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Article

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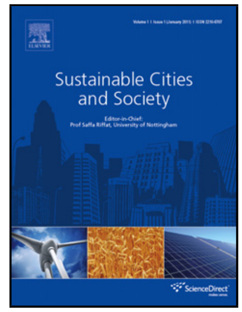

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Plant biomass ashes in cement-based building materials. Feasibility as eco-efficient structural mortars and grouts

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Highlights

- Plant biomass ash as partial replacing binder in cement-based structural compounds.
- Pollution mitigation and structural performance.
- Advantages and disadvantages as cement substitute are highlighted.
- GWP and EE are calculated.
- Properties that require additional research are pointed out.

Abstract

The use of plant biomass ash, as partial replacing binder in cement-based structural mortars or grouts, is an interesting eco-friendly alternative within the building industry. Besides, recycling those ashes makes possible to reduce the polluting wastes that are accumulated in landfills, improving sustainability. On the basis of the data obtained from the literature, this paper analyses the feasibility of using plant biomass ashes in eco-efficient structural mortars or grouts. The research focuses on issues that are directly related to the pollution mitigation and to the structural performance. Physical-chemical properties (pozzolanic activity and mechanical characteristics), rheological behaviour, setting times and drying shrinkage, durability and environmental features are analysed. In addition, the global warming potential and embodied energy of the plant biomass ashes- based mixtures are calculated, assuming that they will be used to grout hollow concrete units (CMUs), in order to obtain green grouted blocks. Advantages and disadvantages of each waste as cement substitute are highlighted. Besides, the properties or characteristics that require additional research are pointed out (e.g. durability and environmental impact). Conclusions from this work could be used to foster further research on the use and development of those eco-efficient building materials.

Keywords

Eco-efficient materials; Cement substitute; Biomass ash; Plant wastes; Eco-friendly construction; Environmental impact (GWP and EE).

1. Introduction

Every year, the cement industry is responsible for approximately 5-8% of the worldwide CO_2 emissions, provoking a significant environmental impact. Building construction is highly responsible for contamination due to energy demand and CO_2 emissions [1]. Thus, the use of eco-efficient building materials and the re-use/recycling of building structures are great challenges for the present-day architecture and civil engineering. In order to minimize this negative effect, it is crucial to find out alternatives to conventional cement. It is worth noting that the pollution is caused not only by the energy consumption, but also for the high amount of wastes that are produced.

Alternatives to Portland cement are also regarded in Codes (e.g. Eurocode EC2 and ACI standards) and are a current area of active research. The literature offers a wide range of different organic and inorganic replacing materials, analysing different features. Thus, Aprianti et al. [2] review the potential uses of agricultural wastes as cementitious material in the production of concrete, focusing on rice husk ash, palm oil fuel ash, bagasse ash, wood waste ash, bamboo leaf ash and corn cob ash. Vo and Navard [3] review the treatments of plant biomass for cementitious building materials. Brás and Faustino [1] analyse the potential of using non-classical additions in concrete and mortar compositions such as coal bottom ash (BA) and biomass ash (Bio), as partial replacing binder of ordinary Portland cement, by means of rheological optimisation. [1]. Madurwar et al. [4] review the application of agro-waste for sustainable construction materials. Rajamma et al. [5] characterize some biomass fly ashes obtained from a thermal and co-generation power plant to study new cement formulations. Salvo et al. [6] valorise biomass ashes and evaluate their use as supplementary cementitious material in the cement industry, analysing ashes from woodchip and straw power plants. Paris et al. [7] review waste products that are utilized as supplements to OPC in concrete, analysing four plant ashes (sugarcane bagasse, rice husk, palm oil and biomass combustion ashes).

Usually, organic waste materials are burnt to reduce their volume or to obtain energy. After that, when their use has finished, they are disposed into landfills. Contaminant compounds such as heavy metals are part of those wastes [8, 9]. According to Demirbas [10], the ash properties depend on the plant species and growth conditions (including the soil contamination). Additionally, Vamvuka [11] assures that heavy metals contained in the ash residues may pose a significant risk to the environment, due to the possible leaching into underground and surface waters, affecting health. Recycling those ashes allows lengthening their life, reducing the polluting wastes that are accumulated in landfills, and improving sustainability.

Under those premises, this research (after reviewing a number of published works) analyses the feasibility of partially replacing the ordinary Portland cement (OPC) by different wastes, in particular biomass ashes. The review presented in this paper focuses on issues that are directly related to the pollution mitigation and to the structural performance.

This review is organized as follows: after providing a general description of each plant biomass ash, the second part analyses the main physical-chemical properties, focusing on pozzolanic activity and mechanical properties. After that, the third part studies the rheological behaviour, analysing flow spread, consistency, workability and morphological features obtained from SEM images. In the following section, setting times and drying shrinkage, of each waste are analysed. The fifth part is devoted to durability and it focuses on resistance to chloride ion penetration and sulfate resistance. The following parts deal with environmental issues. In addition to the review and analysis, the global warming potential and embodied energy are provided, assuming that the OPC/biomass-based compounds will be used to grout hollow concrete units (CMUs), in order to obtain green grouted blocks. The last part of the paper offers a summary of the main insights, analysing the feasibility of using these compounds as eco-friendly materials. Additionally, the properties or characteristics in which further research is still required, in order to complete databases, are pointed out.

2. Plant biomass ashes: general description

On the basis of the literature review, the following plant biomass ashes will be analysed: rice husk ash, palm oil fuel ash, sugarcane bagasse ash, wood waste ash, bamboo leaf ash, corn cob ash, olive biomass fly ash, agave biomass ash, cork waste ash, wheat straw ash, waste paper sludge ash and coconut shell ash. In the next sections, a general description of each plant waste is provided.

2.1. Rice husk ash (RHA)

Rice is, among the analysed raw materials, the most abundant agricultural product. Around 740.2 million tons of rice were produced in 2015 [12], being China the main producer (around 200 million tons annually [13]). From those quantities, a high volume of rice husk is obtained (more than 20%) which is the agricultural residue obtained from the outer covering of rice grains during milling process [14]. Rice husk ash is a carbon neutral green product gained from raw rice husk that is converted into ash using a combustion process (**Fig. 1**). Different combustion procedures can be applied but generally, it is carried out in a furnace at 600ºC-800ºC [2]. The combustion of rice waste has been widely used for heat and power generation in Europe and North America [15] and some underdeveloped countries find in rice a potential opportunity to generate energy (e.g. [16]). RHA has been widely used as an adsorbent of organic dye, inorganic metal ions, waste gases and as support catalyst [17].

2.2. Palm oil fuel ash (POFA)

Palm oil is one of the largest edible oil, with approximately 25% of the global production [19] [20]. Although it has received negative criticism related to its nutritional facts and environmental impacts [20], different research (e.g. [21] [22]) have proven that it is a sustainable crop. Palms generate a large amount of waste in form of empty fruit bunches, fibres and kernels [23]. Those by-products are normally used as fuel to heat up boilers for electricity generation in palm oil factories [24]. The ashes that are obtained from the combustion process of palm oil (POFA) can be used as cement substitute [25], (**Fig. 2**).

2.3. Sugarcane bagasse ash (SCBA)

The worldwide production of sugarcane is around 1,700.00 million tons [26]. When juice is extracted from the sugarcane, the solid waste material is known as sugarcane bagasse. Bagasse and molasses are by-products from the sugar industry that are commonly used in energy plants [27]. When bagasse is burned under controlled conditions, the ashes exhibit good properties to be used as cement-replacing [28] (**Fig. 3**). In addition, sugarcane bagasse ash is used for fertilization of sugarcane fields [27].

2.4. Wood waste ash (WWA)

Wood waste ash is generated by the combustion of wood, generally to produce energy (**Fig. 4**). Wood wastes are one of the more preferable fuels for biomass furnaces because, when compared to other herbaceous and agricultural wastes, less residual materials are produced [29]. The applications of wood fly ash are the following: 70% is disposed as landfill waste, 20% is recycled as supplement to improve alkalinity of soil, and 10% is used for several applications, including construction materials, metal recovery and pollution control [30]. An interesting option is the wood pellet ash. The world's production of plant fuel pellets is roughly 13 million tons per year, and pellets' consumption in Europe is predicted as 50 million tons per year in 2020 [31].

2.5. Bamboo leaf ash (BLA)

Bamboo is the common term applied to a broad group (1,250 species) of large woody grasses [32]. Total bamboo forest is around 0.8% of the world’s land area (31.5 million ha), and 5.7 million ha of bamboo forest are in China [33] . The worldwide production of bamboo generates large volumes of leaf wastes, which are deposited in landfills or burned in an uncontrolled manner, with negative environmental effects. The ash obtained by calcination of the bamboo leaf waste is known as bamboo leaf ash and shows good properties as supplementary cementing material for the production of blended cements [34] (**Fig. 5**). It is considered as one of the fastest-growing and highest-yielding renewable natural building material, and its use provides the most economic and socially useful outlet for bamboo chips [35].

2.6. Corn cob ash (CCA)

Corn cob is an agricultural waste product obtained from maize or corn, both important elements of the food industry [37]. The corn cob ash is a fineness waste that is produced in the boilers of the animal feed industry [38] (**Fig. 6**). It is used to obtain energy, as corn cob has a high content of cellulose and hemicellulose. Therefore, it is one of the most potent feedstock for production of biofuels using biochemical process [39]. The worldwide production is around 589 million tons of maize, being South Africa and Nigeria the main producers [40].

2.7. Olive biomass fly ash (OBFA)

The worldwide production of olive fruit is around 3.10 million tons per year [42], being Spain one of the main producers (e. g. there are 1.4 million hectares of olive crops only in Andalusia [43]). Around 3.7 million tons of olives per year are used to make olive oil (800,000 tons/year) and the rest to obtain olives (300,000 tons/year), to be consumed as table olives [43]. Furthermore, olive crops generate 4.2 million tons/year of pruning residues [44]. In Andalusia, there are 19 plants that use biomass to generate a total of 205.3 MW of electrical energy [44] and the majority of these installations use olive trees residues as fuel [43]. The OBFA is obtained from the combustion in cogeneration plants of olive-pomace and olive stones [44] [45] (**Fig. 7**).

2.8. Agave biomass ash (ABA)

Agave bagasse is a by-product generated in the mezcal industry [47]. Mezcal is an alcoholic beverage and it is used in other products such as food and candies [48]. The agave wastes (roots, leaves, bagasse and vinasse) represent almost 50% of the plant weight [49]. Usually, after being dried and burned, a by-product is generated in the form of residual ash, which is polluting and is called agave biomass ash [47] (**Fig. 8**). It is also used to produce energy in power plants [50]. Corredor González et al. [51] estimated that approximately 4.5 million tons of agave salmiana, the most efficient specie as grows in semiarid regions, are produced annually [52]. It is important to take into account that there are several barriers to the large-scale implementation of agave, because it is an expensive feedstock [49].

