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GASIFICATION OF BIOMASS FROM RIVER MAINTENANCE AND CHAR APPLICATION IN BUILDING MATERIALS PRODUCTION

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Abstract

This paper exposes the research activities regarding REBAF (Energetic Recover of River Biomasses) project, focused on the maintenance operations self-sustainability of the Secchia river (Italy). Poplar was found as the most abundant and representative wood plant of Secchia riverbanks, with a good behavior during gasification process: from 1 hectare of maintenance every three year, it was possible to produce 23 MWh of electrical power and 31 MWh of thermal power. The biochar obtained was characterized and mixed with local red clay to create both lightweight aggregates (LWAs) for green roofs applications and bricks. Ashes coming from the gasifier cyclone were characterized and used to create bricks. The aims are the saving of raw materials and the obtaining of weight-lightened products with high porosity. Biochar and ashes were found to be suitable for this purpose given their organic carbonaceous nature, according to X-ray diffractometry, Loss on Ignition (LOI) and TG-DTA results. Application on LWAs by substituting 15%wt of the clay with biochar leads to a weight-lightening of the material. To optimize LWAs pH, spent coffee grounds (SCG) were added with proportion of 85% clay-15% biochar/SCG. A greater decrease in weight and pH values in the neutrality range were observed. Adding 20%wt biochar or ashes on bricks led to a significant reduction of materials bulk density (from 2 to 1.5 g/cm^3) and the achievement of 40-45% porosity. With higher additions (until 40%wt) bulk density gets lower (1.2 g/cm^3–1.3 g/cm^3), but the material results weaker with a worst mechanical strength.

Key words: bio-char, biomass, brick, gasification, lightweight-aggregate

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1. Introduction

Biomass from river maintenance is not widely used for bioenergy production. In fact, the high moisture, the high ash content and the variable size distribution decrease the quality of these feedstock which it is less exploitable into power plants compared to wood chips or wood pellets (IEA, 2012). However, the wide availability of biomass per hectare of riverbed justifies the cost of power plants optimized for these kinds of feedstocks, in fact wetland crops like *A. Donax* produce up to 42 Mg ha^{-1} year^{-1} in Italy (Ceotto et al, 2013; Spinelli, 2005). Over the energy convenience of the conversion processes, river maintenance is a vital operation to ensure the safety of banks and to prevent ruinous floods. The vegetation on the river bed reduces the velocity of the water waves, thus increasing their height and the pressure-related stress on the river banks. Flood waves can pull out the vegetation together with part of the bank, this fact further erodes the soil of the banks (Silingardi, 2007). In this paper, we summarized the first activities and results regarding the project of the REBAF project of the Emilia Romagna region. During several field surveys near the Secchia riverbanks, we found out that the dominant arboreal species are poplar, willow, alder and elm. About the grass biomass, the most abundant species are Typha L., *Phragmites*, rushes and sedges, *Rumex L.* and *Equisetum*. There are also some species such as reeds and panic with characteristic in between

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wood and grass biomasses. About wood biomasses suitable for gasification, poplar is the most abundant plant which can be collected from river maintenance (Spinelli, 2005). The cut of poplar is made regularly every 3 years. For this reason, in the REBAF project we consider that the composition of the biomass can be assimilated to that of poplar. In addition, willow and poplar woods have similar composition and higher heating value (ECN, 2018). Literature suggests that about 50-70 ton/ha of biomass is obtainable from maintenance of rivers located in Northern Italy every 3 years (Spinelli, 2005). The initial moisture of this biomass is very high. Basu (2010). suggests about 40-50% of moisture for freshly cut wood chips. This work investigates the problem in the worst case: amount of 50 ton/ha only of poplar wood chips with moisture content up to 50% and the cut is made every 3 years. Experimental gasification tests of wood chips from river maintenance were done in a commercial gasification power plant All Power Labs PP20 (All Power Labs, 20187).

The by-product of this process is biochar: a fine-grained vegetable carbon extracted from the bottom of the gasifier. If added to the soil it can improve its chemical-physical properties thanks to the strongly stable nature of organic C, which is not subject to degradation and mineralization, either because it is a very porous material with a high reaction surface, which increases water retention for example of sandy soils. Further, the improvement is related to the increasing soil fertility and crop yield because of it is often used as soil improver. A further advantage of the storage of biochar in the ground is the reduction of CO_2 emissions into the atmosphere (Glaser et al., 2002; Lehmann, 2007; Van Zwieten et al., 2008; Yamato et al., 2006),) thanks to the carbon sink process where carbon dioxide is subtracted from the cycle of carbon.

If the use of biochar as soil or substrate improver has been studied a lot in the last 15 years, the application of this substance in building materials or other composites is starting to gain more attention recently. Indeed, in addition to the great advantage of carbon sequestration, the use of biochar can reduce the energy associated with the production process of such materials, by decreasing firing temperature, as well as the consumption of raw materials. Furthermore, in many applications, for example cement or other materials, an improvement of various physical properties is found when biochar is added. A growing interest can be seen in cement composites application: Gupta et al. (2017), for example demonstrated the feasibility of using biochar in cementitious materials, focusing on carbon sequestration. Choi et al. (2012), after testing mixture with 5, 10, 15 and 20% of biochar, reported that introduction of 5% biochar in cement mortar increased 28-day compressive strength with no significant decrease in flowability. All the specimens prepared with biochar had less moisture evaporation and better water retention, so biochar seems to act like a self-curing agent for cement material. Addition of 1% of hazelnut and peanut shell biochar in cement paste was found to increase flexural toughness because biochar particles act as obstacle to cracks propagating, increasing its tortuosity, with the corresponding increase in toughness and fracture energy (Khushnood et al.,2016). Ahmad et al. (2015) also found an increase in compressive strength by 30% when 0.20% of bamboo biochar when added to cement mortar. Other recent uses of biochar in the building sector can be identified in the field of composite materials and asphalts. Wood-polypropylene composites, which belong to the first typology, are materials widely used in automotive and building sector. DeVallance et al. (2015) added hardwood biochar at 5, 15, 25 and 40wt% instead of wood flour in these materials, with a substantial increase in flexural strength, tensile strength and tensile elasticity. For the second typology, Zhao et al. (2014) mixed 10wt% of switchgrass biochar with asphalt components and compared its properties to carbon black and carbon fiber additions. The results indicate that biochar reduces the temperature susceptibility in asphalt binders and induces a higher rutting resistance.

