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Pyrolysis Process for the Recycling of Cork Dust Waste from the Processing of Cork Agglomerate Caps in Lightweight Materials

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Abstract: This study aimed to investigate the possibility of recycling cork scraps derived from the production of agglomerated bottle caps containing organic additives (glues and adhesives) in addition to virgin wood. The study involved pyrolysis treatment followed by the use of char to obtain lightweight material prototypes. The scrap was pyrolysed in order to achieve the thermal degradation of unwanted molecules with decomposition temperatures lower than the pyrolysis temperatures, but also to achieve the reduction in mass and size of the starting material. The substitution of 15% by weight of weight-lightening agent (char from pyrolysed cork, or half char and half spent coffee grounds) into the clayey matrix made it possible to obtain lightweight aggregates with pH and conductivity values that could be exploited in an agronomic context. The substitution of clay with of 5 to 15% by weight of pyrolysed cork char in the production of specimens pressed at 25 bar and fired slowly at 1000 °C led to lightweight ceramics with particularly interesting porosity (from 41 to 68%) and bulk density (850–1600 kg/m^3) values.

Keywords: carbonization; cork residues; cork caps; pyrolysis; char; lightweight aggregates; porous ceramics

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1. Introduction

Cork is a plant tissue that has always been used for multiple purposes, and it is considered a sustainable and environmentally friendly raw material [1]. It is composed of cells that, once dead, are replaced by air, creating an airy and light material that is elastic and compact [2]. Cork is also a natural material that is compressible and flexible, and it has very low thermal conductivity [3].

One of the various uses of cork is the manufacturing of caps for wine bottles, champagne, cognac, vinegar, etc. There are several advantages of using this material for bottle capping. A cap retains more CO_2 than it releases during production (approximately 309 g absorbed against 300 g sold) [2]. In the production of corks, waste arises that must be managed; hence, the purpose of this research was to investigate this waste. In particular, we focused on the scrap produced by a company in northern Italy in the agglomerate cork trimming phase. This cork residue is about 80% wt. cork (imported from Portugal, which is the largest cork producer [4]) and 20% wt. additives (polyurethane glue, paraffin and others).

There are currently agreements to return this residue to the Portuguese supplier involving high environmental and economic costs related to transport; therefore, an alternative valorisation on the territory would appear to be an interesting option.

One possible recovery strategy, alternative to the one proposed in this work, was proposed in a study conducted in Portugal in 2017 [5]. It concerned the feasibility of gasification of industrial cork waste using a semi-batch fluidized bed reactor. The tests were carried out using air as an oxidizing agent and sand particles as the bed material at a bed temperature of 780–900 °C. Cork waste pelletization to allow its use as fuel for direct combustion or gasification was proposed by Nunes et al. [6].

The study presented here included an initial phase concerning the optimization of the cork-waste pyrolysis process, aimed at obtaining a carbon residue (char) to be included in the formulation of lightweight silicate matrix materials. The second phase corresponded to a feasibility study of the material realisation. To the best of the authors' knowledge, there are no previous scientific studies concerning the pyrolysis process involving the production of two kinds of porous ceramics for cork waste valorisation.

Pyrolysis is an endothermic process where biomass is heated up in the absence of oxygen at temperatures in the range from 300–800 °C and thermal decomposition of large hydrocarbon molecules into smaller molecules in the forms of gases (such as CO and CO_2), liquids and solids (char) takes place [7]. In this case, the objectives were the thermal degradation of the unwanted components and the reduction of the size and mass through the carbonization process. In addition, received cork powder (not yet pyrolysed) has previously shown unsatisfactory performances in the clayey matrix [8]. Char is the solid product of the pyrolysis process and has the ability to retain a part of the carbon that would be dispersed into the atmosphere in a solid form recalcitrant to decomposition for hundreds of years [9]. Furthermore, if char is returned to agricultural land, it can permanently increase the carbon content of the soil and create a carbon sink for atmospheric CO_2. However not all chars are suitable as soil amendments. Only a specific niche of chars, called biochars, can be used for agronomic applications. Biochars need to meet specific characteristics defined by the European Biochar Certificate or the International Biochar Initiative [10,11]. One of the key requirements consists in the absence of toxic impurities in the biomass [10,11]. In this work, the starting feedstock consisted of a blend of cork scraps containing organic additives (glues and adhesives) and virgin cork. The char obtained could not be directly used as a soil amendment, and it was tested as a weight-lightening agent within the clayey matrices for the obtainment of lightweight aggregates (LWAs) and porous ceramics. Regarding LWAs, preliminary tests were conducted to assess possible agronomic applications.

An LCA study demonstrated that the addition of organic wastes in the clay matrix represented an improvement over the traditional aggregate (without residue) with which it was compared. Among the waste considered, coffee grounds were the waste that proved to be the most efficient in reducing the carbon footprint in the manufacture of ceramic materials under conditions of sintering at high temperatures and with reduced times [12]. The char was then reused in the production of two types of materials: LWAs and porous ceramics. The char content for LWAs was 7.5 wt% (in combination with spent coffee grounds (SCGs)) and 15 wt% and between 5 and 15 wt% within porous ceramics (bricks).

The lightweight aggregates were characterised from chemical (pH, electrical conductivity), physical (density, porosity, weight loss, water absorption, hygroscopic absorption and release a closed, open and controlled environments), mineralogical (X-ray diffraction) and microstructural (SEM analysis relating to the surface of the LWA sample) points of view.

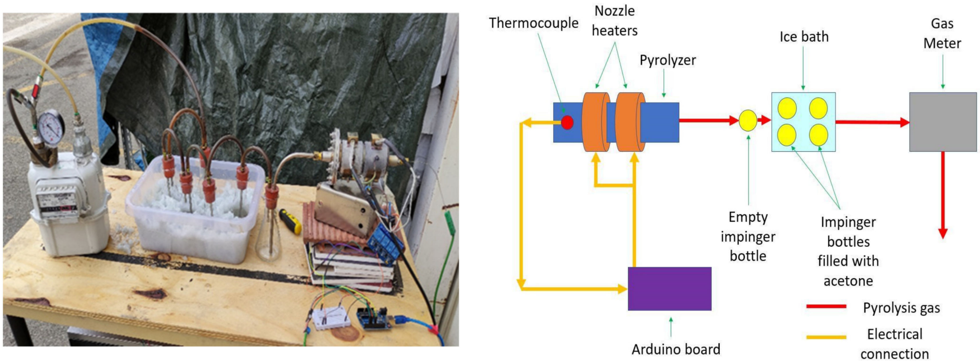
The tests performed on the porous ceramics included tests of the static absorption in distilled water for 24 h, weight loss, drying and firing shrinkage, bulk density and total porosity.