2.9. Cork waste ash (CWA)

Cork is a natural product obtained from removing (each 9 years) the outer bark of the cork tree. Their extraordinary mechanical and physical properties have been analysed by different research [53, 54]. The main cork applications are the by-products [55]. Recent research focus on the feasibility of using cork as contributor to the improvement of sustainability and a less consume of energy [56]. That product is predominantly located in Portugal, Spain, and Algeria [57]. The worldwide production is approximately 340 thousand tons per year and Portugal leads the production (52% of the total) [58]. Europe produces more than 80% of the worldwide production, and annually 68,000 to 85,000 tons are considered waste materials [56]. Around 20% to 30% of the raw cork received at the processing units is discarded, mainly as cork dust [59]. That cork powder is generated from grinding, cutting and finishing operations throughout the industrial cork process [60]. Cork waste ash is the result of cork industries where the cork powder is used mainly as fuel [60]. The CWA is generally deposited in landfills, increasing pollution [60]. But, due to its good properties and compatibility with cement, it is possible to reuse it. Before using the CWA, it must be dried at 105±5 Cº for 24 h [60].

2.10. Wheat straw ash (WSA)

Wheat straw is the main agricultural by-product of the wheat producing process. The annual worldwide production of wheat is around 653 million tons [26]. Part of the wheat straw is used as feedstock for the paper industry, fuel of biomass power plants and cattle food [61]. Wheat straw ash (**Fig. 9**) is generally obtained following this procedure: straws are collected and reduced to sizes and packed, and after that, they are burned in electric furnaces and then cooled [62]. Some wastes are burnt out directly in the farmland after harvesting [63] without productive use, causing environmental pollution [64].

2.11. Waste paper sludge ash (WPSA)

The global paper and paperboard worldwide production is approximately 394 million tons, and China is currently the largest producer (23.5% of the total production) [66]. That high production causes high waste generation. For instance, in the United States, waste paper accounts for approximately 40% of the total waste, which is equivalent to almost 72 million tonnes of wastepaper annually [67]. In Europe, 11 million tonnes of waste are produced annually (70% from the production of de-inked recycled paper [68]). Paper sludge is a solid waste material composed of short pulp fibres, contaminants and other papermaking components such as clays and fillers [69]. The paper sludge is burnt in fluidized beds where two types of ashes are produced: fly ash and bottom ash [70]. Both ashes are potential building materials.

2.12. Coconut shell ash (CSA)

Cocos Nucifera trees, also known as coconut palm trees, grow abundantly along the coast line of Equatorial countries, with a worldwide production of 12.5 million tons (for coconut flesh) [71]. A healthy coconut tree will produce approximately 120 watermelon-sized husks per year, each with a coconut imbedded inside [72]. Large quantities of the shells can be obtained in places where coconut meat is used in food processing. Coconut shells have little or no economic value and the disposal is expensive and provokes environmental problems [73]. Indeed, the shell is considered as a potential environmental pollutant. The coconut shells are collected, and generally are burnt in the open air (uncontrolled combustion) during three hours. When the combustion is carried out under controlled procedures, pyrolysis is the preferred method [73]. CSA can be used as pozzolan in partial replacement of cement in mortar production [73].

To summarize and as an orientation to estimate the potential of obtaining ashes, **Table 1** depicts the worldwide production.

3. Physical-chemical properties

Since analysing the feasibility, as eco-efficient structural mortar/grout component, of different biomass ashes is the main concern of this research, the analysis of the physical-chemical properties is a crucial issue. The aforementioned properties are directly related to the chemical components (type of waste, sand, water, superplasticizer and so on), ratios (e.g. water/binder ratio, percentage of cement substituted by biomass ash among others) and particle size (e.g. fineness and granulometry). Mixture properties, density or porosity are also related to the mechanical performance. Both, the chemical composition and the reaction between cement and biomass ash, yield specific properties that are directly linked to the mechanical behaviour.

In the following sections a review and analysis of pozzolanic activity, which is directly related to mechanical characteristics, and general physical-mechanical properties is provided.

3.1. Pozzolanic potential and activity

It is known that siliceous or siliceous- aluminous materials chemically react with calcium hydroxide at ordinary temperature, forming compounds that possess cementing properties [74]. That property, which is called pozzolanic activity, is directly linked to the chemical composition.

According to ASTM C618, in order to present pozzolanic activity, silicon dioxide (SiO_2) plus aluminium oxide (Al_2O_3) plus iron oxide (Fe_2O_3) should be part of the chemical composition, in a proportion greater than or equal to 70% [75]. A component with the aforementioned percentage is classified as fly ash Class F, and if the percentage is between 50% and 70% is Class C. Moreover, it is important that the ratio CaO/SiO_2 is greater than 1, in order to maintain the basicity index in the material [76]. Goldman and Bentur [77] state that the capability of pozzolanic materials enhances the strength of cementitious systems, having more physical (size, shape and texture of the particles) than chemical effects. It is worth noting that the pozzolanic activity also depends on silica crystallization phase, size and surface area of ash particles [78].

As far as the analysed wastes are concerned, most of them present $SiO_2 + Al_2O_3 + Fe_2O_3$ content higher than 70%. That is because plants obtain various minerals and silicates from earth during the growth process. Inorganic materials, especially silicates, are found to be higher in annually grown plants than in long-lived trees. Thus, the plant residues are a potential source of cement replacement material with pozzolanic reactivity [79]. **Table 2** summarizes the $SiO_2+Al_2O_3+Fe_2O_3$ content of the analysed biomass ashes.

BLA presents a high $SiO_2 + Al_2O_3 + Fe_2O_3$ content, 80.4% SiO_2, 1.22% Al_2O_3 and 0.71% Fe_2O_3 [36]. Villar-Cociña et al. [36] determined the pozzolanic activity of BLA by means of the electric conductivity method, obtaining a high activity at early ages (between 0 and 5 hours). For SCBA and RHA the oxide content is also high. In the case of SCBA, Arif et al. [80] report the ($SiO_2 + Al_2O_3 + Fe_2O_3$) content of SCBA from different sources: 74.5%, 63.2%, 90.2% and 86.5%. In their research the oxide content is 78.5% SiO_2, 7.3% Al_2O_3 and 3.85% Fe_2O_3. Martirena et al. [81] provide the following chemical content for SCBA: 72.74% SiO_2, 5.26% Al_2O_3 and 3.92% Fe_2O_3. Regarding the pozzolanic activity, Arif et al. [80] conclude that although cement-SCBA pastes show little activity, at 5% cement replacement level, SCBA is potentially pozzolanic. Regarding RHA, it is rich in silica content, and it is considered a highly pozzolanic substance, when compared to other mineral admixtures (e.g. silica fume or fly ash) [78]. Zain et al. [78] provide a number of values of RHA oxide content, obtained from different combustion methods. In all cases the SiO_2 is higher than 79%: (i) 79.84% SiO_2, 0.14% Al_2O_3 and 1.16% Fe_2O_3; (ii) 80.72% SiO_2, 0.08% Al_2O_3 and 1.10% Fe_2O_3; (iii) 86.49% SiO_2, 0.01% Al_2O_3 and 0.91% Fe_2O_3. Abbas et al. [82] provide the following composition for RHA: 76.81% SiO_2, 6.17% Al_2O_3 and 4.19% Fe_2O_3. They also determined the pozzolanic reactivity of RHA by means of the strength activity index and thermal analysis. Results from that research show that mixtures incorporating RHA up to 30% could be classified as active pozzolans, as the activity index was higher than 75%. The chemical composition of WSA, CSA, POFA and CCA also contains more than 70% of $SiO_2 + Al_2O_3 + Fe_2O_3$. CCA has an oxide content around 72% when is treated at 600ºC for 4 hours (63.91% SiO_2 + 4.01 % Al_2O_3 + 3.95 % Fe_2O_3 [38]) with a pozzolanic activity index of 103% (higher than 75%, and therefore a suitable value for being considered as pozzolanic material). WSA is composed by high amount of SiO_2 (73.06%), being the rest of compounds in quite low proportion (Al_2O_3 3.90% and Fe_2O_3 1.75%) [62]. Regarding POFA, in spite of its oxide content and pozzolanic potential (SiO_2 63.41%, Al_2O_3 5.55% and Fe_2O_3 3.74%) this waste exhibits a slow pozzolanic activity, provoking low early compressive strength in cement-based materials [83, 84]. CSA contains SiO_2 37.97%, Al_2O_3 24.12% and Fe_2O_3 15.48% [85]. Utsev and Taku [85] analyse the pozzolanic activity index at various OPC-CSA replacement levels and age. A decrease of that index is observed for 15% and 30% replacement, when the curing age increases. However, the relation between pozzolanic index and curing time is no clear for 10%, 20% and 25% replacement levels. According to that research, when the CSA amount increases the pozzolanic activity decreases.

In the case of WWA, if the oxide content exceeds the minimum 70%, the waste is chemically reactive, and the pozzolanic activity index value is 75.9% [29]. The pozzolanic activity could be low if the wood ash contains appreciable amount of un-burnt carbon [86]. Different oxide contents have been obtained from the literature: (i) 67.20% SiO_2, 4.09% Al_2O_3 and 2.26% Fe_2O_3 [87] (ii) 78.92% SiO_2, 0.89% Al_2O_3 and 0.85% Fe_2O_3 [88] and (iii) 31.80% SiO_2, 28.00% Al_2O_3 and 2.34% Fe_2O_3 [86].

The OBFA oxide proportion is low (e.g.: (i) 56.16 % (33% SiO_2 + 16.66 % Al_2O_3 + 6.5% Fe_2O_3 [45]) and (ii) 15.82 % (11.84% SiO_2 + 2.60 % Al_2O_3 + 1.38% Fe_2O_3 [89]). Cruz-Yusta et al. [45] determined a low pozzolanic activity for OBFA, by measuring the Ca^{2+} and OH^- concentrations.

For CWA, Ramos et al. [60] obtain 43.75% (SiO_2 + Al_2O_3 + Fe_2O_3) content (38.15% SiO_2 + 3.65 % Al_2O_3 + 1.95% Fe_2O_3). After determining the pozzolanic activity, as prescribed in EN 196-5, a negative result was obtained (CaO concentration around 13.6 mmol/l and OH- concentration of 48 mmol/l) [60].

According to Azmi et al. [90], the chemical composition of WPSA is SiO_2 15.16%, Al_2O_3 6.06% and Fe_2O_3 1.11% and the possibility of transforming an inert material such as paper sludge into a highly pozzolanic product directly depends on its clay mineral content (mainly kaolinite), activation conditions (temperature and retention time), scale of operations (laboratory or industrial) and fineness [91]. As a result of the aforementioned, the chemical composition of activated paper sludge varies. García et al. [92] determined the composition and pozzolanic activity of calcined paper sludge waste, concluding that to obtain satisfactory pozzolanic properties, the optimal calcination conditions are given by a temperature of 700ºC during 2h.

Regarding ABA, the potential of pozzolanic reaction does not exist because the contents of compounds forming CSH gel and the SiO_2 percentage are not significant (around 1.4% [50]).