Considering the introduction of a waste, such as biochar, into a production process, we can see that the building materials industry has interesting receptive features as can absorb a wide range of waste even in large quantities. In particular ceramics as bricks, cement materials and polymers, thanks to their own matrix structure, are the best building materials not only for receiving but also for inertising several types of residues. Building materials industry has also large margins of improvement from an environmental and economic point of view: the consumption of natural resources such as sand, rocks or water is so high that the only construction industry consumes more raw materials than any other activity.

In this work two types of waste were characterized: biochar (with grain size under 4 mm) coming from the gasification reactor and ashes coming from the soot collection vessel of the cyclone. Original feedstock consists in woodsy biomass from river maintenance. Chemical, thermal and physical analyses were made to fully characterize the materials and understand their nature and behaviour. The previously characterized biochar and cyclone ashes were then applied in various building materials such as bricks and LWAs (lightweight aggregates) for green roofs. SCG (spent coffee grounds) were also used in the preparation of LWAs. SCG are the majority of coffee residues and they are obtained from the brewing process or from soluble coffee industry (Cruz et al., 2012).

2. Material and methods

2.1. Gasification facility

The small gasification power plant used in this work is depicted in Fig. 1. It is a commercial All Power Labs PP20 gasifier. The reactor architecture consists in an air-blown Imbert type downdraft gasifier, typical of mall scale reactors (Vakalis and

Baratieri, 2015). Wood chips are loaded in the hopper that has a volume of about 300 liters. The chips are moved to the gasification reactor by an auger and they are converted in producer gas and biochar. About 5% in mass of the inlet biomass is converted into biochar and extracted from the bottom of the reactor through an auger connected to a vessel. The producer gas is filtered in a cyclone, cooled down and purified in the final char candle filter. After the filtration, the producer gas is mixed with air and it is burned into the engine that drags an alternator to produce electrical power. The engine is equipped with a heat exchanger that extracts about 20 kW of thermal power form the engine coolant when the electrical generator produces 15 kW of electrical power. System specification are summarized in Table 1. The temperature within the reactor reaches its maximum at the throat. In this point, the air blasted through the nozzles creates a combustion stage with peak temperatures around 880-950°C. In the part of the reactor below the throat, char reduction takes place. This endothermic process makes the temperature to drop from 950 to 650°C approximately.

Fig. 1. All Power Labs PP20 gasifier (All Power Labs, 2018).

Table 1. Specification of the All Power Labs PP20 with CHP auxiliary subsystem

Characteristic	*Value*
Continuous electrical power rating	15 kW_{el} @50 Hz
Continuous thermal power rating	20 kW_{th} at 15 kW_{el}
Biomass P16 W10 consumption	1.2 kg/ kWh_{el}
Biomass moisture content	5-30% dry basis
Electrical efficiency with P16 W10	18.5 %
Thermal efficiency with P16 W10	24.6 %
Installed foot print	1.36 x 1.36 m
Run time with hopper fill	3 hours at 15 kW_{el}

2.2. Chemical characterization

Riverbanks and red spruce biochars and cyclone ashes samples (one specimen for each type) were examined by scanning electron microscope (SEM) “ESEM-Quanta 200 FEI”, to evaluate particle structure and surface morphology of the materials. Energy Dispersive Spectroscopy (EDS), coupled with SEM, was also carried out to identify the atomic elements in these materials and their relative proportions (%). With EDS total carbon content was evaluated also for different biochar. The content of C, H, N, S in gasification biochar and ashes was measured on an elemental analyser “CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112”. The test refers to a sample of biochar and ashes coming from red spruce and was made in order to confirm the results given by EDS analyser. The materials were grounded prior to this analysis. For pH measurements of the biochar, an "XS Instruments, pH 6" pH meter was used. Biochar samples and cyclone ashes (10 g) were immersed in deionized water at a ratio of 1:5 and 1:10 by weight and 1:5 by volume and kept for 1 hour under magnetic stirring prior to the pH measurement following UNI EN 13037 (2012). The pH meter was previously calibrated with standard buffers at pH 4, 7 and 10. The measurement of specific electrical conductivity is directly linked to the presence of salts in solution, the dissociation of which generates positive and negative ions. The analyses were conducted on the same eluates analysed with pH meter with reference to the UNI EN 13038 (2012). The measurement was carried out with the “Oakton CON 6/TDS 6” model conductivity meter. The determination of major crystalline phases present in the biochar and ashes was achieved by using an X-ray diffractometer “Phillips PANalyticalPW3710” on grounded and dried material. Carbonates analysis was made using a “Dietrich-Fruhling” calcimeter. The material was grounded and dried prior to the analysis.

2.3. Thermal characterization

Moisture content was determined following UNI EN 13040 (2008) standard in a stove at 105°C for 24h. The loss of mass and thermal behavior with increasing temperature were determined by Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA), using a “Netzsch STA 409” analyser. The temperature range was set between 20°C and 1300°C, with a heating rate of 10°C/min. The mass of biochar and ashes in the platinum crucible ranged from 5 to 20 mg. Three different Loss on Ignition (LOI) tests at 700°C, 900°C and 1100ºC were also performed on biochar samples (three measurements for each temperature using 10g sample) to compare the results achieved in TG-DTA. The material was weighed and placed in ceramic crucibles. After each two-hours-heating test in a muffle furnace, the biochar was allowed to cool completely in the oven before weighing. The data reported are an average value of the three obtained.