2. Materials and Methods

2.1. Pyrolysis Test and Char Characterization

The cork powder used came from the smoothing phase in the production of agglomerated cork caps and was directly collected through a cyclonic air-filtering system. The average diameter of the powder particles was in the range 0.063 mm < d < 1 mm. The ratio of virgin cork and additives (polyurethane glue, paraffin and others) was 83/17.

The prototype pyrolyser used consisted of a small cylindrical chamber made of stainless steel and operated in a retort configuration [13,14]. The pyrolyser was heated by means of two electric resistors (nozzle heater) connected to a thermocouple for the measurement of the temperature inside the cylinder (Figure 1). Multiple tests were carried out in order to calibrate the pyrolysis process. The various tests were performed by modifying the parameters of the temperature control strategy implemented in an Arduino relay board; the control algorithm allowed the temperature trend to be as linear as possible. The residence time at the target temperature (400 °C or 600 °C) was set to 30 min. These operating conditions were consistent with slow pyrolysis; that is, the pyrolysis mode in which char yield is maximized at the expense of liquid and gas production [15].

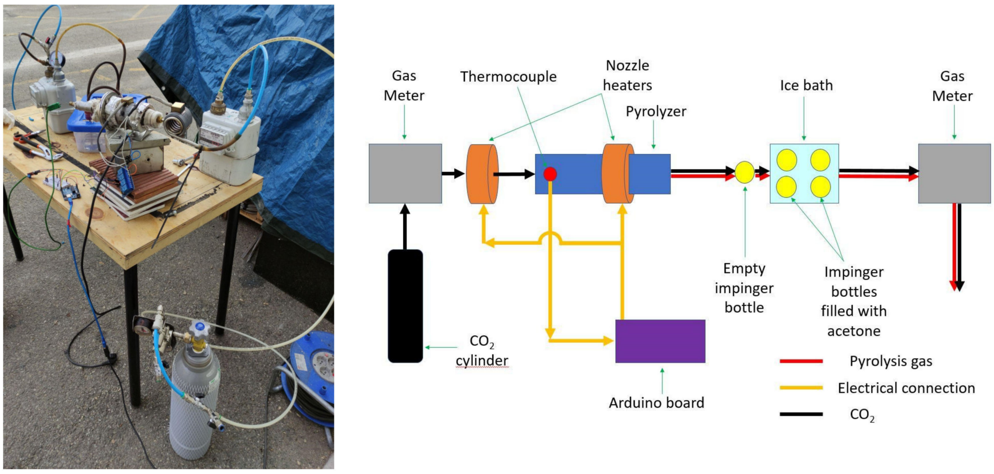


(**a**) (**b**)

Figure 1. Pyrolyser setup: (**a**) picture; (**b**) scheme.

Tar and particulate contents in the pyrolysis gas were estimated with a simplified procedure deriving from the Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases [16]. The gas produced flowed through a series of impinger bottles filled with acetone, after which distillation was performed [17]. Particulate matter larger than 7 μm was measured by filtering the acetone with Whatman quantitative filter paper 1452-150, separating the particles from the solvent.

In order to determine if flushing with an inert gas would create a better distribution of the temperature in the pyrolysis chamber, a flushing test with CO_2 was carried out (Figure 2).



(**a**) (**b**)

Figure 2. Fluxed pyrolyser setup: (**a**) picture; (**b**) scheme.

In this test, one of the two resistances was moved from the pyrolyser and placed on a spiral pipe in order to heat up the flow of CO_2 that flowed inside. Two flow meters were positioned to measure the input and the output flows of CO_2 together with the produced gases. To avoid the cork, which was of fine size, being transported away by the CO_2 flow and moved up to the flasks, a metal mesh was placed in the closing section of the pyrolyser.

Elemental analysis (using a Flash 2000 Organic Elemental Analyzer) and ash analysis were performed on both the dried cork powder and the obtained char in order to establish the percentages of C, H, N, S and ash.

2.2. Lightweight Aggregate (LWA) Preparation and Characterization

Expanded clay is a product resulting from the firing of clay at around 1200 °C in a rotary kiln that is obtained as a pellet [18] and commercialized under different brand names, such as LECA (Light Expanded Clay Aggregate) and LIAPOR (Porous Lias Clay). It retains its characteristics over time; does not release toxic substances, disperse fibres or particles or require stabilizing treatments; and is used in the agricultural, construction and road sectors and as a material with sound-absorbing properties and fire, mechanical and thermal resistance [19]. The UNI EN 206-1: 2006 standard [20] defines lightweight aggregate as an "aggregate of mineral origin having a density of granular particles dried in a stove $\leq 2000\ \mathrm{kg/m^3}$ determined according to UNI EN 1097-6 or a density dried in a kiln $\leq 1200\ \mathrm{kg/m^3}$ if determined according to UNI EN 1097-3".

In this work, samples were produced based on 85 parts clay and the remaining 15 weight-lightening agents, such as pyrolysis char obtained from the carbonization of cork waste at 420 °C. These percentages were optimized in a previous work [21]. Some samples were produced starting from clay, char and spent coffee grounds (Sample 1, Char 7.5%), which have been previously studied in the formulation of this type of material [22], or from clay and char (Sample 2, Char 15%). In detail:

1. Char 7.5%:
    a. 85 wt% clay (<1000 µm);
    b. 7.5 wt% char from pyrolysis at 420 °C of the cork scrap (<1000 µm);
    c. 7.5 wt% powder from exhausted, dried and sieved spent coffee grounds (<250 µm).
2. Char 15%:
    a. 85 wt% clay (<1000 µm);
    b. 15 wt% char from pyrolysis at 420 °C of the cork scrap (<1000 µm).

In the first composition, the lower amount of char was compensated with SCGs (post-consumer residue) with good performance as a porous agent. In both formulations, char from pyrolysed cork waste was used but not as it was received because in the first attempt we had problems when making prototypes that resulted in cracks, particularly following the introduction of 15% cork powder [8].