3.2. Physical-mechanical properties

As aforementioned, the pozzolanic activity is determined by the oxide content (SiO_2+Al_2O_3+Fe_2O_3). Diaz et al. [93] state that the combination of materials, rich in those compounds such as fly ashes, with a highly alkaline solution and soluble silicates provides the formation of strong binders. According to Wang et al. [94] high amounts of reactive SiO_2 and Al_2O_3 result in higher degree of geopolymerization and consequently higher mechanical strength.

Following the key factors of their potential reactivity, the particle size distribution is the physical characteristic of ashes that most strongly affects reactivity. Furthermore, the effect of ash particle size distribution in the mortar resistant behaviour is very important [95], having an effect on the compressive strength [50]. The compressive strength is generally reached completely at 28-day, and depends on the component proportion, e.g. water/binder ratio or percentage of cement substituted by biomass ash, among others.

The incorporation of plant biomass ash in the cement mortar can either increase or decrease its compressive strength. Generally, it is associated with the pozzolanic activity but this is not the only decisive issue.

SCBA exhibits both one of the highest pozzolanic potentials and a satisfactory compressive strength, when added to cement mortar. The compressive strength of SCBA-cement mortar increases with SCBA up to 10%, and then at 20% SCBA the compressive strength attains the equivalent value as observed for control mortar. According to Ganesan el al. [96] 20% replacement is the optimal limit, and the following increases with respect to the control specimen were obtained: 19.39, 19.60 and 13.25 for 5%, 10% and 15% replacement, respectively.

In the case of POFA, some authors state that the best percentage of substitution to maintain or improve the mechanical properties is around 20% (e.g. [97]). Usman et al. [98] conclude that the 28-d strength for samples containing up to 20% POFA was higher or equal to OPC mortar. For 10% or 15% replacement, the 28-d increase is around 2%. The strength increase could be due to the formation of secondary C-S-H owing to the pozzolanic reaction between the cement hydration product and the reactive silica of POFA [98].

Martínez-Lage et al. [99] analyse the mechanical properties of WPSA-cement mortars, concluding that their compressive strengths is higher than the value of the reference mortar (between 4% and 19% increase). For 10% replacement, the flexural strength is similar to that of the reference specimen, but a 10% decrease is obtained for a 20% substitution.

WSA cement-binder mortar presents higher strength than the reference cement mortar at early ages [100], due to the filler effect of the ash particles. However, at later stages, the mechanical properties become worse. In 15%wt WSA specimens, the 28-d compressive strength decreases approximately 1.5% and the flexural strength maintains the reference value.

Adesanya [101] analysed the compressive strength from different CCA replacement proportions and specimen ages. The 28-d compressive strength of 1:3 and 1:6 CCA-cement mortars was 19.8% and 15.13% higher than the value of the reference mortar, but for a mix ratio of 1:1, the strength of the blended mortar is less than that of the OPC mortar (around 15% decrease).

It is interesting to highlight that RHA, SCBA and BLA present similar oxide content (with more than 80% of $SiO_2 + Al_2O_3 + Fe_2O_3$ in their chemical composition), but only SCBA improves the mechanical performance. RHA and BLA have a similar decrement in the compressive strength, around 16%. According to Potty et al. [102], 1:3 (binder to sand ratio) RHA strengths show a decreasing trend when the percentage of replacement increase. That is because the RHA particles are coarser than cement particles, provoking a porous surface with more voids. However, the compressive strength of 1:4 (binder to sand ratio) RHA mortars increase at 5% replacement and decrease thereafter. The compressive strength of 1:3 RHA mortars is higher than that of the 1:4 RHA mortars at all RHA replacements. When 20%wt of cement is substituted by RHA, the compressive strength decreases around 16%, (with 0.50 w/b ratio and 1:3 binder to sand ratio). In BLA compounds, although the compressive strength increases with time, the values are lower than those of the reference mortar. Thus, around 16% decrease is observed in the 28-d compressive strength when 20%wt BLA is added to cement mortar [103].

According to González-López et al. [50] the compressive strength of ABA cement mortars depends on the burning temperature, owing to the chemical composition and particle size. In that research, ashes were obtained through combustion with temperature between 500ºC and 700ºC and the apparent particle size was between 25 and 32 μm. The results suggest that the best temperature is 500º. The 7-d compressive strength, with 5% replacement in mass is 90% higher than the OPC strength, due to the semi-reactive characteristics of the ash components. However, around 9.26% decrease in the 28-d compressive strength is obtained.

Cheah and Ramli [29] provide an overview on the implementation of WWA as a partial cement replacement material in concrete and mortars. The aforementioned research concludes that although, in general, WWA reduces the mechanical strength, the use at replacement levels up to 10% by total binder weight could yield acceptable strength properties. García and Sousa-Coutinho [104] analysed specimens with different levels of WWA. In all the cases, the increase of the ash replacement up to 28 days is inversely proportional to the compressive strength. For instance, the minimum replacement of 5%wt of WWA provides a compressive strength around 4% less than that of the control mortar without WWA, and when 10%wt is replaced the compressive strength decreases more than 11%. Regarding flexural strength, that decrease is higher [104].

Regarding OBFA, Cruz-Yusta et al. [45]) analyse the compressive strength at 28-d for M5 mortar with partial cement replacement. When OBFA content increases, a continuous decrease in the compressive strength is observed. The compressive strength from OBFA-cement is generally low, only specimens with 10%wt of replacement exhibit adequate resistance for commercial use due to its low pozzolanic activity (around 8% less than the cement mortar without OBFA).

When CWA is added to the cement matrix, strength is reduced and that loss is directly related to the replacement percentage [60]. The strength decrease may be attributed to the increased amount of free water. It is due to the reduced amount of material that is available to react with water, since CWA is not fully pozzolanic and consists of larger particles and, thus lower specific surface is available. According to the aforementioned research [60], if cement is substituted by 10%wt of CWA, the compressive strength decreases 9.70% and in the same way, the flexure strength also decreases 13.25% (when 10%wt of cement is substituted).

In CSA cement compounds, the compressive strength decreases when the percentage of cement substituted by CSA increases [73]. Thus, if 10% of cement is substituted by CSA, the 28-d compressive strength decreases approximately 7% and if the substitution is by 20%, the 7-d compressive strength is even 37.16% less than that of the mixture without CSA.

Figure 10 summarizes the compressive strength of the plant biomass ashes, showing the increase or decrease with respect to the control cement mortar. Nominal values of mortars are given in **Table 3.**

In conclusion it is worth noting that regarding the compressive strength, the best mixtures are those containing SCBA, WSPA, POFA and CCA (1:3 and 1:6) as they improve the reference strength.

4. Rheological behaviour

Consistency and workability are also essential fresh state properties, if analysing the feasibility as eco-efficient structural material is the main concern.

According to Kosmatka et al. [105] the consistency is the ability of freshly mixed concrete or mortar to flow. They provided also a definition of workability very similar to that of given by the American Concrete Institute (ACI) which state that the workability is the property of freshly mixed concrete or mortar that determines the ease and homogeneity of being mixed, placed, compacted, and finished.

The most commonly used test to determine workability in practice is the slump cone test [106]. A truncated metal cone, open at both ends and sitting on a horizontal surface, is filled with mortar, and lifted quickly. The mortar will slump or move only if the yield stress is exceeded and will stop when the stress (or weight of the mortar/area) is below the yield stress [107]. This test is a useful quality control tool because it can help to detect changes in the composition, e.g., changes in the amount of mixing water [108]. All the reviewed data follow the Codes ASTM C 109 [109] and ASTM C 230 [110] and, as expected, results depend on the percentage of substituted cement.

4.1. Flow spread

It is important to highlight that the current state of research has sparse information with respect to flow spread. Thus, with regard to POFA, BLA, CCA, OBFA, WPSA and CSA, no nominal values have been found. **Figure 14** summarizes the obtained information.

Figure 11 clearly shows that SCBA-mixture presents the highest variation with reference to the cement specimens. The flow value is 164 mm, when 10% of the cement content is substituted by SCBA. The higher porous texture of SCBA increases the water demand and consequently decreases the flow value [111]. Experimental results show that the flow spread of fresh mortars would decrease with an increase of SCBA replacement [111].

In the same way, POFA decreases the flow tendency due to the porous and spongy nature of its microstructure and to the increased fineness or surface area [83]. Yan and Sagoe-Crentsil [112] point out that the flow decreases when the WPSA amount increases.

CWA, ABA and WSA cement mixtures exhibit similar values to SCBA. If 10% of cement is substituted by CWA, the obtained flow is 186 mm [60] whereas if 10% of WSA is added, 155 mm of flow are obtained [100]. ABA-cement mortar presents 168 mm of flow with 5% cement replacement [50].

Additionally, in **Figure 11** it is possible to distinguish the biomass ash-cement mortars that decrease in relation to the reference cement mortar specimens, achieving similar nominal values (i.e. RHA-cement mortar and WWA). The RHA-cement mortar flowing ability decreases with the higher RHA content and W/B ratio [113]. Regarding WWA-cement mortar, Elinwa et al. [114] state that the slump value has a gradual decrease under this condition: the water binder ratio of the mortar mix has a constant value (0.60 w/c). For 5% of cement replaced, slump is 250 mm, 7.41% less than the control specimen.

4.2. Consistency and workability

Workability is complementary to flow spread. It is worth highlighting that as, in general, the particle size of biomass ash is smaller than that of the cement one, worse consistency and water demand to maintain a given workability are found. A higher quantity of water is required to wet the surface of the smaller ash particle [115]. If the water content is high, it becomes a problem in the application of biomass ash as a supplementary cementing material.

Comparing particle size between cement and biomass ash and its relation with workability, the cement particle size is D_{95}<48µm [116] and, for instance, in the case of WPSA its size is less. It is worth noting that the maximum size of the ash particles is 200 µm and the percentage of particles smaller than 0.15 µm is 15% [99]. Besides, the water absorption of hardened mortar decreases when WPSA content increases at ambient temperatures [112]. Thus, the workability of mortar decreases whereas the substitution of WPSA increases.

A similar situation is presented by CWA particles. The particles are coarser than the cement ones, and workability worsens [60]. Ramos et al. [60] state that D_{50} of CWA is 31.59 µm. In addition, D_{90} of CWA is 71.25 µm.

Regarding WWA, although approximately 31% of wood fly ash passes on sieve nº 325 (45 µm) [29], the addition of this waste as a partial substitution of OPC (10% by total binder´s weight) has no adverse effect on the water demand. This was compared to the control mortar mix in order to achieve a similar level of workability using solely OPC as binder material [29]. Workability decreases when the percentage of WWA increases [117].

Mortar with OBFA-cement binder presents normal consistency and acceptable workability due to size distribution, which is multimodal with particles of different size. The OBFA's particle size is not the smallest (from 0.6 to 450 µm, with 26.3% ranging from 2 to 20 µm, and 68.7% from 20 to 300 µm) [45].

In ABA cement mortars, when the surface area is very large (the apparent particle size of ABA on average is between 25 and 32 µm), deficient workability and consistency reduction are expected [50].

Another key factor is the porous volume created in the mixture. In the SCBA mortar, the higher porous texture increases the water demand [111].

To summarize, **Figure 12** represents both the increase and decrease of workability in mortars. It is concluded that if the quantity of OPC that is replaced increases, the quantity of required water for normal consistency and workability also increases.