2.4. Physical characterization

The particle size distribution of the biochar and ashes was determined using a stainless-steel sieve set (mesh 2, 1, 0.5, 0.25, 0.125 mm) placed in a vibration sieve shaker for 15 minutes. The materials were analysed as received, without pre-treatments. Another analysis was also carried out with a laser granulometer “Malvern mastersizer 2000” in the range of 0.1-2000 µm, after an ultrasound treatment, to better understand the behavior of the finer fraction of the two materials. Specific surface area was determined by the Brunauer-Emmett-Teller (BET) method by nitrogen gas sorption with a “Gemini V” analyser; the biochar was outgassed for 24 h at 105°C prior to the measure. Particle density was measured by helium pycnometer “AccuPyc II 1340, Micromeritics” with precision on standard deviation and on mean of 0.0001 g/cm^3. Bulk density of the two materials was evaluated experimentally by adding a known amount of specimen mass into a graduated cylinder to measure the volume. Before both measurements, the samples were dried in an oven at 105°C. Porosity ε (Eq. 1) was evaluated with the following formula (Brady and Weil, 1996; Flint and Flint, 2002):

$$\varepsilon = 1 - (\rho_b / \rho_p) \tag{1}$$

where: ε [ad] is the char porosity, ρ_b [kg/dm^3] is the char bulk density and ρ_p [kg/dm^3] is the char particle density. Multiplying the result obtained by 100 it was possible to obtain the value expressed in %.

2.5. LWA samples production

For the production of LWAs, two distinct types of preparations were made. The first, aimed at demonstrating the feasibility of inserting the biochar in these materials, involved the preparation of aggregates with biochar (with a particle size of less than 250 µm) and two different types of local red clay (with a particle size of less than 1 mm): clays were named a and b. Both samples were prepared with 85wt% clay (a or b)-15wt% biochar and were named BCa (85wt% red clay a, 15wt% biochar) and BCb (85wt% red clay b, 15wt% biochar). These two specimens were compared with control samples named ROa (100% red clay a) and ROb (100% red clay b).

The second, aimed at optimizing aggregates with biochar, saw the inclusion of a second waste in substitution of biochar, spent coffee grounds (SCG) collected from some local commercial activities, dried and sieved under 250 µm, in order to obtain an improvement in terms of pH of the finished product. The ratio in this case was 85% clay b-15% biochar/SCG and the sample was named CBCb. All the raw materials used were previously dried in an oven at 105°C to remove all traces of free water. The homogeneous mixing between the clays and residues was carried out inside a ceramic container; then, distilled water was added to the powders to obtain a workable paste. Once the homogeneous mixture was obtained, LWAs were manually made, trying to make the samples similar in weight and shape to the most known commercial LWAs (0.6-0.8 cm diameter); from each mixture a variable number of spheres was obtained (between 35 and 60 elements). All the obtained aggregates were dried at 105°C for about 24 hours to remove excess free water used in the preparation process. The aggregates were than subjected to a firing treatment in a static oven at 1000°C for 1h. Finally, some important parameters were assessed for the use of aggregates in green roofs:

- weight loss during drying and firing were obtained by difference between the weight before and after drying stage and firing stage using a "Bel Engineering M124A" analytical balance, with 120g scale and accuracy of 0.0001g;
- pH value, according to UNI EN 13037 (2011) standard, was measured using a pHmeter "XS Instruments, pH 6";
- specific electrical conductivity (EC), according to UNI EN 13038 (2011) standard, was measured using an “Oakton CON 6 / TDS 6” conductivity meter;
- static absorption in water over 24h was evaluated by difference between the weight before and after the residence time in water;
- surface microstructure of the materials was evaluated by a scanning electron microscope (SEM) “ESEM-Quanta 200 FEI”.

2.6. Bricks samples production

Before the specimen preparation, TG-DTA (“Netzsch STA 409”) tests were performed on three types of mixtures to test the behaviour of the biochar and cyclone ashes during firing. R100 (100% red clay) as standard composition, B70 (70wt% red clay – 30wt% biochar) and A70 (70wt% red clay – 30wt% cyclone ashes) were prepared and tested from 20°C to 1300°C, with a heating rate of 10°C/min. Later, several cylindrical specimens (40mm Ø x 4mm) with biochar and cyclone ashes ratios from 5 to 40% and a red local clay were created by pressing at 22bar after a 7% humidification of the mixtures. Materials used were previously dried in an oven at 105°C to remove all traces of free water.

Biochar and cyclone ashes were sieved under 250 µm and clay under 1 mm. All the obtained samples were dried at 105°C for about 24 hours and then were subjected to a firing treatment in a static oven at 950°C for 30 minutes. Weight loss in drying and firing was evaluated by difference between the weight before and after drying and firing stage using a "Bel Engineering M124A" analytical balance, with 120g scale and accuracy of 0.0001g. Drying and firing shrinkage were evaluated by difference between the specimen diameter before and after drying and firing stage using a digital caliper. Bulk density of the fired samples was evaluated by measuring their volume and weight.

3. Results and discussion

3.1. Wood chips from river maintenance gasification tests

Three gasification tests with a total duration of 15 hours using about 250 kg of wood chips from river maintenace were performed and the specific consumption and the power delivery was found in line with the manufacturer data. However, a biomass drying to 10% is required in order to not afflict the performance and to not increase O&M costs. This drying can be done using the heat from the engine heat exchanger or the sensible heat of the exhaust of the engine thar are currently discarged at about 300°C. Considering a biomass drying to 10% of moisture, from one heactare of rivernbanks maintenance made every 3 years it is possible to obtain about 27.8 tons of wood chips that can be used to produce about 23 MWh of electrical power and 31 MWh of thermal power. In addition, considering a biochar of 5% in weight, about 1.4 tons of biochar is disposed from the char vessel of the plant.