The clay, first suitably ground with a fast ball mill, was then mixed in an agate mortar along with the two pouring agents mentioned above by means of a spatula, with distilled water carefully added, in order to obtain a workable paste. It was important in this phase to ensure semi-plastic behaviour in the compound, so as to be able to create a row that could be positioned on a mechanism that would allow it to be separated into balls [23].

Small spheres with weights varying between 1.5 g and 2 g were then obtained manually from the dough, with the samples intended to be similar in weight and shape to commercial LWAs (diameter 0.6–1.0 cm).

Once the LWAs spheres were produced, they were first dried in the oven at 105 ± 5 °C for 24 h in order to remove the excess water used in the dough preparation process and then fired inside ceramic crucibles in an electric static oven preheated to a temperature of 1000 °C for 1 h in an air atmosphere. This process subjected the aggregates to a thermal shock similar to that which they would undergo in industrial processes; these latter, however, occur at higher temperatures (from 1200 °C to 1400 °C) [23]. Finally, some important parameters for the use of the aggregates were evaluated, as described below.

- **Shrinkage after firing (SF%):** this was calculated based on two measurements of diameter, post-drying (D_d) and post-firing (D_f), for ten LWA samples per formulation. Equation (1) is used:
$$SF\% = (D_d - D_f)/D_d * 100 \quad (1)$$
- **Water absorption after 24 h (WA%):** this test is governed by the UNI EN 772-21: 2011 [24] standard, and it involved the execution of a water absorption test at room temperature in which the aggregates (ten beads for each formulation) are immersed in distilled water, in such a quantity as to cover them entirely (about 200 mL of water in a beaker), and left in a static condition for 24 h. The following day, they were removed from the water, dried and weighed. The sample, after drying, was weighed before (W_i, initial weight) and after testing (W_f, final weight) with the immersion in water. The water absorption percentage WA (%) was quantified using Equation (2):
$$WA\% = (W_f - W_i)/W_i * 100 \quad (2)$$
- **Apparent density:** for the calculation of the bulk density, a GeoPyc 1360 was used in which a first "tare" analysis was carried out with graphite powder (Dryflow). The test was carried out on both samples, for each of which two aggregates were sampled in order to obtain data redundancy and greater accuracy. Some preset values were kept constant in the instrument, such as the force = 28 N and the conversion factor (in our case for spherical samples) = 0.12840. The instrument carried out five measurement cycles for each sample so that the data obtained were for the mean values and gave a standard deviation.
- **True Density:** the true density of the aggregates was measured with a He pycnometer, which calculates the volume of a porous solid (Micrometrics Accupyc 1340). Previously, ten LWA spheres were ground into a powder with a small agate mortar. The total porosity percentage (TP (%)) was obtained by processing the absolute (Mycrometrics Accupyc 1340) and apparent (Enveloped Density Micrometrics Geopyc 1360) density data, indicated as ρ_{abs} and ρ_{app}, using Equation (3):
$$\text{Total Porosity } (\%) = (\text{True density} - \text{Bulk density})/(\text{True density}) * 100 \quad (3)$$
- **pH and conductivity measurements:** pH and electrical conductivity measurements were carried out as reported in UNI EN 13,037:2012 (pH rule standard) [25] and UNI EN 13,038:2012 (conductivity rule standard) [26]. Bulk specimens (10 g) were placed in distilled water with a solid/liquid ratio of 1:5 under stirring conditions (360 rpm) for 1 h at room temperature. The liquid was filtered in order to obtain a transparent liquid fraction; with this eluate, the pH and electric conductivity were measured.
- **Mineralogical analysis:** mineralogical analysis was carried out with an X-ray powder diffraction analyser (PW 3710, Philips Research Laboratories, Eindhoven, the Netherlands) with Ni-filtered CuKa radiation in the 5–70° 2θ range and a speed of 1°/min, operating at 40 mA and 40 keV. Highscore Plus software version 3.0 coupled to the International Centre for Diffraction Data (ICDD) cards database was used to identify the crystalline phases with a qualitative method.
- **Microstructural analysis (SEM):** microstructural analysis was performed using SEM (Model XL40, Philips Research Laboratories, the Netherlands) coupled with X-EDS equipment (Model QUANTAX-200, Bruker, MA, USA) and the following beam voltage operative conditions: 25 KW; spot size: 5.0; pressure: 0.60 Torr; working distance: 12–13 mm. Thanks to the scanning electron microscope, it was possible to carry out investigations relating to the morphology and microstructure of the materials in order to analyse the shape and size of the grains, the porosity and the defects and inclusions present. It was also possible to perform mineralogical characterizations to identify the phases within a material, determine their concentrations and search for the presence of heavy metals. The following samples were subjected to microstructural analysis: (i) char sample produced by pyrolysis at 420 °C; (ii) char sample produced by pyrolysis

at 640 °C; (iii) LWA char 7.5% internally and externally; (iv) LWA char 15% internally and externally.

2.3. Preparation and Characterization of Porous Ceramics

Nowadays, porous materials are considered very interesting and find different applications in catalysis, separation, lightweight structural materials, biomaterials and so on. In the construction sector, their application allows energy saving and thermal and acoustic insulation [27].

Several cylindrical specimens (40 mm Ø × 4 mm) with char ratios from 5 to 15% and a local red clay were created, all pressed to 30 MPa after humidification (7% distilled water) and then left to rest in an air-free container for 1 h in order to homogenize the humidity. All the samples obtained were then first dried at 105 °C for about 24 h, to eliminate all traces of free water, and subjected to thermal treatment in a static stove, placed in a cold stove and fired with a heating rate of 10 °C/min up to 1000 °C for 1 h. The weight loss between the drying and firing phases was evaluated by weight difference using a Bel Engineering M124A analytical balance with an accuracy of 0.0001 g. The shrinkage from firing was evaluated from the difference between the diameter of the dried specimen and the diameter of the fired one using a digital calliper. Finally, the bulk density of the fired samples was evaluated by measuring their volume and weight. Two families of porous ceramic materials were created:

1. A series obtained by substituting 5, 10 and 15 wt% of clay for char produced by pyrolysis at 420 °C and sieved below 1000 μm in order to keep the particle size as close as possible to that of the clay matrix;
2. A series based on finer char, below 250 μm, in order to investigate whether reducing the cork grain size would make it possible to improve the compaction and density of the brick created. In this case, 5 and 10 wt% of the total clay was substituted for char.