4.3. SEM images analysis

The morphological features of the material particles can be examined using Scanning Electron Microscopy (SEM) analysis [118]. Spherical or elongated particle forms are fundamental in order to predict the viscosity and flow performance. The second one present preferential orientation inside the fresh mortar when flow occurs and that provides a decrease of viscosity [119].
SEM ashes images, **Figure 13**, which have been obtained from the literature review, are studied in this section.

From the analysed images, it is possible to distinguish three predominant forms. **Figures 13 a, c and k** show spherical particles in OPC, POFA and WPSA**.** This shape provides the best rheological behaviour. OPC exhibits the best viscosity behaviour. In the images, the WPSA particles present spherical shapes, but their size is too big and do not improve viscosity. Ramos et al. [60] state that CWA particles show spherical and spongy shape, being the spongy shape-particles greater than the first ones. However CWA particles are coarser than cement, and the viscosity is not improved.

The second possible form is elongated particles. RHA, SCBA and ABA present elongated particles that decrease the viscosity, due to preferential orientation inside the fresh mortar.

Regarding WWA, BLA, CCA, OBFA, WSA and CSA particles, the particle form is similar to a sponge. That shape indicates that more water quantity is absorbed during the mortar making process, having a detrimental effect on flow and viscosity.

5. Setting times

Setting time is a crucial factor in workability, and it is usually measured by rather conventional methods (e.g. Vicat aparatus). After beginning of setting one cannot mix anymore, and after end of setting the mix is not workable anymore. The general trend in bio-ash mixtures is for longer initial and final setting times. **Figure 14** and **15** show the values of initial/final setting times of biomass ash-cement mixtures, and the relative change of setting time as a percentage of the setting time in reference OPC compounds.

The increase in setting time provided by CSA is quite high. The initial and final setting times increase when the percentage of cement substituted by CSA increases [73]. Thus, the initial setting time increases from 65 minutes without CSA, to 253 minutes with 10% of CSA and to 289 minutes with 20% of CSA. Regarding the final setting time, it changes from 83 minutes in mortar without CSA, to 330 and 375 minutes with 10% and 20% of CSA, respectively [73].

More moderate values are presented by BLA, CCA, WSA and WPSA. In the presence of 10% BLA, the setting times increase (initial setting time at 200 minutes and final setting time 260 minutes) whereas in the presence of 20% BLA the setting times are proportionally increased (155 min. initial setting time and 200 min. final setting time) [127]. In the same way, the initial and final setting times are directly proportional to the CCA content of CCA-blended cement. Thus, if the amount of cement substituted by CCA increases, the initial and final setting times increase too [128]. For instance, when 10% of cement is replaced, mortar presents 208 min. initial setting time and 328 min. final setting time [128]. The use of WSA also provides an increase in setting times, while WPSA produces a decrease in initial setting time. When 10% of the cement content is substituted by WSA, retardation in initial setting time (52% with respect to OPC mortar) and final time (50% with respect to OPC mortar) are seen [100]**.** Oppositely, initial setting time is 23.5% shorter in cement with 10% WPSA [129].

A 10% replacement of SCBA provides an increase of 23.1% at the initial time, and 13.3% for the final time [96], whereas RHA increases the initial time (38.5%) but decreases (12.7%) the final setting time [14].

Finally, in the case of WWA the initial and final setting times are proportional to the wood ash content. Initial and final setting times were 100 min and 160 min for the reference OPC mortar. Setting times doubled for 10% WWA mixtures (218 and 334 min) [86].

6. Drying shrinkage

Drying shrinkage is a volume reduction resulting from the drop in the internal relative humidity in the pores of the cements materials, during drying of moisture to the environment [130]. If the volume reduction due to shrinkage is hindered by internal or external constraints [131], residual tensile stresses build up, and warping and/or micro- and macro-cracking could appear [130]. Eventually, damaged concrete structures experience reduced durability and service life due to that phenomenon, which has a tremendous economic impact [130].

As shown in **Table 4**, for WWA, RHA, BLA, CCA, OBFA, ABA, WSA AND CSA biomass mortars, data have not been found.

Regarding POFA, when 30% of this material is added, the shrinkage increases 19% [132].

However, for mixes with SCBA and WPSA, the drying shrinkage values are lower than that of the control mix [111, 112]. Mixes with 10% of SCBA, at 25-day, show a drying shrinkage of 8%, as low as that of OPC specimens. Thus, from the drying shrinkage point of view, 10 % of SCBA is found to be the optimal limit [111].

In WPSA, the drying shrinkage decreases almost linearly when the paper sludge content increases up to 5 %, and then moderately decreases for higher sludge contents [112]. The 91-day drying shrinkage of mortar specimens with 2.5% and 10% of sludge ashes is 34% and 64% less than the reference mortar [112].

7. Durability

Resistance to chloride ion penetration, resistance to sulfate, and carbonation are key factors for the durability in cement compounds. However, sparse information is available with respect to the last one.

Regarding carbonation, it was only possible to get information for WWA. According to Aprianti et al. [2], cement mixtures using WWA show a carbonation depth greater than pure Portland cement compounds. In the next sections, the information related to resistance to chloride and sulfates is provided.

7.1. Resistance to chloride ion penetration

The resistance to chloride penetration of mortar and concrete is one of the most important issues concerning durability, especially if corrosion minimisation is a main concern. It is generally accepted that the incorporation of pozzolan improves the resistance to chloride penetration [133]. This is mainly due to the reduction of permeability/diffusivity, particularly to chloride ion transportation of the blended cement mortar [133, 134].

In order to measure the resistance to chloride penetration, it is necessary to prepare the specimens following specific prescriptions (e.g. as described by the Code ASTM C39 [135]). Additionally, to predict the service life in marine environments, it is necessary to know the flow rate of chloride ions through unit area of mortar. It is measured by means of the chloride diffusion coefficient, using the migration test [136] [137] or quantifying the charge passed in coulombs [138].

Figure 16 shows the percentage of improvement or worsening of chloride ion penetration under $AgNO_3$ solution. The diffusion coefficient is measured in x10^{-11} m^2/s and the charge passed in Coulomb.

RHA is the analysed ash that presents the best resistance to chloride penetration. According to Chindaprasirt et al. [133] when 20% RHA is added, the depth is 3.5 mm, 4.5 times less than 16.0 mm observed for OPC mortar. Regarding the diffusion coefficient, it is only 5.24×10^{-11} m^2/s, being 25.10×10^{-11} m^2/s the value exhibited by OPC. This represents a 79.12% variation [139].

In the same way, the presence of POFA improves the resistance of mortar to chloride penetration. For instance, a decrease of 12 mm of thickness is obtained, when 40% by weight of cement is substituted by POFA, after 30 days of immersion in 3% NaCl solution [133].

Better behaviour under chloride ion penetration is found in CCA-cement mortar. The results of the reaction of CCA blended mortar specimens with HCl acid water are presented by Adesanya and Raheem [140]. The best results are obtained for 1:1 mix proportion. The resistance against HCl attack increases from 11.1% to 58.3% when the CCA substitution increases from 2% to 15%. These results show that the incorporation of CCA improves the resistance to chloride attack.

As shown in **Figure 16**, for biomass compounds BLA, OBFA, ABA, WSA, WPSA AND CSA no data have been found. However, it is known that chloride permeability is reduced by < 20 % replacement of cement with SCBA [111], being 10% the optimal limit based on the results of resistance chloride penetration. In contrast, García and Sousa-Coutinho [104] concluded that the WWA does not improve the chloride penetration. Regarding diffusion coefficient, the mortar with 10% CWA presents a more permeable structure and exhibits 2.28×10^{-11} m^2/s (90.95% worsening) whilst the mortar with 20% substituted has 2.06×10^{-11} m^2/s (91.83% worsening) [60].

The resistance of grout to chloride ion ingress is determined by means of the charge passed through grout specimens measured in coulombs [141]. The charge passed of all specimens, evaluated at 28 days, is shown in **Figure 16.**

In all the analysed compounds, the charge passed decreases. RHA cement based mortar presents the highest value, 89.67% decrease with respect to the reference mortar, when 20% is substituted [142]. Mortars with 20% of POFA present a decrease of 74.44%, with respect to the reference mortar, and nominal value of 1905 Coulomb [142].

With regard to SCBA [143], when 20% of cement is substituted by this waste, the charge passed is 2720 Coulomb (67.90% less than reference mortar), while if it is substituted by 10%, 6829 Coulomb are obtained (only 19.41% less than reference cement mortar). This value is the most similar to the reference cement mortar, around 8000 Coulomb.

7.2. Sulfate resistance

Sulfate attack is defined as a deleterious action involving sulfate ions [144]. The mortars manufactured with pozzolans, together with OPC improve resistance against sulfate attack as revealed by several studies (e.g. [132]).

In CCA mortars, when the replacement is up to 10%, the loss in specimen weight due to H_2SO_4 attack is reduced. The sulfate resistance with respect to the control mix, is 38.7% for 10% replaced, with 1:1 ratio [140].

The use of RHA in mortars has a positive effect in decreasing the expansion of mortars when exposed to sulfates. The effects of RHA in the compressive strength loss are positive or negative, depending on the type of sulphates and on the mix proportion. A mixture with w/b ratio 0.55 and 10% substituted, provides a 6% decrease of the compressive strength at 7-d and 10% at 28-d [145]. Increasing the proportion of RHA tends to reduce the compressive strength loss due the increase in density and impermeability related to pozzolanic activity [145].

Regarding CWA, when 10% CWA is added, the resistance to sulfate is reduced [60]. According to Ramos et al. [60], in specimens with CWA mortar, expansion rates were low at the beginning, and increased substantially after 10 weeks of immersion in Na_2SO_4. That is because as CWA is not fully pozzolanic, portlandite (CH) reacts with sulfates, promoting the formation of gypsum, which causes the expansion and cracking of cement-based materials [146].

As far as POFA is concerned, after being immersed in 5% $MgSO_4$ solution for 24 months, mortar with a rate of 10% by weight of POFA shows the same sulfate resistance, in terms of expansion and loss in compressive strength, that the OPC mortar [147].

Table 5 shows the aforementioned data. It is worth noticing that for SCBA, WWA, BLA, OBFA, ABA, WSA, WPSA and CSA no data have been found.

8. Environmental issues

Both cement production and plant waste generation provide several environmental problems. It is known that cement production consumes a high amount of energy, generating CO_2. Plant waste production yields some environmental problems associated to: local sources, amount of produced wastes or required treatments in order to be discarded. Some plant products studied in this research have an environmental beneficial role as cement substitute as they are CO_2 neutral emitter [5]. Besides, the production of energy from agricultural residues is a developing industry with strong environmental potential [148].

In the case of rice more than 20% of rice husk volume is residue [149]. The rice husk obtained during the rice refining yields disposal problems. The handling and transportation of rice husk ash are also problematic [150]. Most of the rice wastes are burnt or dumped in landfills. Burning of rice husk in open field causes environmental and health problems in the surrounding areas, especially in developing countries. Therefore, it is very important to fully utilize those ashes [150].