3.2. Chemical characterization results

Three different methods to measure pH, as shown in Table 2, were performed to verify the alkalinity of the materials, widely documented in literature studies. pH values are generally lower for biochar produced at lower pyrolysis temperatures. A substantial increase in pH usually occurs at higher temperatures due to the increase in the relative concentration of inorganic elements such as Ca and Mg of the original raw materials that have not been pyrolyzed and of the formation of surface oxides. pH changes depending on the maximum process temperature and residence time (Novak et al., 2009; Rehrah et al., 2014).

Table 2. Results of pH, specific electrical conductivity and $CaCO_3$ analysis

Chemical analysis	*Units*	*Materials*	
pH and specific electrical conductivity		***Biochar***	***Cyclone Ashes***
pH (deionized water) 1:5 w/w 1h (UNI EN 13037, 2012)	pH unity	11.8	12.2
pH (deionized water) 1:10 w/w 1h	pH unity	12.1	12.4
pH (deionized water) 1:5 v/v 1h	pH unity	10.7	11.0
EC (deionized water) 1:5 w/w 1h (UNI EN 13038,2012)	mS/cm	5.7	8.6
EC (deionized water) 1:5 v/v 1h	mS/cm	5.3	8.3
$CaCO_3$	%	7.1	8.1

Observing Table 2, it’s possible to note in all the measurements that biochar and ashes are strongly alkaline; indeed, the high temperatures reached during the gasification process strongly influence the pH of the final products, causing alkalinity. This parameter is important because a very alkaline pH could influence the final material in the application that will be chosen, altering its acceptability in a certain range of values, as following reported. The values of biochar specific electrical conductivity are in the range 5-6 mS/cm and they are consistent with values found in literature studies. Li for example (Li et al., 2013), finds an increasing variability for rice straw biochar from 4.09 to 7.72 mS/cm by changing the charring temperature from 100 to 800°C. The analysis with a calcimeter shows a significant presence of calcium carbonates, later confirmed by the EDS and XRD analyses data. Yuan et al. (2011) found a linear correlation between alkalinity and carbonate content, although also carboxyl and hydroxyl groups may contribute to the pH of biochars.

The EDS chemical analysis, coupled with SEM, was carried out on different samples of biochar and ashes (coming from both river biomass and red spruce) with a focus on different areas of the single sample. The average content of element was the average content of all the dots and areas for a sample analysed. The result shows a wide range of values that well represents the high variability of the material analysed compared to the starting biomass. As we can see from Table 3, the total carbon content in different biochars and ashes (coming from different biomass) can change from 45% to 85%. These values are in agreement with literature studies on various types of biochars from different feedstocks and different processes: Al-Wabel for example found a C content of 82.93% for conocarpus biochar obtained at 600°C, Li found a C content of 77.24% for rice straw biochar obtained at 600°C (Al-wabel et al., 2013; Kim et al., 2012; Li et al., 2013; Xie et al., 2014). The values obtained from elemental analysis, referred to the red spruce biochar and ashes, fall within the ranges identified by EDS analysis.

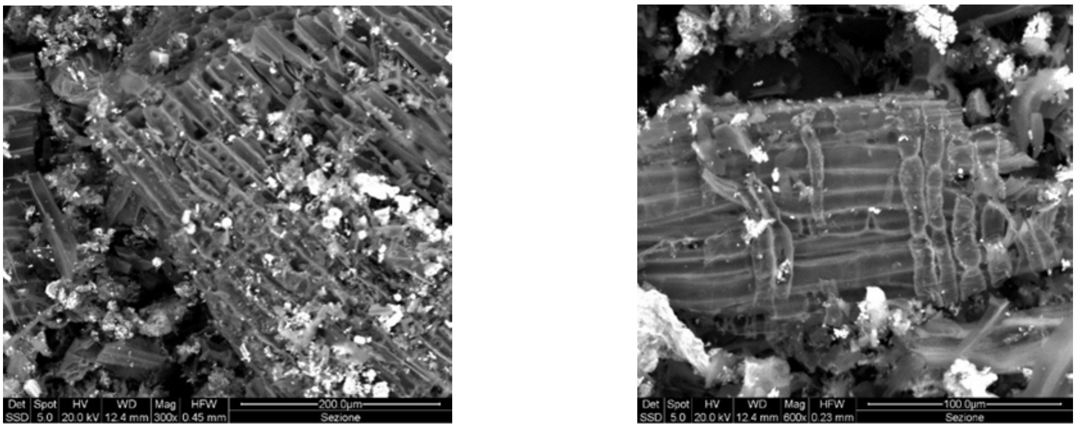
Table 3. Results of EDS and elemental analysis

Chemical analysis	*Units*	*Material*	
EDS chemical analysis *(range values from both river biomass and red spruce)*		***Biochar***	***Cyclone Ashes***
C	%	45-85	55-70
O	%	10-21	15-18
Ca	%	4.5-9	7.5-10
K	%	2-3	2-3
Si	%	0.5-1.4	0.5-3.5
Fe	%	\	1
Elemental analysis (from red spruce)			
C	%	53.90	67.54
H	%	1.00	1.26
N	%	0.33	0.26
S	%	0.00	0.00

According to Zhao et al. (2013), biochars derived from woody materials (like those analyzed in this study) has a low ash content (often less than 3%) and a medium-high content of C. This content of C is to be referred to unburnt coal, organic compounds of different complexity and carbonates, as confirmed by the thermal analysis. Figs. 2a-b show the SEM images of biomass riverbanks biochar particles at 300x and 600x magnifications. The pores created in the biochar during the gasification process are visible on the surface of the material and are attributable both to the nature of the original feedstock and to the release of volatile and organic substances during the thermal process. Wood, indeed, is a material made of fibers, where we can find gas and water transport channels creating walls; the size of these channels determines the following size of the pores in the biochar (Warnock et al., 2007). The pores created during the gasification of the original biomass can be subdivided into micropores (<2 nm), meso-pores (2 nm-50 nm) and macro-pores (50 nm). Structures attributable to the original biomass with an evident macro-porosity can be seen in the two figures at different magnifications. Figs. 3a-b show the SEM image of biomass riverbanks cyclone ashes particles at 300x and 600x magnifications.

