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Evaluation of Physical, Chemical, and Environmental Properties of Biomass Bottom Ash for Use as a Filler in Bituminous Mixtures

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Abstract: The road construction sector is one of the most raw material-intensive sectors in existence. As a result, it has a significant impact on the environment. For this reason, there are several research projects in which industrial by-products are used as raw materials. In turn, energy production from biomass combustion is considered to be one of the most promising energy sources. However, this type of energy produces a number of wastes that need to be treated, such as biomass bottom ash. This research evaluates the properties of biomass bottom ash for use as a filler in bituminous mixtures and quantifies the environmental advantages of its use. For this purpose, the chemical composition of the ashes was analysed and their properties were physically characterised to confirm their suitability as a filler. Subsequently, the advantages of its processing compared to limestone filler, lime, or cement were calculated with SimaPro software. The results showed acceptable properties of biomass bottom ash for use as a filler, as well as a drastic reduction in the environmental impact of its processing. In short, this research presents the basis for the development of further bituminous mixtures with biomass bottom ash, reducing the extraction of raw materials and avoiding landfill disposal.

Keywords: biomass bottom ash; energy production; characterisation; filler; bituminous mixture; waste; life cycle assessment; circular economy; sustainable construction

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Citation: Suárez-Macías, J.; Terrones-Saeta, J.M.; Iglesias-Godino, F.J.; Corpas-Iglesias, F.A. Evaluation of Physical, Chemical, and Environmental Properties of Biomass Bottom Ash for Use as a Filler in Bituminous Mixtures. *Sustainability* **2021**, *13*, 4119. https://doi.org/10.3390/su13084119

Academic Editors: Mayca Rubio-Gámez and Ana Jiménez del Barco Carrión

Received: 2 March 2021
Accepted: 6 April 2021
Published: 7 April 2021

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1. Introduction

The construction sector is essential for society, as it brings important benefits to the population. However, this sector is one of the most polluting sectors in existence. This is due to the fact that it uses large quantities of raw materials, with their extraction and processing resulting in greenhouse gas emissions [1].

More specifically, the construction of road infrastructure consumes a significant amount of raw materials. In addition, high temperature processes are used to conform the materials used, usually bituminous mixtures. These processes are fuelled by fossil fuels, so the carbon footprint of these operations is considerable. Nevertheless, roads are essential for the welfare of the population, avoiding economic and social inequalities, as well as favouring the economic development of the population. On this basis, it can be deduced that the construction of roads is necessary but with more sustainable processes, obtaining, as a consequence, materials that are more respectful of the environment [2].

According to the hypotheses developed, and taking as a basis a new circular economy in which waste is the raw material for new materials [3], various research projects have been carried out in which industrial by-products were used in bituminous mixtures [4,5]. The wastes used in bituminous mixes have been ladle furnace slag [6,7], electric arc furnace slag [8], reclaimed asphalt pavement [9,10], scrap tyres [11], recycled glass [12], ceramic dust [13], etc. In most cases, the results were acceptable and demonstrated the feasibility of incorporating waste into bituminous mixtures for roads, reducing the environmental impact through their use [14].

On the other hand, different nations—encouraged by a greater environmental awareness of the population—are implementing, developing, and investing in new, more sustainable forms of energy production [15]. Among these new industries is the production of energy from biomass combustion [16].

This form of energy production currently accounts for 14% of the world's energy supply [17] for population and industry and is therefore one of the most promising energy production systems available, so much so that by the year 2100, the total energy production from biomass is expected to be 25% to 46% [18].

In Europe, energy production through biomass combustion has increased considerably in recent years [19]. More specifically, in Andalusia (Spain)—the area where this research is being carried out—there are currently 18 plants producing energy through biomass combustion, producing a total of 257.48 MW [20].

However, although biomass energy production seems to be a sustainable solution, it has a number of disadvantages that need to be evaluated for remediation. Among the main disadvantages is the production of different wastes that must be treated to avoid subsequent environmental pollution [21]. It should be borne in mind that Spain alone produces 120,000 tons of waste per year from biomass combustion [22]. Of this waste, 64% corresponds to biomass fly ash and 36% to biomass bottom ash [23].

At the same time, it should be noted that the waste produced depends on the industrial process carried out and, to a greater extent, on the biomass used. In other words, the biomass used will condition the physical, chemical, and even mechanical properties of the residue obtained, whether it is biomass bottom ash or biomass fly ash. For example, biomass ashes from the combustion of municipal solid waste contain high percentages of highly polluting metallic elements and must therefore be treated appropriately. Therefore, it is essential to know the biomass used by the producing industry, as well as the properties of the waste for its possible valorisation in new materials [24]. More specifically, in the area of Andalusia (Spain) where this research is being carried out, the biomass used usually comes from the olive tree and the by-products obtained from its processing [25].

As mentioned, there are two very different types of waste produced by the biomass electricity generation industry [26]. These wastes are biomass fly ash and biomass bottom ash. Biomass fly ash is collected from the gases produced in the combustion of biomass. Therefore, its particle size is small and it has a number of volatile components. These biomass fly ashes, due to their high production and their physical and chemical characteristics, have been studied by different researchers for their valorisation. This research includes the reuse of these fly ashes as a partial substitute for cement [27], as an additive to concrete [28], for the production of geopolymers [29], for the improvement of soils low in nutrients [30], and even for nanotechnology [31].