Regarding the palm oil, this is one of the main contributors to the pollution problem in some countries, such as Malaysia [151]. In those countries a huge amount of wastes is obtained, for instance around 3.13 million tons of palm shell wastes are produced in Malaysia [152]. Moreover, the waste amount increases every year [153].

The sugar industry also emits harmful gases and solid particles in air and water, which directly affects the environment in terms of global warming, acidification and eutrophication [27]. For instance, in India 67,000 ton/day of bagasse ash is directly disposed to nearest land, causing environmental problems [154]. The increase of sugarcane production implies a proportional waste increase, provoking severe environmental problems due to the lack of sustainable solutions for the waste management [155].

Wood waste is considered both a renewable and CO_2 neutral energy resource [5]. According to Tortosa et al. [156] when the wood burning reaches 800º the majority of the mass loss is produced by the release of CO_2. A reduction of the impact related to electricity consumption could be theoretically possible by replacing the boiler with a co-generation unit [157].

A product similar to the wood is bamboo, which contributes to the environment protection in a similar way. Bamboo plant absorbs CO_2 producing oxygen [158] and is a fast-growing plant. Furthermore, the BLA formation process is carried out at 600ºC for 2 hours in a furnace [159]. That is a fast and eco-friendly process.

In spite of the environmental benefits provided by biomass energy, it is important to consider the wastes that are generated. For instance, conventionally, the energy stored in corn cob is released through combustion to obtain heat. As a result, hazardous products such as SO_2 and NOx are formed and emitted, causing air pollution. Besides, the energy conversion efficiency is low, leading to a significant waste of fuel [160].

As far as OBFA is concerned, the technology for olive oil extraction in Spain has progressed significantly towards a more sustainable process [161] [162]. The new technology only produces two effluent streams (olive oil and alperujo) avoiding the production of alpechín, which is extremely hazardous to the environment [162]. In addition, the resulting waste of the chemical extraction (“orujillo”) can be used for co-generation of electrical power [161]. The olive biomass can produce energy through three methods: pyrolysis, gasification and combustion [163].

Agave also presents an opportunity for bioenergy production with important economic and environmental benefits, and without impacting global food production or causing indirect land use change [164]. That is because agave is a Crassulacean acid metabolism (CAM) specie [52]. CAM is a photosynthetic adaptation that facilitates the uptake of CO_2 at night, and thereby optimizes the water-use efficiency of carbon assimilation in plants that grow in arid habitats [164].

Regarding cork fly ash and cork bottom ash, the main problem is the unused ashes. Those ashes have detrimental effects on the environment such as air pollution, due to fineness, and groundwater quality, due to possible leaching of metals from the ashes [165].

The paper industry is also a polluting industry. Paper sludge is regarded as a threat to environmental safety, as most of it is disposed via landfill or incineration, which can cause severe soil, water or air pollution [166]. However, efficient waste paper recycling has a significant role in the sustainable environment [167] and the re-use of recycled paper is growing (Europe recycled 71.7% of the paper and cardboard used in 2012 [91]), it is worth noting that waste paper cannot substitute virgin paper at a 1:1 ratio [168]. At least 20% should be substituted by virgin paper [168], thus a part of used paper always become waste and will be incinerated and rejected in landfills [167].

Finally, CSA also presents problems associated to agricultural production. Coconut production is an important contributor to pollution problems because 80–85% of the coconut's raw weight is treated as solid waste residue in the form of husks [169].

In the following Sections, two issues that are directly related to the feasibility of using the plant biomass ashes in eco-efficient cement materials are analysed: the Global Warming Potential and the Embodied Energy.

8.1. Global Warming Potential (GWP)

In the built environment, global warming contribution is the cumulative quantity of greenhouse gases (CO_2, methane, nitric oxide, and other global warming gases), which are produced during the direct and indirect processes related to the creation of the building, its maintenance and end-of-life. This is expressed as *CO_2 equivalent* that has the same greenhouse effect as the sum of GHG emissions [170].

Table 6 summarizes the GWP of the analysed ashes. It is worth noting that SCBA is responsible for the highest global warming value, whereas the other wastes exhibit similar values.

Ramjeawon [172] shows the productive process of SCBA. In this process, 1GWg and 35,600 kg CO_2-eq are produced. At the same time, when 4615 tonnes of bagasse are used by 1GWh, 69225 kg of ash is generated. Thus, 0.51 kgCO_2/kg SCBA is obtained.

Prasara [171] stated that, if the the rice husk ashes are obtained from electricity production, the global warming emissions from 919 MWh is 1.02E+4 kgCO_2-eq. In that case, 1.775E5 kg of ashes were produced. Therefore, the GWP value is 0.057kgCO_2/kg ash.

The GWP of wood ash generated in a wood combustion plant is around 76.07 kg CO_2-eq, when it is working 7000 hours [173]. Under those conditions, the plant consumes 200 kg of wood per hour and generates 8.2 g of ash from each kilogram of wood. Thus, the consequence is 0.0066 kgCO_2-eq/kg WWA. At the same way, EE is 27.75 kg oil eq [176]. It is necessary to know this value in the same unit systems, therefore the unit change followed is that of proposed by Goedkoop et al. [177] where 1 kg oil eq has the same value that 42MJ. Thus, the EE total is 1165.5MJ and 0.101 MJ/kg WWA for each kilogram of ashes.

Regarding POFA, CCA, ABA, CWA, WSA, WPSA and CSA no data have been found. Regarding agave combustion, the whole process is not completely analysed from an environmental point of view [178]. In some cases, the environmental analysis does not distinguish among ash and other components (e.g. the life cycle assessment of wheat provided by Jeswani et al. [179]).

It is important to highlight that a great number of the analysed ashes are not produced in combustion process or co-generation plant. For instance, bamboo is a common material used in construction activities, but it is rarely burnt to provide energy. For this reason, its EE is not found in literature review. Van der Lugt et al. [174] state that the carbon footprint of bamboo waste is 0.779 kg CO_2, and 10% of this waste is ash, so the GWP is considered 0.0779 kg CO_2-eq/kg BLA.

Cossu et al. [175] study the environmental impact of bottom ash from olive waste. Taking account that between 4-12% of the waste is ash, and that the environmental impact of 1 ton of waste is 4.04kg CO_2-eq and 220MJ-eq, the impacts per kilogram of ash are: 0.05 kgCO_2-eq/kg ash and 2.75 MJ/kg ash.

8.2. Embodied Energy (EE)

In the built environment, Embodied Energy is the total amount of non-renewable primary energy required for all the direct and indirect processes related to the creation of the building, its maintenance and end-of-life [170]. It is measured in energy units, Megajoules (MJ).

Table 7 summarizes the EE data of the analysed ashes. Regarding POFA, BLA, CCA, ABA, CWA, WSA, WPSA and CSA no data have been found.

The ash with the minimum value of embodied energy is the WWA, whereas SCBA presents the highest value of EE. Ramjeawon [172] analyses embodied energy from those ashes and the result is as follows: 261000 MJ EE of SCBA when it is produced 69225 kg of SCBA, that is, 3.77 MJ/kg SCBA.

RHA and OBA are in the medium range. Prasara [171] states that RHA is responsible for 4.04E+03 kg oil eq. The units proposed by Goedkoop et al. [177] are used where 1 kg oil eq has the same value as 42MJ. No data have been found for the other ashes.

It is worth noting that SCBA is the highest global warming contributor, presenting also the highest level of embodied energy. That is due to the long ash production process. OBFA presents similar values, whereas the rest of by-products exhibit less value.

9. Discussion

In order to make easier the analysis of these plant biomass ashes as cement substitutes, **Table 8** and **9** summarise both nominal values and increase/decrease percentage with respect to the reference OPC compound. **Table 8** depicts the physical-chemical properties and **Table 9** shows durability features.

From a structural performance perspective, the most suitable mechanical behaviour is expected from POFA, SCBA, CCA and WSPA. The worst mechanical behaviour is provided by RHA and BLA, despite the pozzolanic potential. OBFA is the mixture that has normal consistency and acceptable workability and POFA has a potentially satisfactory rheological behaviour. The initial setting time provided by RHA, SCBA, BLA, CCA, WSA, WPSA and CSA are satisfactory as an increase with respect to the OPC reference value is observed. As far as the final setting time is concerned, although all the nominal values are acceptable, only the final setting time of the RHA decreases with respect to the reference mortar. The drying shrinkage values of SCBA and WPSA are more satisfactory than those of the control mix. RHA, CCA, POFA and SCBA improve the resistance to chloride penetration. Regarding the service life in marine environments, although sparse information is available, RHA and CWA exhibit worse behaviour with respect to OPC. As far as sulfate resistance is concerned, RHA and CCA mortars have a satisfactory improvement, CWA worsens and POFA behaviour is similar to the reference mortar.

On the basis of environmental impact values obtained from the review, GWP and EE are calculated, assuming different ash replacement percentages (from 0% to 20%). The following GWP have been considered (from SimaPro 7.3): 0.73151 kgCO_2-eq/kg for cement, 0.00371 kgCO_2-eq/kg for sand and 0.057000 kgCO_2-eq/kg for water. Regarding EE, the values are as follows: 3.21652 MJ/kg for cement, 0.05468 MJ/kg for sand and 0.00477 MJ/kg for water.

In order to obtain POFA, CCA, ABA, CWA, WSA, WPSA and CSA values it is assumed that standard concrete units are reinforced by means of OPC/biomass-based mortars (in order to obtain green grouted blocks), and that, approximately, 50% of the total volume is grout mortar.

Figure 17 shows the GWP nominal values. BLA exhibits the best GWP value (57.52% smaller than the reference cement mortar) and SCBA has the minor decrease (9.46% in relation to reference cement mortar). All the analysed biomass-based mortars improve the cement mortar emission.

The Embodied Energy value is calculated in the same way that GWP, and values are shown in **Figure 18.** RHA, and WWA reduce the EE values (17.02% and 17.45% respectively) whereas the improvement provided by SCBA is less (1%).

Figure 19 summarizes the main characteristics of the analysed plant biomass ashes-based mortars from a qualitative perspective.

10. Conclusion

The feasibility of using plant biomass ash, as partial replacing binder in cement-based structural mortars or grouts, has been analysed in this work. This research has focused on issues that are directly related to the pollution mitigation and to the structural performance. GWP and EE have been estimated assuming that the OPC/biomass-based mixtures will be used to grout hollow concrete units (CMUs), in order to obtain green grouted blocks. Thus, a main goal is to gather data and knowledge to use more eco-friendly mortars.

From the data obtained in the review, the advantages and disadvantages of each waste as cement substitute have been analysed. The following conclusions can be drawn:

- Those materials are a very strong eco-efficient alternative, as they make possible to obtain more eco-friendly materials and to improve sustainability (reducing the amount of polluting wastes that are in landfill).
- The high worldwide production of the analysed wastes shows their significant prospective as building materials.
- POFA, SCBA, CCA and WPSA cement-based mixtures have potential to improve the OPC mortar compressive strength.
- The pozzolanic potential is not always linked to the mechanical improvement, e.g. RHA, WWA, BLA, WSA and CSA based compounds have pozzolanic potential and do not improve the compressive strength.
- POFA mixture has a potentially satisfactory rheological behaviour, and OBFA-cement based has normal consistency and acceptable workability.
- Final and initial setting times are satisfactory for all the analysed compounds.
- Regarding durability, RHA, CCA, POFA and SCBA- based mixtures improve the resistance to chloride. RHA and CCA compounds improve the resistance to sulfate.