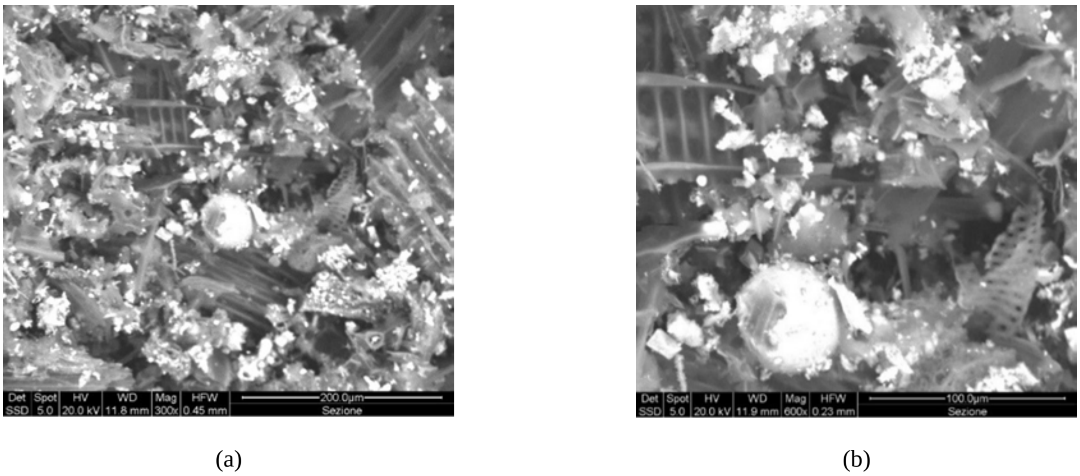
From these it can be visualized an inhomogeneous structure. Some structures attributable to the nature of original feedstock, similar to biochar sample. Additionally, there is a greater presence, compared to biochar, of mainly inorganic spherical structures, with diameters from 10 to 30 µm, probably due to a faster cooling of the material. These spheres show by EDS analysis compositions rich in Si (around 17%), K (13%) and Al (7%).

The X-ray diffractometry patterns are visible in Fig. 4. At high process temperatures, as 900 °C in our case, the biochar and cyclone ashes obtained show a predominantly amorphous nature. Indeed, the peak attributable to cellulose disappears when 400°C of process are reached, with a consequent weight loss of around 300 and 400°C (Wang, Cao and Wang, 2009). In this case, the only crystalline phases present can be identified mainly as calcite ($CaCO_3$), with traces of quartz (SiO_2). The presence of calcium carbonate, according to EDS and carbonates analysis, is confirmed by the peak at $2\theta = 29,4°$, and can also be found in other literature studies (Devi and Saroha, 2013).



(a) (b)

Fig. 2. Biochar particle structures at: 300x (a) and 600x (b) magnifications



(a) (b)

Fig. 3. Cyclone ashes particle structures at: 300x (a) and 600x (b) magnifications

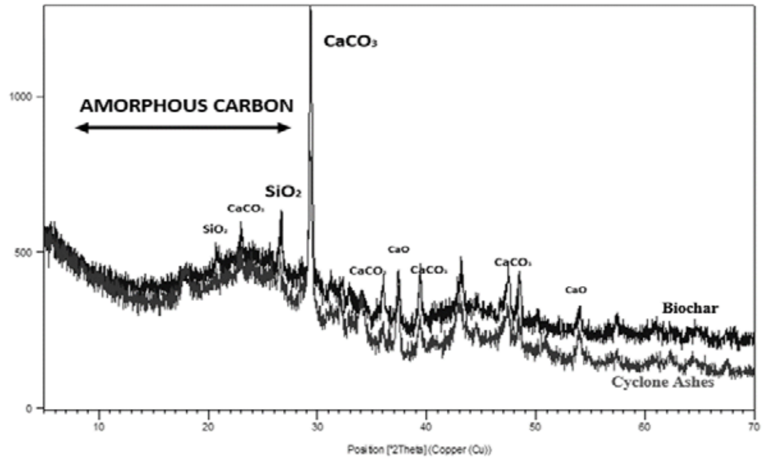


Fig. 4. X-ray diffractometry patterns of biochar and cyclone ashes

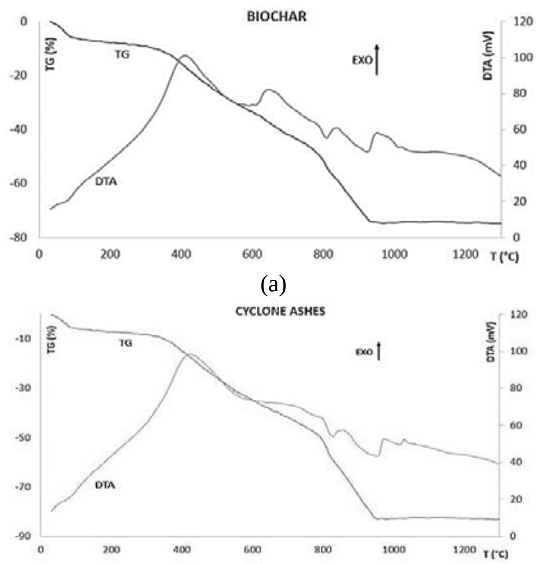
3.3. Thermal characterization results

During the drying time at 105°C the sample achieved zero weight loss and a "oven-dried" biochar was obtained. The amount of water present in the biochar can vary greatly, depending on how it was produced and if it has accumulated moisture during the next storage. In this case the values (1.5% for biochar and 3.1% for cyclone ashes) are similar to average values found in literature (1-15%) (Brown, 2009) but it's important to underline that the humidity removed at 105°C is only part of the actual humidity contained in a sample of biochar. In fact, the strong hygroscopicity and the high absorption capacity for water vapor of this material, require a more intense drying, at 200°C, to remove all the absorbed water and thus determine a biochar base "without humidity".