For each series, the following were calculated:

- Linear shrinkage (LS%)

$$LS\% = (d_{\text{mean initial}} - d_{\text{mean final}})/d_{\text{mean initial}} * 100 \tag{4}$$

which was calculated after drying using the diameters of the fresh and dried specimens and after firing using the dried and the fired specimens

- Weight loss (WL%):

$$WL\% = (W_i - W_f)/W_i * 100 \tag{5}$$

- Volume of the fired cylinder;
- Bulk density of fired ceramics (which took into account the internal porosity).

3. Results

3.1. Pyrolysis Test and Char Characterization

Table 1 summarizes the main results of the pyrolysis tests. T-Const and T-Max are the average temperature and the maximum peak temperature reached during the pyrolysis process, respectively. It can be seen that the loss in mass was slightly greater in the higher temperature test (as was expected). The gas production during the fluxed pyrolysis was not detected because the outlet gas flow was very similar to the CO_2 flow of about 2.1 L/min; a more accurate measurement system would have been needed to detect small flow differences.

Table 2 reports the results of the filtration and distillation tests using the tar and particulates sampling method [16]. The non-fluxed pyrolysis tests, despite the temperature difference, did not show substantial differences (slightly less dust but more tar in the lower temperature test); however, there was an important difference in the powders of the fluxed test, which were 10 times higher than their non-fluxed counterparts, a fact probably deriving from the turbulent influence of the fluxed CO_2 on the transport of the powders themselves. Fluxed pyrolysis also resulted in higher tar yield. This was in accordance with the literature; in fact, gas sweeping drags the hot vapours and organic compounds out of the pyrolysis zone, stopping secondary reactions such as repolymerisation [28,29].

Table 1. Temperatures and mass losses from the pyrolysis tests.

Test	T-Const (°C)	T-Max (°C)	Initial Mass (g)	Final Mass (g)	Mass Loss (%)	Gas Production (L)
Pyrolysis T = 420 °C	420	517	19.44	8.31	57	1.8
Flux pyrolysis T = 420 °C	415	475	20.81	10.42	50	-
Pyrolysis T = 640 °C	638	650	18.60	6.88	63	1.5

Table 2. Tar and particulates sampling analysis results.

Sample	Particulates (g)	Tars (g)
Sample pyrolysed at 420 °C	0.0077	1.8090
Sample pyrolysed at 640 °C	0.0103	1.4241
Sample pyrolysed at 420 °C (fluxed)	0.0771	2.5664

The elemental analysis, summarized in Table 3, did not reveal substantial differences between the char obtained from the various tests, but there was a slightly higher carbon and ash content in the higher temperature one.

Table 3. Elemental analysis results.

Material	N%	C%	H%	S%	ASH%
Dry cork powder	0.88	63.33	8.53	-	0.52
Dry cork powder pyrolysed at 420 °C	0.76	73.95	9.95	-	0.76
Dry cork powder pyrolysed at 640 °C	1.32	76.75	7.84	-	1.71
Dry cork powder pyrolysed at 415 °C (fluxed)	1.27	71.11	9.09	-	1.10

To measure pH and electrical conductivity, 10 mL of char powder was sampled, diluted in a 5:1 ratio in distilled water (50 mL), placed on a stirrer for 1 h and then filtered. The results listed in Table 4 show that, although a more basic pH was possessed by the sample pyrolysed at 640 °C, this latter had a lower electrical conductivity (which represents the dissolved salts), indicating a lower ionization. It should also be remembered that, for use in the agronomic field, materials must have a pH between 6.5 and 7.5 [25] and an electrical conductivity of less than 2 mS/cm [26].

Table 4. pH and electrical conductivity of the pyrolysed samples.

Property	Char 420 °C	Char 640 °C
pH	7.05	7.70
Electrical conductivity (mS/cm)	0.396	0.340

By measuring the on and off times of the resistors and knowing their operating power, it was possible to measure the specific energy consumption for these particular experimental setups. Figure 3 shows the specific energy spent in heating the cork waste for different types/temperatures of pyrolysis. It does not take into account the relative energy losses of the system. Among all the analysis shown, none of the fluxed pyrolyses at 420 °C produced a completely carbonized material using the lower amount of energy; for this reason, only chars obtained with this process were used for the following material formulation.

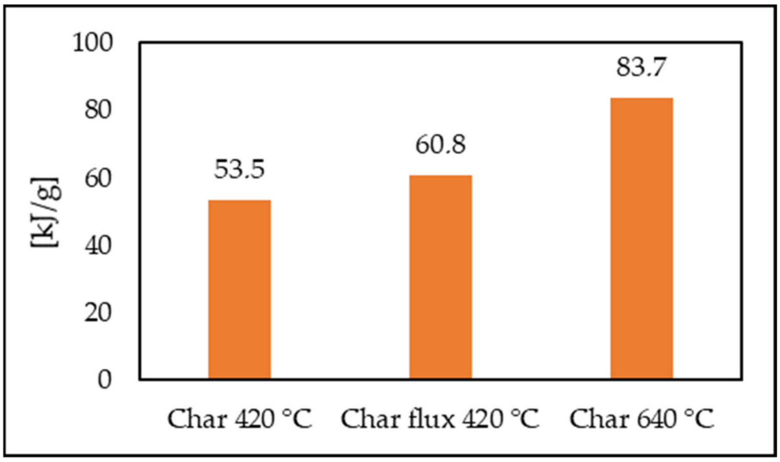


Figure 3. Specific energy used to pyrolyse cork waste samples under different conditions.

3.2. LWA Characterization

3.2.1. Physical and Chemical Properties

Table 5 summarizes the properties of the LWAs obtained; the data were compared to the reference sample containing only clay.

Table 5. LWA characterization results.

Property	Char 0% (Only Clay)	Char 7.5%	Char 15%
Water absorption (%)	7.27	24.14	26.26
Weight loss (%)	16.50	23.40	20.40
Shrinkage after firing (%)	7.50	7.19	6.75
True density (kg/m^3)	2690 ± 1.1	2725 ± 1	2715 ±0.4
Apparent density (kg/m^3)	1330 ± 2.0	951.7 ± 2.4	924.0 ± 1.7
Porosity (%)	50.55	66.10	64.94
pH	7.16	7.22	7.41
Electrical conductivity (mS/cm)	1.15	0.345	0.311

The percentage of weight loss is an index that helps to understand how much water, organic material and other volatiles are lost from the aggregates subjected to the various thermal cycles mentioned above. After firing, the weight loss was slightly greater in Char 7.5% (due to the presence of coffee in this sample (23%)) compared to the sample containing only char (20%), so we can assume that the added char and coffee waste behaved in similar ways.