Regarding the global warming potential and embodied energy of the plant biomass ashes- based mortars:

- The greenhouse gas emissions of RHA, SCBA, WWA, BLA and OBA are lower than those of the OPC reference mortar (from 57.52% decrease for BLA to 9.46% decrease for SCBA).
- The Embodied Energy values of the analysed plant waste-based mortars (RHA, SCBA and WWA) are lower than those of the OPC reference mortar (17.02% decrease for RHA, 17.45% decrease for WWA and 1% decrease for SCBA).

To summarize, the analysed mixtures have a great potential as eco-efficient alternative to OPC. However, much more data and research are still required, as clearly observed in **Figure 19**. Results from this work could be used to foster further research on the use and development of plant biomass cement-based mortars or grouts as eco-efficient building materials.

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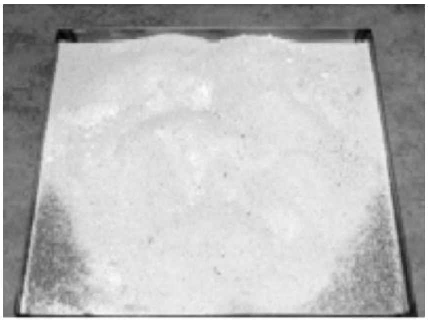

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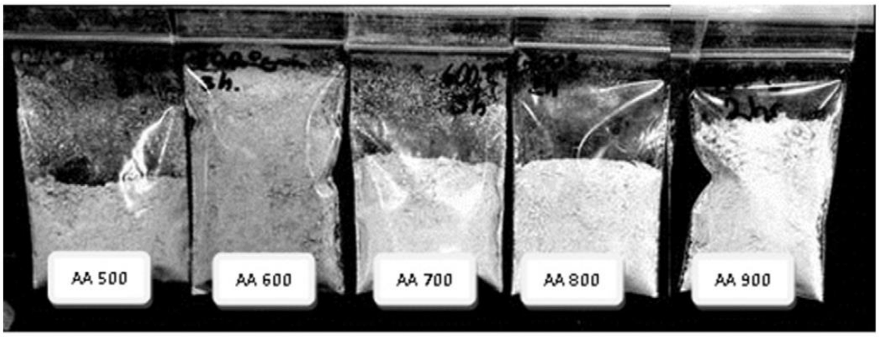

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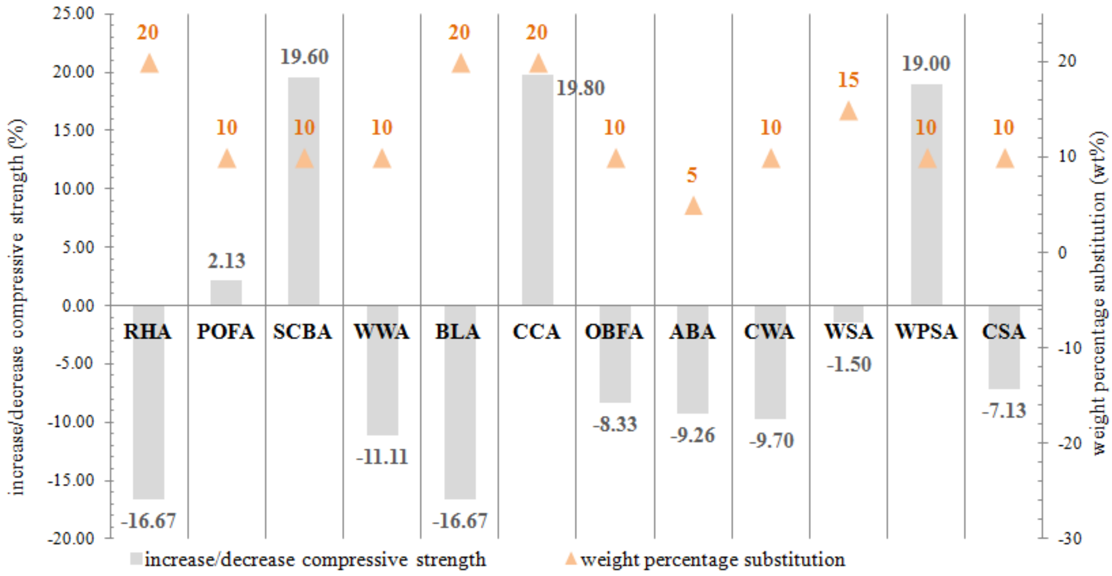

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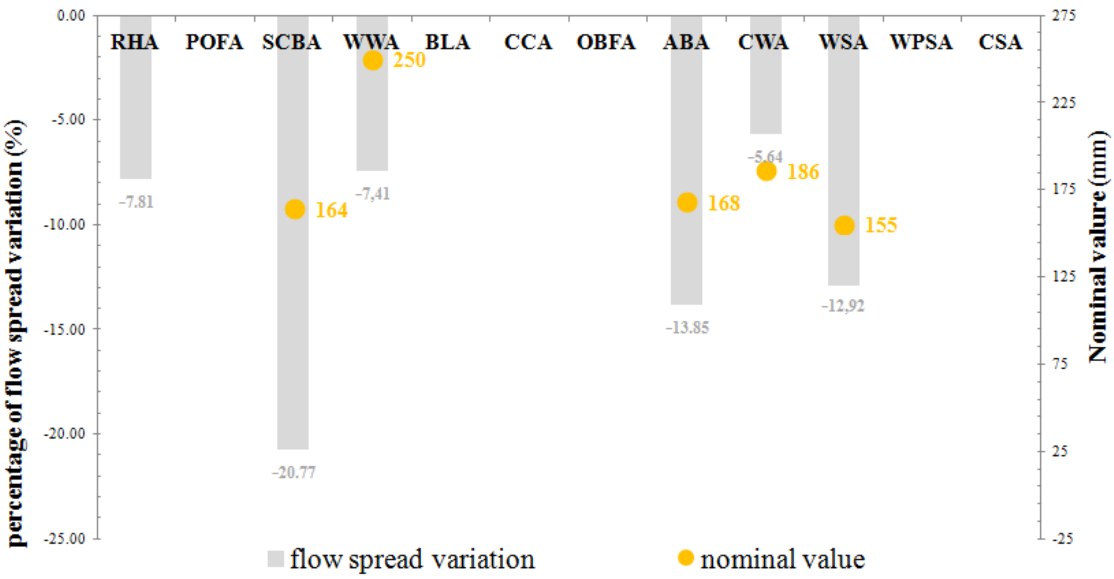

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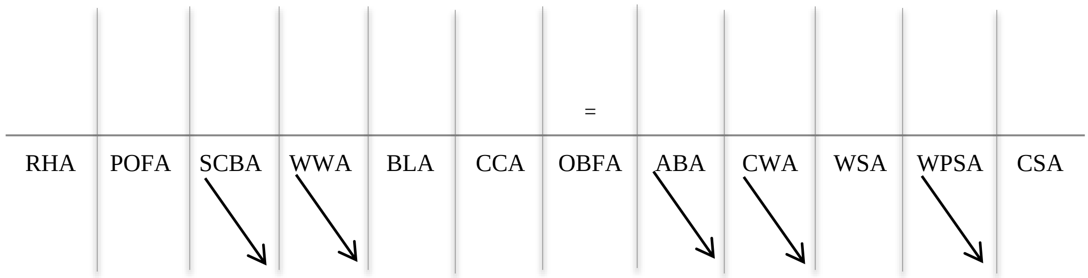

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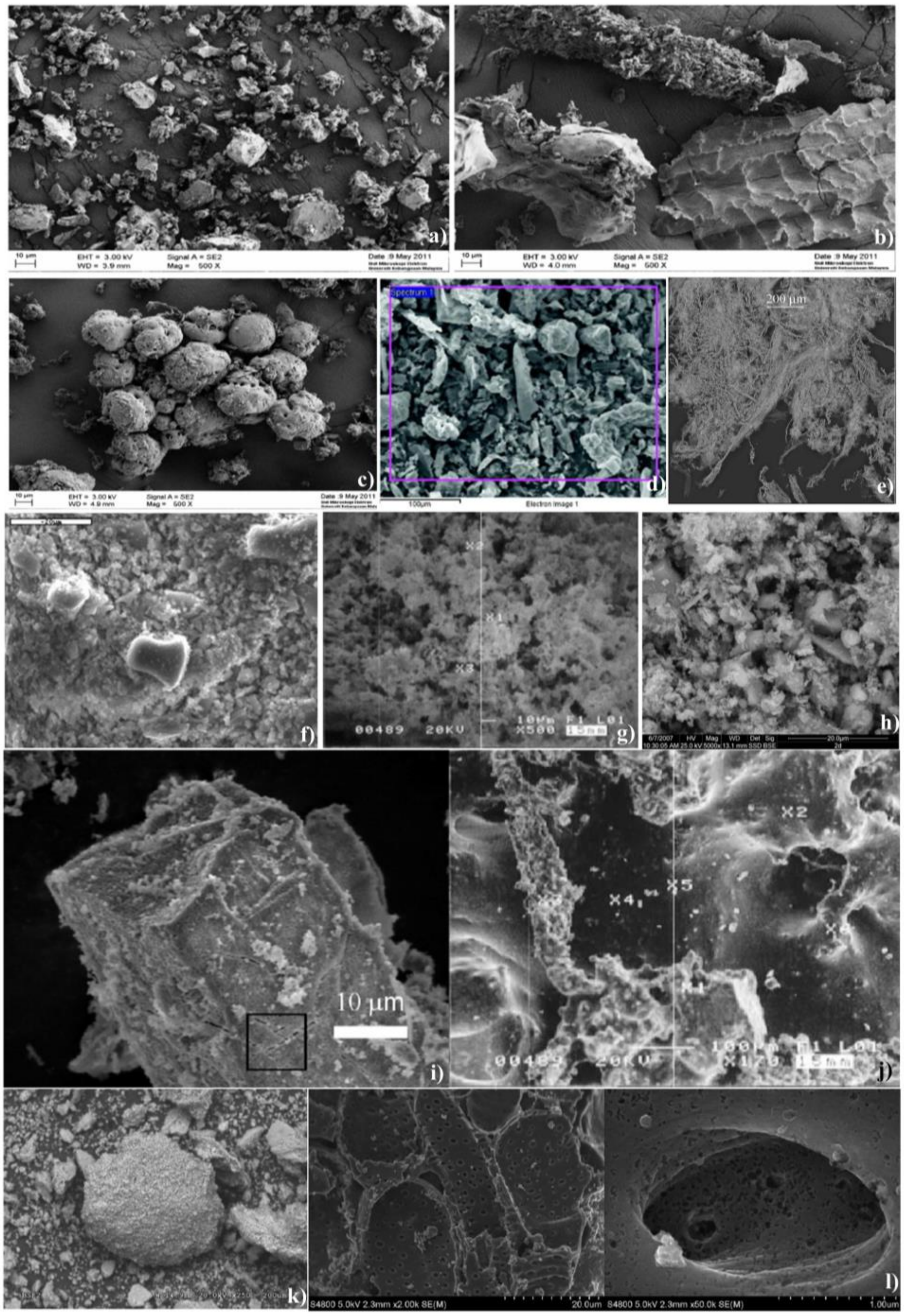