In Fig. 5a-b we can see the TG-DTA curves related to biochar and cyclone ashes respectively. The trends of both the TG and DTA curves are very similar in the two materials. The first slight weight loss is from room temperature up to about 200°C and corresponds to the loss of moisture and highly volatile organic compounds. Subsequently a loss of organic matter is visible corresponding to an exo-peak around 400°C followed by a decarbonation at higher temperatures (800/950°C) that was expected considering the previous analyses. The final loss is about 82% and occurs within 950°C, a temperature above which there is no longer any weight decrease.

3.4. Physical characterization results

In the context of a characterization concerning the physical properties of the materials, a sieve analysis was made on both wastes "as received". Knowledge of biochar particle size is important for determining the predisposition or not for each chosen application. Particle size distribution is mainly influenced by the biochar original feedstock (biochar from crop residues have generally a finer structure than biochar from woody biomass) and by the conditions in which thermal process occurs (particle size decreases with increasing temperature) (Cetin et al., 2004; Downie et al., 2009). The results obtained by a sieve analysis are displayed in Fig. 6a-b. Looking at the biochar (a), we can notice a fairly uniform subdivision of particle sizes between the various bands, each one ranging from 10 to 20% of the total. 43% of the analysed material remains over 1 mm Ø sieve. The cyclone ashes (b), on the other hand, have a finer composition. Only 9% of the material analysed does not pass below 1 mm Ø sieve and a large percentage, about 40%, has a grain diameter of less than 100 µm. Both materials, excluding the fraction above 2 mm Ø, were than subjected to analysis with a laser granulometer. The results, in Table 5, show how, after an ultrasound treatment, the granulometric classes of the two materials looks very similar. The biochar has a slightly finer particle size than the cyclone ashes (80.7% of the material passes under <0.045 mm Ø against 72.2% of the ashes). This result could be due to the fact that biochar "as received" occurs in a state of aggregation of granules greater than cyclone ashes.

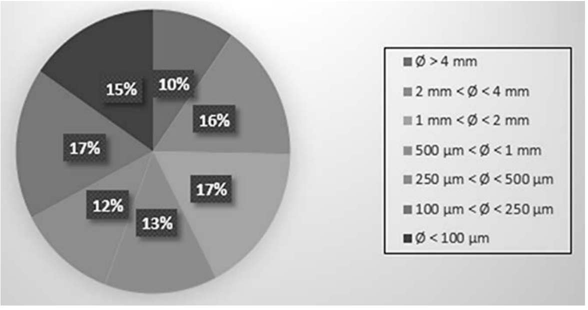


(b)

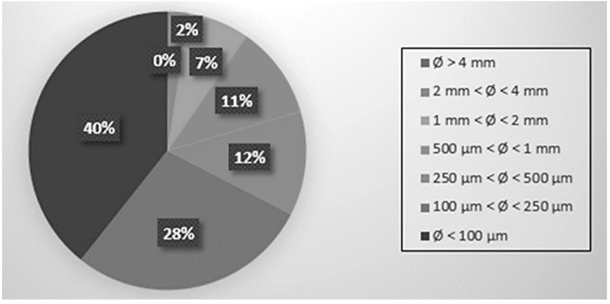
Fig. 5. TG-DTA curves related to biochar (a) and cyclone ashes (b)

Table 4 LOI and EDS analysis results on biochar samples

Biochar	*LOI (wt%)*	*C (%)*	*O (%)*	*Ca (%)*	*K (%)*	*Fe (%)*	*Si (%)*
700°C	34.78	66	19.6	6.9	2.7	1.4	0.6
900°C	50.90	53	20.7	17.4	3.4	1.3	0.6
1100°C	70.97	39.5	28.5	20.5	2.4	3.2	1.5



(a)



(b)

Fig. 6. Results of sieve analysis on biochar as received (a) and cyclone ashes as received (b)

BET analysis, performed on the dried material, shows the physical adsorption of gas molecules on the biochar and cyclone ashes solid surface with the aim to quantify the specific surface area of the materials. As can be seen in Table 5., the biochar has a larger specific surface than the cyclone ashes, in accordance with the previous granulometric analysis. The value of surface area (210.50 ± 5.94 m^2/g) is on average if compared to other literature studies (Bedussi, 2015; Brewer et al, 2014) although much lower than a commercial activated carbon (500-3000 m^2/g). The increase in the maximum process temperature and residence time in the pyrolyser/gasifier can lead to an increase in the porosity of the char and thus influences the surface area value (Brewer et al., 2014). Biochars coming from high temperature treatments generally have higher surface area values (Giorcelli et al, 2016). Biochar bulk density can vary with feedstock and process.