Water absorption after 24 h was around 25%, with no significant differences between the two kinds of samples.

As regards density, it is possible to note from the results that the LWAs obtained had an apparent density < 1200 kg/m^3, which is characteristic of light aggregates, a positive parameter that resulted in their lightness and high porosity. The Char 0% sample without a pore-forming agent did not fulfil the requirements. Furthermore, it can be seen that the LWAs containing only char (Char 15%) were slightly lighter than those with char and coffee (Char 7.5%). The true density depends on the composition of the aggregates, and it can be seen that there were no significant differences between the two prepared compositions, which are very close to the true density of the sample containing only clay. Further, the total porosity was calculated using the bulk and true densities with Equation (3). The aggregates (both Char 7.5% and Char 15%) had porosity percentages around 65%, compared to 50% for Char 0%, due to the fact that, during firing, the unburned organic matter present in the pyrolysed char and present in the SCG burned with the development of gas, which allowed the formation of pores. From these results, it can be seen once again how the char used behaved similarly to coffee waste, a positive factor in its reuse since it is suitable both as a pore-forming agent and as a weight and density reducer. Figure 4 shows the LWAs obtained using the high percentage of Char (15%).

Figure 4. LWA material obtained with 15 wt% Char in the composition.

Two tests were carried out for both pH and electric conductivity in order to improve reproducibility. The data obtained showed how the pH settled at neutral values for the LWAs created, which are optimal for subsequent use in the agronomic field. As regards the specific conductivity of the aggregates (measured in mS/cm), in general, 2 mS/cm represents the limit at which the soil is suitable for any type of crop and, consequently, is not subject to any risk [30,31].

In this case, all the results obtained fell well below this limit, which allows us to think about the use of these aggregates in any type of soil.

It should be noted that, on average, the Char 15%, while presenting a greater amount of char, resulted in LWAs with a lower electrical conductivity.

Given its neutrality and its low electrical conductivity, Char 15% was selected as the best sample for agronomic use, as it allowed reuse of an amount of pyrolysis waste double that of Char 7.5%.

3.2.2. Mineralogical and Microstructural Analysis

XRD patterns of the two LWA formulations (Figure 5) indicated that there were no particular differences between the two from the qualitative point of view. The crystalline phases identified were the same and derived from the fact that the clay was rich in iron and the carbonatic phase, demonstrating that char introduced in the clayey matrix did not change the type of mineralogical composition.

SEM was used to analyse the microstructure of the biochar obtained after pyrolysis (Figure 6). The pores formed in the biochar during the pyrolysis process were visible on the surface of the material and were attributed to both the nature of the original input material and to the release of volatile and organic substances during the thermal process. The concentration of C in the biochar was determined using EDS.

Regarding the LWAs obtained, the cross-section images for Char 7.5% (Figure 7) show a particular morphology. The images (Figure 7a,b) show how the porosities were homogeneously distributed, with the presence of very small pores, between 1–5 μm. EDS (Figure 7c) was used for the elementary semi-quantitative analysis, which confirmed a silicate matrix given the strong presence of Al, Si, K, Ca, Mg and Fe.

On the external surface (Figure 8), there was both a lower porosity and a smaller average pore size (1–2 μm) compared to the internal section. This was certainly due to the formation of a glassy phase during the flash-firing, which improved the sintering. From the SEM images (Figure 8b), it is possible to notice the presence of small, white crystals of about 1 μm in size, rich in iron and probably related to the ferruginous clay used.

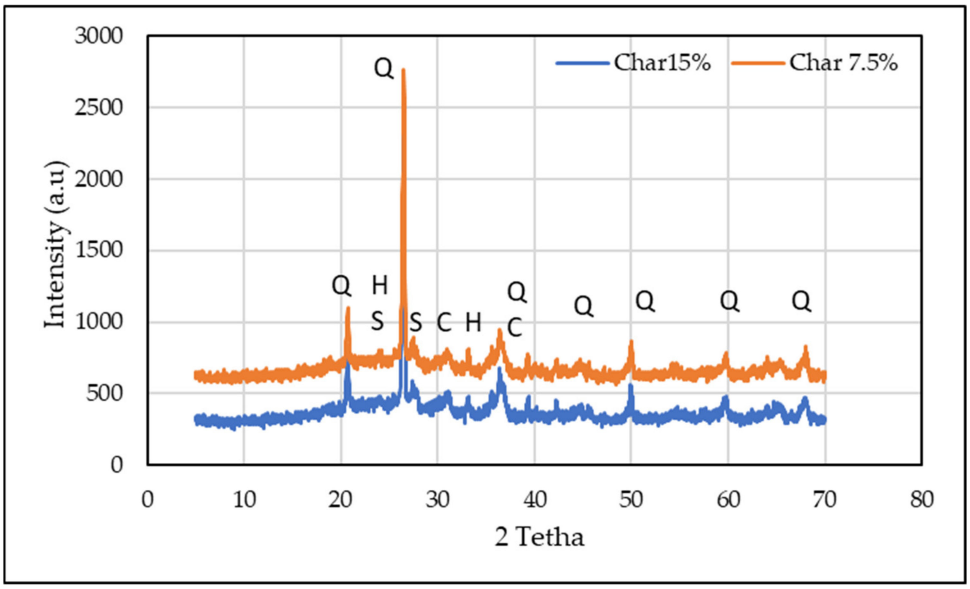
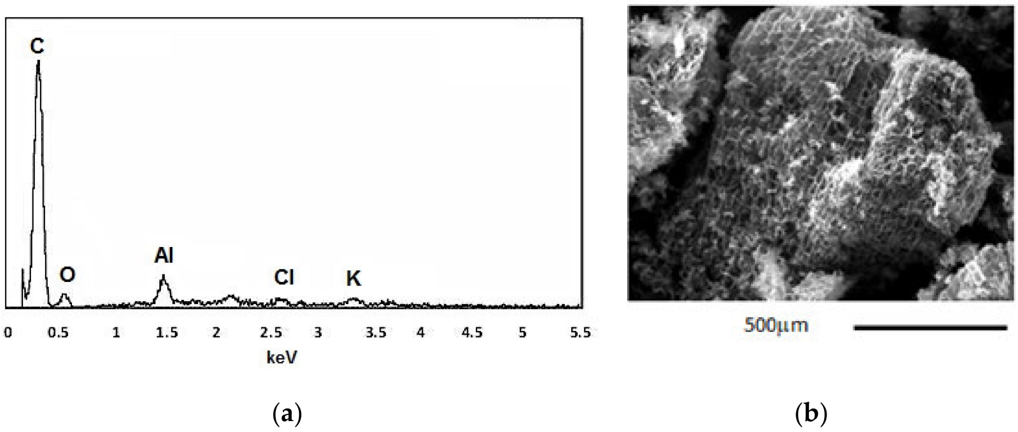
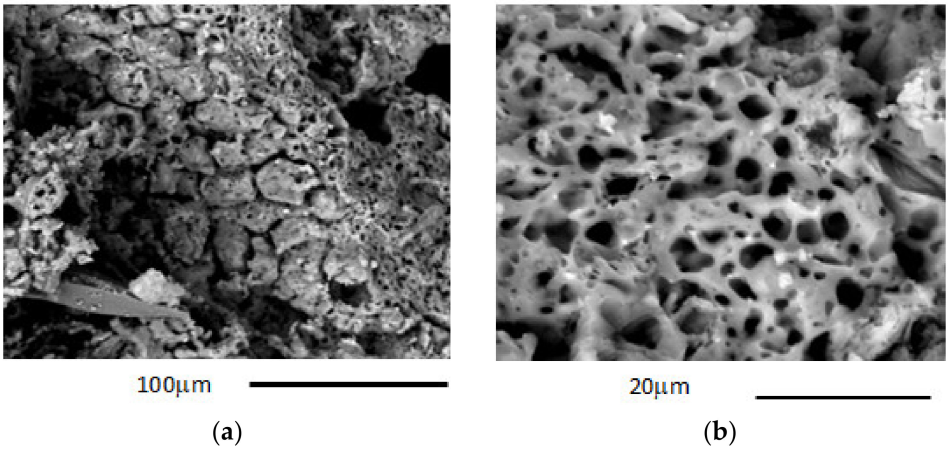