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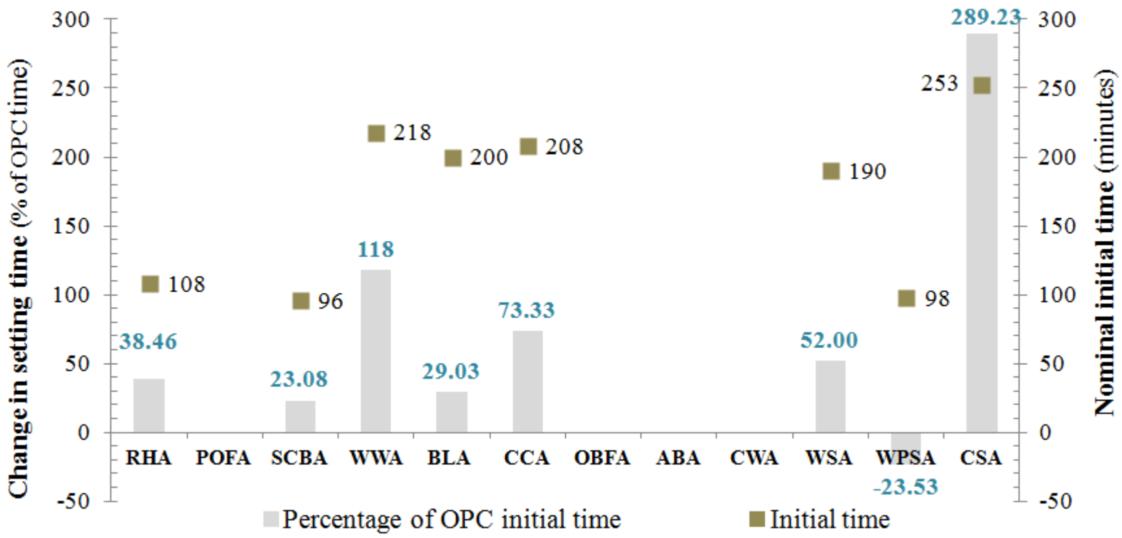

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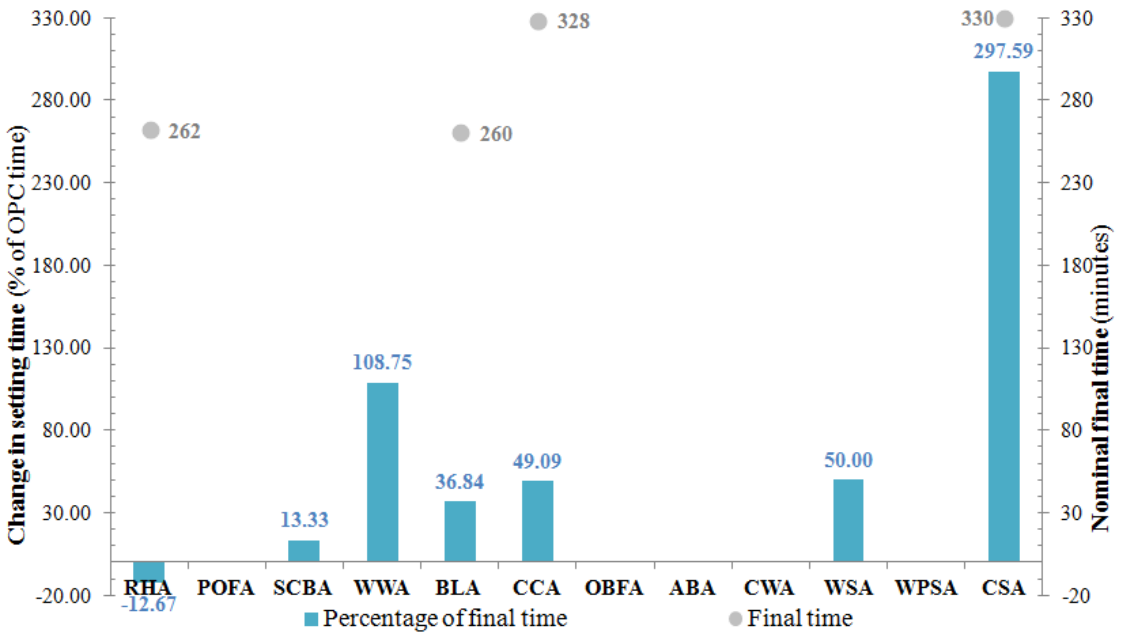

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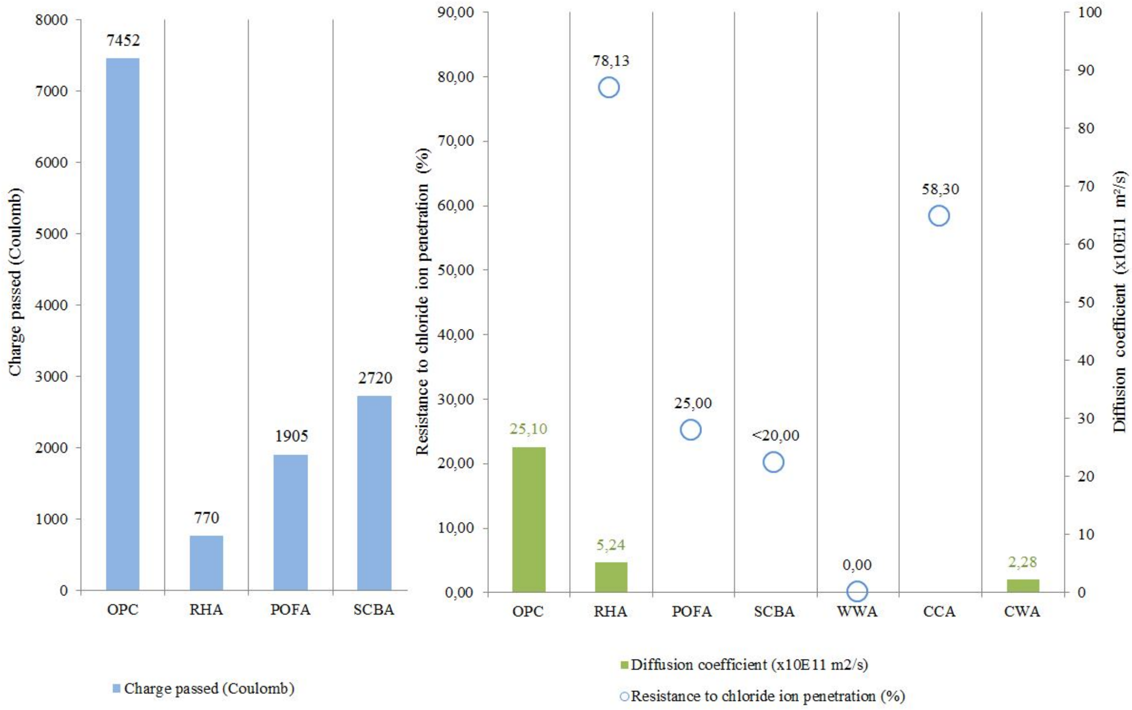

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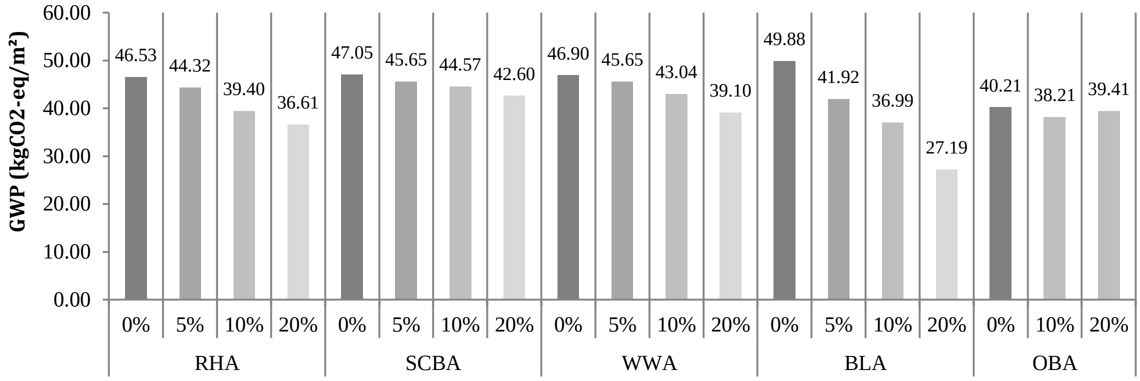

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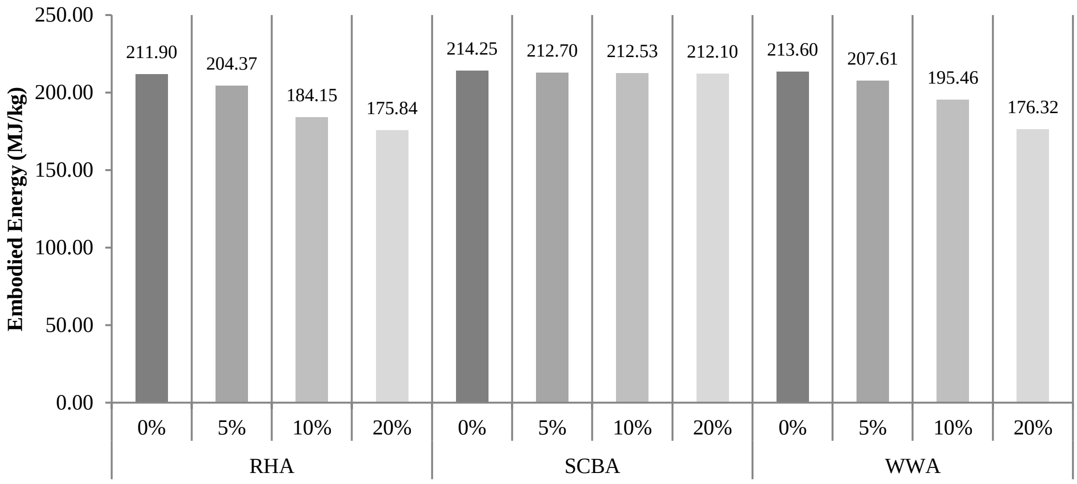