Table 5. BET, Particle size distribution, bulk and particle density and total porosity results on biochar and cyclone ashes

	Unity	*Biochar*	*Cyclone Ashes*
BET Surface area	m^2/g	210.50 ± 5,94	157.18 ± 3.56
Particle Size Distribution			
<0.045mm	%	80.7	72.2
0.045mm-0.125mm	%	18.5	26.8
>0.125mm	%	0.8	1.0
Bulk Density	g/cm^3	0.16	0.19
Particle Density	g/cm^3	2.23 ± 0.004	2.15 ± 0.004
Total Porosity	%	92.8	91.2

The biochar values of 0.16 g/cm^3 is very low, but comparable to other literature results where, for example, a 90% spruce - 10% hardwood biochar it's found to be 0.18 g/cm^3 or a maple biochar it's 0.26 g/cm^3 (Allaire et al., 2015). Particle density is higher than the bulk density for a given solid since pore volume is no longer included. The values found in this study (Table 5) are higher than common values that can be found in literature (Brewer et al, 2014). This is because the analysed biochar comes from a high temperature gasification process and not pyrolysis. Indeed, it's verified that biochar particle density increases with pyrolysis temperature (Brewer et al, 2014). This because, as the temperature rises, solid carbon condenses into a more compact aromatic rings structure with an increasing degree of graphitization, approaching the particle density value of solid graphite (2.25 g/cm^3). The total porosity calculated by Eq. 1, is 92.8% for the biochar. A high value, according to the BET analysis, which is similar to other literature works (Bedussi, 2015).

3.5. Lightweight aggregates

All the samples of LWA prepared were characterised by a good feasibility in processing and showed a good level of final aggregation. No samples showed any breakage during the firing process. The biochar gives a darker colour to the aggregates but, after the firing process, this is lost with a final standard red colour. In Table 6 we can see the results of the characterization tests conducted on all types of samples prepared both with clay a and b and with the addition of SCG.

The addition of 15% of biochar inside the materials leads, with both clays (BCa and BCb), to an increase in weight loss during firing and a consequent weight-lightening of the material (8.32% of the BCa compared to 4.41% of the ROa and 13.64% of the BCb compared to 9.08% of the ROb). Clay b has a higher weight loss in firing; this is probably due to the higher presence of carbonates.

Table 6. Characterization results on LWAs samples

	ROa	***BCa***	***ROb***	***BCb***	***CBCb***
W.L. (%) 105°C 24h	19.8	25.7	22.9	27.1	26.2
W.L. (%) 1000°C 1h	4.4	8.3	9.1	13.6	17.8
pH	6.4	11.9	6.7	9.3	7.9
Specific electrical conductivity (mS/cm)	0.26	3.17	0.32	0.90	0.41
Static water absorption (%) 24h	11.5	18.5	4.7	13.6	12.5

However, the generated porosity does not mean greater water absorption. This is indeed less for clay b, with or without biochar, compared to a. The alkaline pH of the biochar gives at the final product, with both clays, a value beyond the optimal range of plant comfort (6-8). The value of EC is less than 2 mS/cm (optimal range of plant growth) only using clay b. Considering these results, it was decided to continue the study using clay b, which has better pH and EC values. To optimize these parameters, aggregates were created with SCG. The addition involves, as expected, a greater loss in firing and therefore a further weight-lightening. This is because this type of waste is organic, has a LOI of about 98% and has a high theoretical high calorific value. The low pH value of the coffee that remains in the aggregates after firing, gives encouraging results that fall within the optimum values of pH and conductivity.

Fig. 7, at 800x magnification, shows the difference in microstructure between the BCb and CBCb sample. Small pores (even 1-2 μm) in a better-sintered matrix, present in the CBCb aggregate, could be a consequence of SCG combustion.

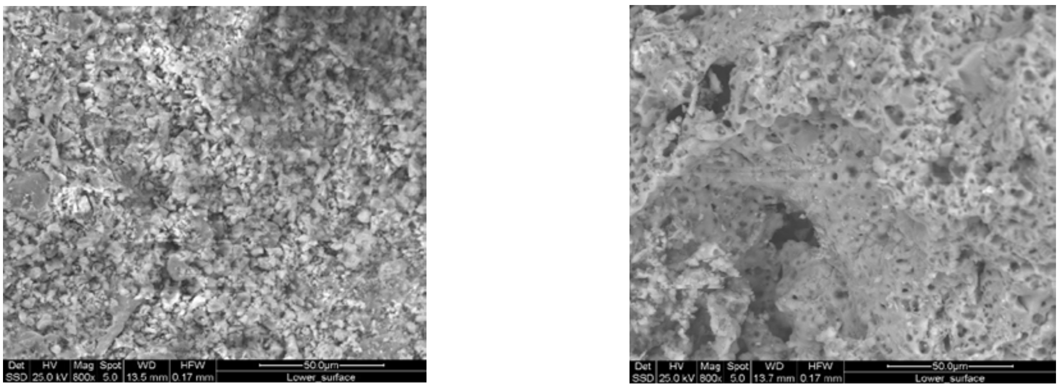
3.6. Bricks

The TG analysis (Fig. 8a) of the two mixtures prepared with a fixed percentage (30%) of pore forming agent, confirms theoretically the weight-lightening effect of the biochar and shows a very similar trend for the cyclone ashes. Indeed, both the mixtures with wastes show values of weight loss far greater than the mixture with only red clay. At about 950°C, ceramic bricks firing temperature, R100 shows a weight decrease of about 4%, while A70 and B70 reach a decrease of about 11%.

The DTA graph (Fig. 8b) shows a marked exo-peak and therefore a release of substances, associated with the presence of biochar and ashes in the mixture, around 400-500°C. These temperatures are higher than those found in systems where other types of weight-lightening waste in bricks are used. In these plants materials such as sawdust release various types of volatile pollutants at around 250-300°C, with relevant problems in fume disposal systems. Further emission studies will be needed on the specimens with biochar and ashes, to verify the negligible impact of these substances on the emissive framework of the furnace.