Figure 5. XRD patterns of Char 7.5 wt% and Char 15 wt% samples. Q = quartz: SiO_2; S = sanidine: (Na, K)(Si_3Al)O_8; H = hematite: Fe_2O_3; C = Calcite: $CaCO_3$.



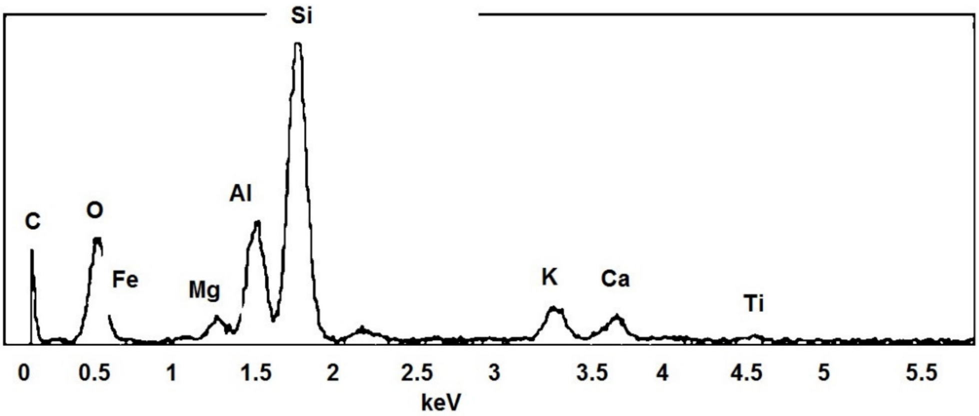
(**a**) (**b**)

Figure 6. EDS spectrum (**a**) and SEM micrograph (secondary electrons) (**b**) of Char pyrolysed at 420 °C.



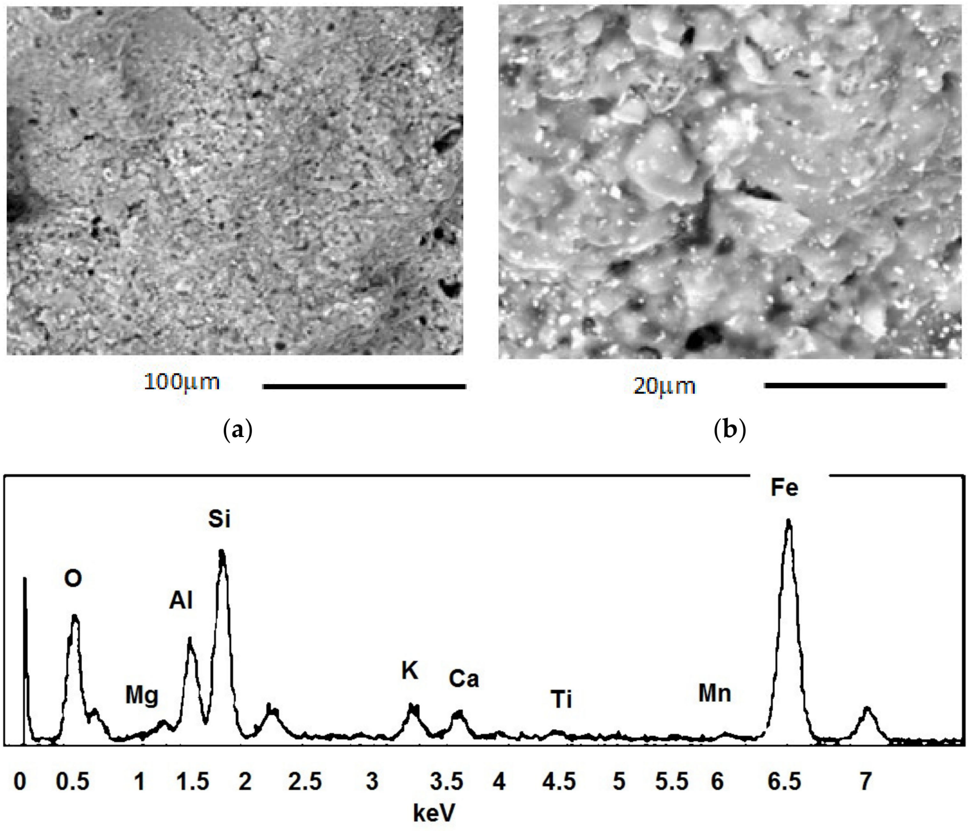
(**a**) (**b**)

Figure 7. *Cont.*



(**c**)

Figure 7. SEM micrographs (backscattered electrons) of a cross-section of the LWA Char 7.5% sample with magnification of 600× (**a**) and 2400× (**b**), along with the relative EDS spectrum (**c**).