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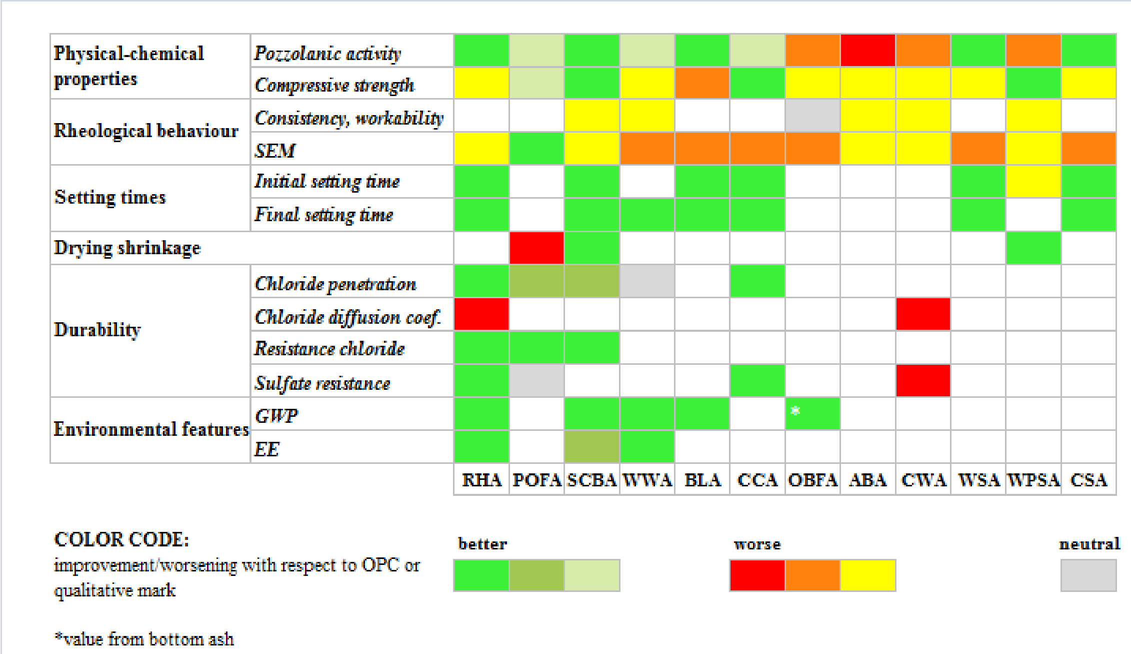

Fig. 19 Main characteristics of the analysed plant biomass ashes-based mixtures from a qualitative perspective

Table 1. Production of crop or raw material in million tons

Crop or raw material	Year of record	Million Tons	Reference	FAO Million Tons	FAO Reference
Rice	2015	-	-	740.20	[12]
Palm	-	-	-	-	-
Sugarcane	2011	-	-	1700.00	[26]
Wood Waste	2009	13.00	[31]	-	-
Bamboo	-	-	-	-	-
Corn Cob	2000	589.00	[40]	-	-

Olive	2013	3.10	[42]	-	-
Agave	2015	4.50	[51]	-	-
Cork	2001	0.34	[58]	-	-
Wheat	2010	-	-	653.00	[26]
Waste paper	2010	72.00	[67]	-	-
Coconut (coconut flesh)	2013	-	-	12.5	[71]

Table 2. $SiO_2 + Al_2O_3 + Fe_2O_3$ percentage in the plant biomass ashes (references in the text)

Biomass cement compound	**SiO_2 (%)**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)**	**Reference**
RHA	79.84	0.14	1.16	81.14	[78]
	80.72	0.08	1.10	81.90	[78]
	86.49	0.01	0.91	87.41	[78]
	76.81	6.17	4.19	87.17	[82]
POFA	63.41	5.55	3.74	72.70	[83]
SCBA	78.50	7.30	3.85	89.65	[80]
	72.74	5.26	3.92	81.92	[81]
WWA	67.20	4.09	2.26	73.55	[87]
	78.92	0.89	0.85	80.66	[88]
	31.80	28.00	2.34	62.14	[86]
BLA	80.40	1.22	0.71	82.33	[36]
CCA	63.91	4.01	3.95	71.87	[38]
OBFA	33.00	16.66	6.50	56.16	[45]
	11.84	2.60	1.38	15.82	[89]
ABA	1.40	-	-	-	[50]
CWA	38.15	3.65	1.95	43.75	[60]
WSA	73.06	3.90	1.75	78.71	[62]
WPSA	15.16	6.06	1.11	22.33	[90]
CSA	37.97	24.12	15.48	77.57	[85]

Table 3. Compressive strength biomass ash-cement mixture (MPa) and reference tests

Biomass cement compound	**Percentage of replacement (%)**	**Nominal Compressive Strength** (MPa)	**Reference tests**			**Reference**
			Standards	**Form**	**Dimensions** (mm)	
RHA	20	25.00	-	Cubes	-	[102]
POFA	10	48.00	-	Cubes	50	[98]
SCBA	10	33.86	-	Cubes	100	[96]
WWA	10	44.30	EN 196-1	Prismatic	40x40x160	[104]
BLA	20	60.00	-	Cubes	4.133	[103]
CCA	20	10.38	-	-	-	[101]
		5.08	-	-	-	[101]
OBFA	10	5.50	-	Prismatic	40x40x160	[45]
ABA	5	55.00	ASTM C311	-	-	[50]
CWA	10	51.20	EN 196-1	Prismatic	40x40x160	[60]
WSA	15	-	JIS 5201-1997	Prismatic	40x40x160	[100]
WPSA	10	54.50	EN 196-1	Semi prism	40x40x160	[99]
CSA	10	31.78	-	Cubes	150	[73]

Table 4. Percentage of drying shrinkage with respect to the reference cement compound (references in the text)

Biomass ash	Drying shrinkage (%)
RHA	**unknown**
POFA	19%
SCBA	-8%
WWA	**unknown**
BLA	**unknown**
CCA	**unknown**
OBFA	**unknown**
ABA	**unknown**
CWA	**unknown**
WSA	**unknown**
WPSA	-64%
CSA	**unknown**

Table 5. Reduction of compressive strength to sulfates attack, in biomass ash-cement mixtures with respect to the reference cement compound (references in the text)

Biomass ash	**Reduction of compressive resistance to sulphate attack (%)**
RHA	6
POFA	Equal to reference cement mortar
SCBA	**unknown**
WWA	**unknown**
BLA	**unknown**
CCA	38.7
OBFA	**unknown**
ABA	**unknown**
CWA	> 0
WSA	**unknown**
WPSA	**unknown**
CSA	**unknown**

Table 6. Global warming potential of the plant biomass ashes

Biomass ash	Global Warming Potential of ashes (kg CO_2-eq/kg ash)	Reference
Rice Husk Ash (RHA)	0.057	[171]
Palm Oil Fuel Ash (POFA)	-	-
Sugarcane Bagasse Ash (SCBA)	0.514	[172]
Wood Waste Ash (WWA)	0.006	[173]
Bamboo Leaf Ash (BLA)	0.078	[174]
Corn Cob Ash (CCA)	-	-
Olive Biomass Ash (OBA)	0.050	[175]
Agave Biomass Ash (ABA)	-	-
Cork Waste Ash (CWA)	-	-
Wheat Straw Ash (WSA)	-	-
Waste Paper Sludge Ash (WPSA)	-	-
Coconut Shell Ash (CSA)	-	-

Table 7. Embodied Energy of the plant biomass ashes

Biomass ash	Embodied Energy of ashes (MJ/kg ash)	Reference
Rice Husk Ash (RHA)	0.955	[171]
Palm Oil Fuel Ash(POFA)	-	-
Sugarcane Bagasse Ash (SCBA)	3.770	[172]
Wood Waste Ash (WWA)	0.101	[176]
Bamboo Leaf Ash (BLA)	-	-
Corn Cob Ash (CCA)	-	-
Olive Biomass Ash (OBA)	2.750	[175]
Agave Biomass Ash (ABA)	-	-
Cork Waste Ash (CWA)	-	-
Wheat Straw Ash (WSA)	-	-
Waste Paper Sludge Ash (WPSA)	-	-
Coconut Shell Ash (CSA)	-	-

Table 8. Physical-chemical characteristics of biomass ash-cement compounds

Biomass ash	$SiO_2+Al_2O_3+Fe_2O_3$		Compressive strength		Flow spread			Setting time					Drying Shrinkage	
								Initial		Final				
	%	Ref.	(1)%	Ref.	(1)%	mm	Ref.	(1)%	min.	(1)%	min.	Ref.	%	Ref.
RHA	81.14	[78]	-16.67	[102]	-7.81	-	[113]	38.46	108	-12.67	262	[14]	-	-
	81.90	[78]												
	87.41	[78]												
	87.17	[82]												
POFA	72.7	[83]	2.13	[98]	-	-	-	-	-	-	-	-	19%	[132]
SCBA	89.65	[80]	19.60	[96]	-20.77	164	[111]	23.08	96	13.30	340	[96]	-8%	[111]
	81.92	[81]												
WWA	73.55	[87]	-11.11	[104]	-7.41	250	[114]	118.00	218	108.75	334	[86]	-	-
	80.66	[88]												
	62.14	[86]												
BLA	82.33	[36]	-16.67	[103]	-	-	-	29.03	200	36.84	260	[127]	-	-
CCA	71.87	[38]	19.80	[101]	-	-	-	73.33	208	49.09	328	[128]	-	-
			15.13	[101]										
OBFA	56.16	[45]	-8.33	[45]	-	-	-	-	-	-	-	-	-	-
	15.82	[89]												
ABA	<50	[50]	-9.26	[50]	-13.85	168	[50]	-	-	-	-	-	-	-
CWA	43.75	[60]	-9.70	[60]	-5.64	186	[60]	-	-	-	-	-	-	-
WSA	78.71	[62]	-1.50	[100]	-12.92	155	[100]	52.00	190	50.00	345	[100]	-	-
WPSA	22.33	[90]	19.00	[99]	-	-	-	-23.53	98	-	-	[129]	-64%	[112]
CSA	77.57	[85]	-7.13	[73]	-	-	-	289.23	253	297.59	330	[73]	-	-

(1) increase/decrease percentage with respect to the reference ordinary Portland cement mortar

Table 9. Durability characteristics of biomass ash-cement compounds

Biomass ash	Durability										
	Resistance to chloride ion penetration		Ref.	Reduction of resistance to sulfates (%)	Ref.	Migration coefficient		Ref.	Charge passed		Ref.
	(1)%	mm				(1)%	$x10^{-11}$ m^2/s		(1)%	Coulomb	
RHA	78.13	3.5	[133]	6.00	[145]	79.12	5.24	[139]	89.67	770	[142]
POFA	25.00	12.0	[133]	-	-	-	-	-	74.44	1905	[142]
SCBA	<20.0	-	[111]	-	-	-	-	-	67.90	2720	[143]
WWA	0	-	[104]	-	-	-	-	-		-	-
BLA	-	-	-	-	-	-	-	-		-	-
CCA	58.30	-	[140]	38.7	[140]	-	-	-		-	-
OBFA		-	-	-	-	-	-	-		-	-
ABA		-	-	-	-	-	-	-		-	-

CWA		-	-	<0	[60]	90.95	2.28	[60]		-	-
WSA		-	-	-	-	-	-	-		-	-
WPSA		-	-	-	-	-	-	-		-	-
CSA		-	-	-	-	-	-	-		-	-

(1) increase/decrease percentage with respect to the reference ordinary OPC