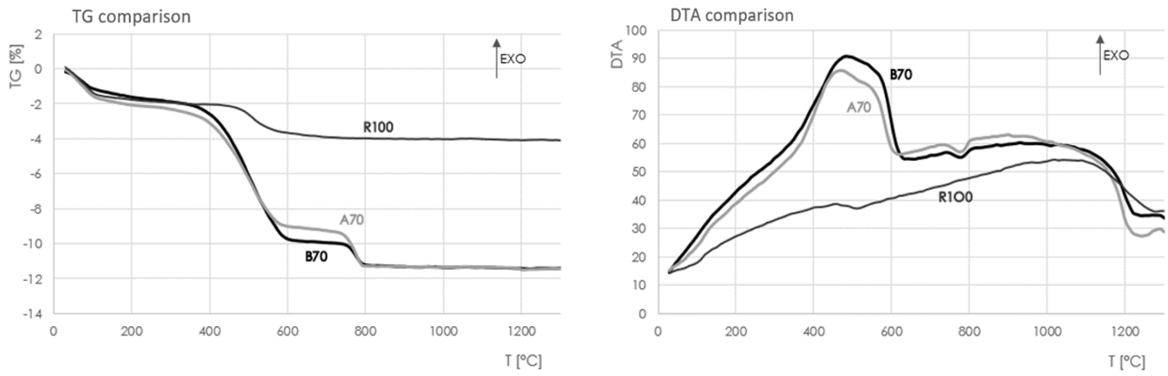
The samples with only clay and with various percentages from 5 to 40 of biochar and cyclone ashes, were then subsequently prepared as previously described and the measurements made are shown in Table 7. An increase in black color was observed when the amount of biochar or ashes introduced was increased. However, after the firing process all the specimens had the same red-clay-color, typical of ceramic bricks. The BC40 sample with 40% of biochar had some problems immediately following the pressing phase, crumbling at the touch. It is considered necessary a greater quantity of water added to the initial mixture, even if after the drying phase the same problem could be found again, due to the low plasticity of the mixture (only 60% of clay). Considering all the other samples, no particular problems (like for example “black heart” defect) have been found and the post-pressing and drying specimens appear to have good consistency and stability.

Table 7. shows that weight loss after firing confirms the results obtained from the TG analyses on the mixtures. The values are very similar as weight loss of 11%, which was related to the introduction of a 30% of biochar/ashes, falls here in the interval between 9.13 (20%) and 15.36 (40%) for the ashes.



(a) (b)

Fig. 7. Microstructure of BCb sample (a) and CBCb sample (b)



(a) (b)

Fig. 8. TG (a) and DTA (b) analysis of the two mixtures prepared with a fixed percentage (30%) of pore forming agent, compared to R100, the mixture with only clay

The material is effectively lightened. The shrinkage of the samples both during the drying phase and the firing phase, remains below 1%. This value can be considered negligible and in line with values relating to industrial processes.

Table 7. Characterization results on brick samples

	% W.L. (%) 950°C 30 min	*Drying shrinkage (%)*	*Firing shrinkage (%)*	*Bulk density (g/cm^3)*
RO	3.34	0.10	0.62	1.99
BC5	4.82	0.03	0.07	1.85
BC10	6.58	0.05	0.32	1.75
BC20	10.25	0.00	0.57	1.47
BC40	\	\	\	\
AS5	4.93	0.02	0.05	1.88
AS10	6.06	0.05	0.37	1.78
AS20	9.13	0.00	0.37	1.58
AS40	15.36	0.10	0.49	1.23

Considering the bulk density measured on the samples, it can be seen how the introduction of biochar/ashes makes possible to reach values around 1.5 g/cm^3, starting from about 2 g/cm^3 of the clay alone. Minor densities of 1.2 g/cm^3 – 1.3 g/cm^3, which can be considered very interesting for the market and a future industrial use, are achieved only by adding 40% of biochar/cyclone ashes in the samples. This, however, weakens the material, which crumbles quite easily to the touch and does not exhibit good mechanical strength. Subsequent thermal conductivity studies will be needed to verify the impact of the biochar/cyclone ashes on this property.

The shape of the alveolus has an important impact on the thermal resistance of the product (Krcmar, 2001) so that even a higher density, due to the introduction of percentages lower than 40%, could however lead to good results. Assuming an average particle density of clay materials of 2.65 g/cm^3 (Blake et al., 2008) and considering the bulk density values shown in Table 7, it is possible to obtain a roughly porosity value of the samples (Eq. 1). For the specimen with only red clay, the total porosity is about 25% but with the introduction of 20% biochar and ashes this value rises to 44.5% and 40.4% respectively.

4. Conclusions

REBAF project activities suggest the possibility to do maintenance on the Secchia River in a sustainable way. Afterwards field survey, the most abundant and representative wood plant is poplar. This wood behaves good in gasification to produce electricity and thermal power. Results suggests that from 1 hectare of riverbanks maintenance every three year, it is possible to produce 23 MWh of electrical power and 31 MWh of thermal power. The biochar and the cyclone ashes produced during the gasification tests was characterized from the chemical, thermal and physical point of view. In particular, by considering an application as weight-lightening agents in clay-based materials, analysis of thermal properties is important. Loss on Ignition (LOI) and TG-DTA curves showed similar trends with loss of moisture, organic matter and decarbonation respectively at 200,400 and 800-950°C. TG final weight loss is about 82% (950°C), a high value indicating the organic carbonaceous nature of the material.

Application on lightweight aggregates for green roofs by substituting 15%wt of the raw clay leads to an increase in weight loss during firing and a consequent weight-lightening of the material. The alkaline pH of the biochar gives the final product a value beyond the optimal range of plant comfort (6-8) and, to optimize this parameter, aggregates were created with addition of spent coffee grounds. This involves, as expected, a greater loss in firing and therefore a further weight-lightening, because this type of waste is organic and has a high calorific value. The low pH value of the coffee that remains in the aggregates after firing, gives encouraging results that fall within the optimum values of pH and conductivity. Application on bricks leads to a weight-lightening effect as well, with a significant reduction in the bulk density of the materials. The insertion of biochar and cyclone ashes is feasible up to a percentage of 20/25%wt, with the achievement of 40-45% porosity.

The positive results about biochar/cyclone ashes reusing can make more sustainable the gasification process by extending its use in different application fields.

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