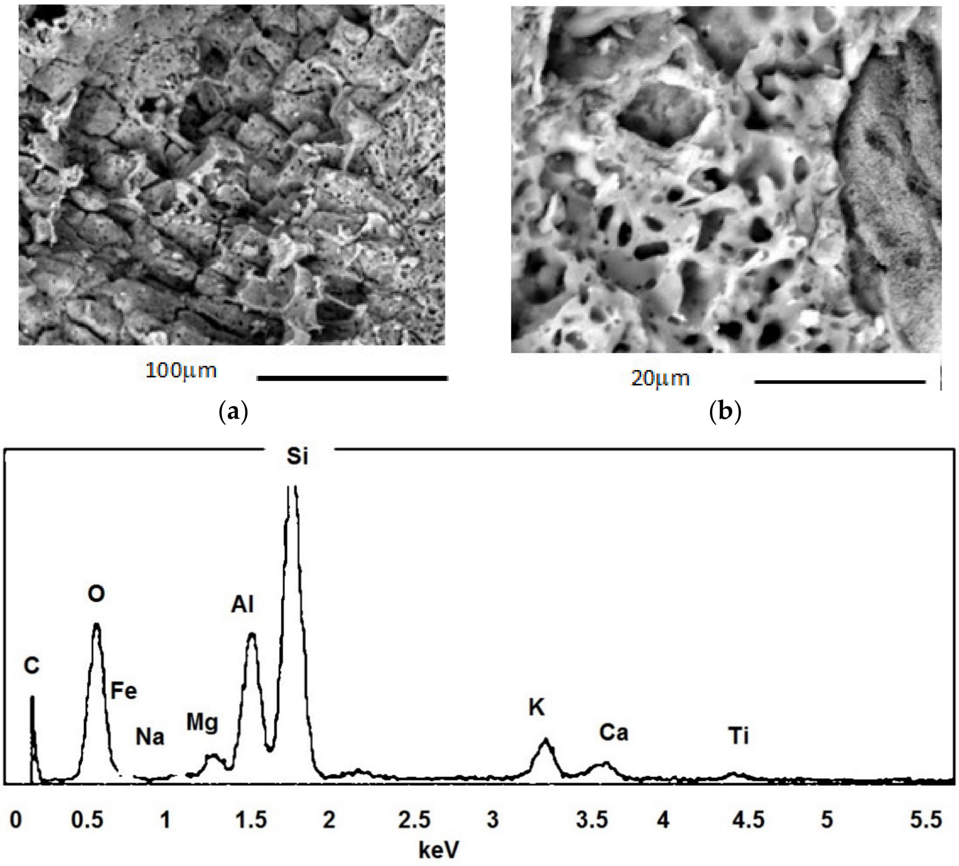
(**a**) (**b**)

(**c**)

Figure 8. SEM micrographs (backscattered electrons) of LWA Char 7.5% external surface with magnification of 600× (**a**) and 2400× (**b**), along with the relative EDS spectrum (**c**).

Concerning the Char 15% sample, it is possible to see from the SEM images at 600× (cross-section) the presence of geometric formations with long-limbed development, probably due to areas of accumulation of char, and which had porous holes of the order of 1–5 µm (Figure 9a). These conformations with particular geometries were composed mainly of clay minerals, confirming the complete decomposition of char, which resulted in porosity slightly more irregular than the Char 7.5% sample.

The SEM image at higher magnification (Figure 9b) shows pores with dimensions slightly smaller than those of the Char 7.5% samples and a more vitrified nature, although the composition remained clay. For the external surface, similar conclusions as for the Char 7.5 sample can be drawn.



(**a**) (**b**)

(**c**)

Figure 9. SEM micrographs (backscattered electrons) of a cross-section of the LWA Char 15% sample with magnification of 600× (**a**) and 2400× (**b**), as well as the relative EDS spectrum (**c**).

The differences between the two LWA samples, such as the different homogeneities of the porosities and the sizes of the pores, were attributed to the much greater volume of char in the Char 15% sample rather than to the different percentages of char used. Indeed, it is possible to see how cork char behaved similarly to coffee as a pore-forming agent, but the difference between the two materials lay in the specific weight and, therefore, in the lower density of the cork, which led to the higher volume used.

3.3. Characterization of Porous Ceramics

In the first series (grain size <1000 micron), three compositions were created using different percentages of char mixed with clay: 5% (PC 5%), 10% (PC 10%) and 15% (PC 15%). Table 6 summarizes the characterization of these samples, which showed acceptable consistency for 5 wt% of char, slightly crumbly consistency for 10 wt% and extremely crumbly consistency for 15 wt%. The data were compared to the reference sample containing only clay (PC 0%).

Table 6. Physical properties of porous ceramics (<1000 µm).

Sample	**Water Absorption (%)**	**Weight Loss (%)**	**Shrinkage after Firing (%)**	**Apparent Density (kg/m^3)**	**Total Porosity (%)**
PC 0%	15.60	12.00	1.15	1550.0	40.80
PC 5%	19.26	12.92	2.42	1576.8	42.15
PC 10%	29.01	17.88	2.96	1134.5	58.35
PC 15%	-	18.25	3.88	918.6	66.2

The total porosity was calculated, as in the case of the LWAs, using the apparent density and the real density (Equation (3)).

Furthermore, as the percentage of char in the compound increased, an increase in the final porosity and water absorption was noted, even if, as previously mentioned, the 10% and 15% samples could not be considered reliable given their high fragility and tendency to deteriorate. As can be observed in Figure 10, the samples containing 15 wt% (the last ones on the right) exhibited flaking and were not perfectly sintered. The weight loss increased with the increase in the amount of char used in the composition due to its thermal decomposition, which also corresponded to a reduction in the weight of the materials obtained.

Figure 10. Porous ceramics containing the three increasing percentages of Char (grain size <1000 micron) from left to right.

As a result of the fragility of the samples containing more than 10 wt% of char, a second series of specimens was realized by using sieved char smaller than 250 µm up to the level of 10 wt% of char due to the high corresponding volume. These samples showed better results (Table 7) as regards the compactness of the porous ceramics created.

Table 7. Porous ceramics (<250 µm) characterization results.

Sample	Water Absorption (%)	Weight Loss (%)	Shrinkage after Firing (%)	Apparent Density (kg/m^3)	Porosity (%)
PC 5%	18.07	12.67	2.73	1653.2	39.3
PC 10%	31.36	17.11	2.68	1266.4	53.6

By comparing the results for the porous ceramics of the first series, below 1000 µm, and those of the second, below 250 µm, it is possible to note that the latter, despite having similar shrinkage and weight loss values, had a slightly higher apparent density, thus resulting in specimens with a lower total porosity due to the higher degree of sintering. Considering that only 8% of the total char obtained by pyrolysis resulted in <250 microns, it is possible to conclude that this operation would not be environmentally viable.

As regards the mineralogical composition of the porous ceramics produced, they were mainly composed of quartz (SiO_2), and hematite (Fe_2O_3) and sanidine ((Na, K) (Si_3 Al) O_8) were also present. Comparing the mineralogical results for the porous ceramic containing 5% char (Figure 11) with the LWA containing 7.5% char (Figure 5), it can be seen that, in the samples pressed and fired in a slow-firing cycle, there was a more pronounced crystallinity (demonstrated by the flattening of the baseline). Furthermore, the disappearance of the calcite occurred, which was certainly decomposed during the thermal treatment.

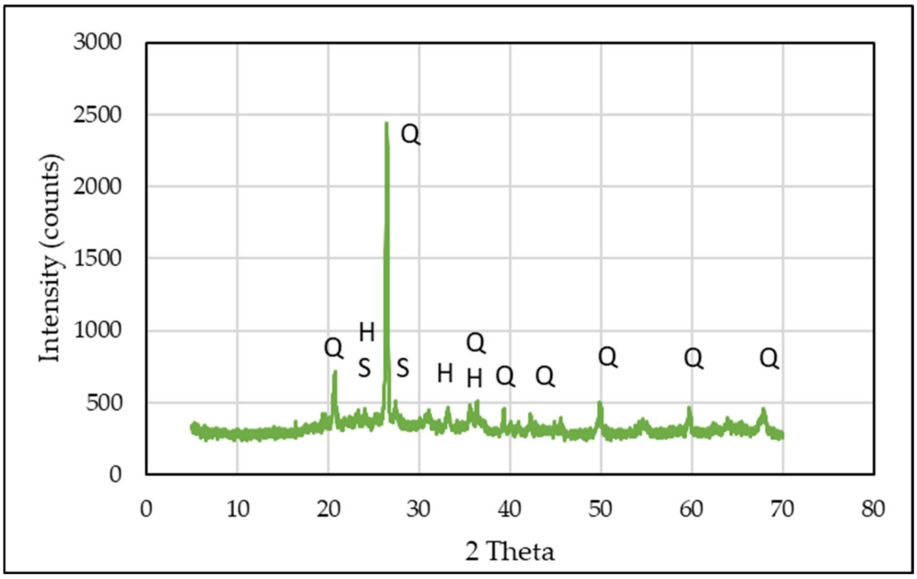


Figure 11. XRD pattern of porous ceramic sample containing char 5 wt%. Q = quartz: SiO_2; S = sanidine: $(Na, K)(Si_3Al)O_8$; H = hematite: Fe_2O_3.

4. Discussion

The main objective of the study was to search for a method of valorisation of industrial cork production waste and obtain the recovery of material to produce two different materials: lightweight aggregates and porous ceramics.

The project activities suggest the possibility of reusing cork waste in a sustainable way, and the fine grain size of the waste makes it possible to directly reuse the material, which therefore does not require prior grinding. In light of its possible application as a weight-lightening agent in clay-based materials, the neutral pH of the char derived from the pyrolysis of cork dust is important, giving the final product (the lightweight aggregates) a value in the optimal range for plant comfort (6–8), favouring pH and conductivity levels that are appropriate for agronomic use. Use in bricks would also lead to a strong weight-lightening effect, with a significant reduction in the bulk density of the materials and an increase in porosity.

The pyrolysis of cork residue was proven to be possible and involved a reduction in volume, mass (60%) and pollutant load; the SEM/EDS analysis also showed the absence of residual heavy metals and high porosity. Analysing all these results concerning the pyrolysis performed at different temperatures, we opted for the use of the char produced at 420 °C (not fluxed), since that produced at 640 °C did not have different characteristics that would justify the higher energy consumption needed to reach this temperature. We also opted for the char deriving from non-fluxed pyrolysis since the greater complexity of the flushing system did not guarantee concrete advantages in heat distribution during the process.

For lightweight aggregates and porous ceramic materials, we concentrated on a characterization that could give information on the porosity of the material, its lightness and its microstructure, as well as its chemical stability. The tests on the aggregates showed how the organic matter decomposed by combustion could obtain a high porosity value, which in turn increased the water absorption value, allowing the retention of water which is so useful for plants. The XRD and SEM/EDS analyses carried out on the prototypes also confirmed that the inclusion of this char in the composition did not significantly affect the crystalline structure of the aggregates, which remained almost the same as that of the waste-free mixture (the red clay (Char 0%)). Comparing the aggregates formed with (Char 7.5%) and without the use of coffee waste (Char 15%), it was seen that the pyrolysed cork waste behaved similarly to the coffee. It can therefore be said that the use of this waste in the production of light and porous ceramic aggregates containing clay is a valid means to enhance the waste from the cork processing industry, offering the possibility of obtaining a resource for agronomic and construction purposes, as well as for roof gardens, green roofs and hydroponic crops.

Positive results were also found regarding the porous ceramic materials (char < 1000 µm); however, they highlighted the impossibility of using the materials created with char percentages higher than 5% (10% and 15%) due to their fragility. In the second formulation of these samples, in which pyrolysed and sieved cork powder smaller than 250 µm was used, characterization results comparable to those for the first formulation were obtained, but with better visual characteristics for the specimens that would allow their use with char percentages up to 10%. However, the fraction below 250 µm represented only 8% of the total char created by pyrolysis; therefore, this path is not recommended because there would be too high a percentage of unused waste, which would not justify the better properties or the increase of up to 10% char in the material. It would therefore be interesting for the future to deepen the characterization for the purposes of construction of porous ceramic products sieved to sizes below 1000 µm and with char percentages of 5% of the total.

Based on the results obtained, it could be very interesting to evaluate other possible applications of these aggregates in a wider context of sustainable construction (weight-lightened concrete, roof gardens and green roofs).

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