On the other hand, biomass bottom ash is the residue deposited on the grate after combustion. This by-product, unlike the previous one, has not been used as extensively. However, some occasional research has used this residue as a substitute for the fine fraction in mortar and even in concrete [32], obtaining a lower weight of the final material [33] and good mechanical characteristics with its addition [34]. It has also been used as a stabilising element in expansive soils, achieving an improvement in the bearing capacity of the soil after its addition and a drastic reduction in expansion [35]. Therefore, and based on the above-mentioned research and the conclusions obtained by the researchers, it can be affirmed that biomass bottom ash has cementitious characteristics that make it suitable for different binders.

This research evaluated the physical and chemical properties of biomass bottom ash from the combustion of almond shells and alpeorujo (a waste product from olive pomace) for their use as a filler in bituminous mixtures. In addition, the environmental effects produced by the processing of these ashes to obtain a filler that can be used in bituminous mixtures were studied, comparing the results with the environmental effects produced to obtain a limestone filler, lime, or cement.

Consequently, the novelty of this study lies in the evaluation of the properties of biomass bottom ash and the determination of the critical points to be taken into account for its use as a filler in bituminous mixtures, as well as the environmental advantages of its use. The evaluation of the properties of the ashes in conjunction with their environmental impact is the only way to objectively determine the benefits of using this waste. It is therefore crucial research for subsequent researchers wishing to incorporate this residue in bituminous mixtures.

In order to carry out this research, and according to the aspects mentioned above, a series of physical and chemical tests were carried out to determine the viability of using biomass bottom ash as a filler in bituminous mixtures. At the same time, an environmental analysis of the processing of these ashes to obtain a marketable filler was carried out in comparison with the conditions produced by the treatment of a limestone filler, lime, and cement. The results showed that the biomass bottom ash had suitable chemical and physical properties for use in bituminous mixtures and that its processing to obtain a marketable filler had a lower environmental impact than the treatment of the commercial materials mentioned above.

2. Materials and Methods

This section describes the materials and methodology used to evaluate the suitability of biomass bottom ash as a filler for bituminous mixtures, as well as the environmental effects produced in its processing to obtain a marketable material. To this end, the materials used in this research are described first, followed by the tests carried out.

2.1. Materials

The material mainly used in this research was biomass bottom ash, hereinafter BBA. Limestone filler, cement, or lime were not analysed as they are commercial materials and only the procedure to obtain them environmentally is compared with the processing that must be carried out on biomass bottom ash to obtain a filler that can be used in bituminous mixtures.

The biomass bottom ash used came from the energy generation industry located in Andalusia, Spain. This type of industry uses biomass from almond shells and alpeorujo to produce combustion and, consequently, energy.

The biomass bottom ash samples mentioned above have been analysed over time. In other words, different production batches were analysed in different months of the year. In this way, it could be observed that the physical properties and chemical characteristics were maintained throughout the production. This is due to the fact that the biomass used is always the same, so the waste produced has practically unchanged properties.

The biomass bottom ash was taken from the producing industry in an unaltered form, i.e., with all its particle sizes and without any further treatment. These biomass bottom ashes were dried at a temperature of (105 $\pm$ 2) °C for 24 h. This process was carried out in order to eliminate humidity and, therefore, not to influence the methodology with unnecessary variables that could disturb the final results. However, the existence of moisture in industry is not problematic, it should simply be taken into account and acted upon.

Subsequently, the dried biomass bottom ash was subjected to different processes to obtain the necessary samples for the different tests. These tests are defined below.

2.2. Methodology

This section describes the tests carried out for the chemical and physical analysis of biomass bottom ash, as well as the procedure used for the evaluation of the environmental impacts of ash processing compared to the processing of limestone filler, lime, and cement.

2.2.1. Chemical and Physical Analysis of Biomass Bottom Ash

The methodology followed in this research consists of various chemical and physical tests necessary to study the feasibility of using biomass bottom ash as a filler in bituminous mixtures.

Firstly, the biomass bottom ash was analysed chemically. In this way, it was possible to identify contaminating or harmful elements that could prevent the use of the ashes as a filler in bituminous mixtures. In order to carry out these tests, the biomass bottom ash was ground to a particle size of less than 100 micrometres. The dry sample, according to the procedure described above and with this treatment, was used for all the chemical tests.

The first chemical test performed was the elemental analysis test to quantify the presence of nitrogen, hydrogen, carbon, and sulphur in the sample. This test consisted of heating the sample of the material to be analysed to a temperature of (950 ± 5) °C. The gases from this combustion were analysed, detecting the presence of the aforementioned elements in the sample tested. The test was performed with LECO's TruSpec Micro commercial equipment (TruSpec Micro, LECO, St. Joseph, MI, USA).

Subsequently, the loss on ignition test was performed. This test consisted of measuring the loss of mass in percentage that exists in the sample when the sample was heated to a temperature of (950 ± 5) °C. Therefore, this test reflects the organic part of the biomass bottom ash corresponding to unburned biomass, as well as the possible existence of carbonates, volatile sulphur, and other compounds that may exist. It should be noted that there are several factors that influence the loss of mass by ignition, so the performance of other parallel tests and the knowledge of the sample will have a significant influence on the interpretation of the results.

In turn, and due to the fact that the chemical composition of the ash is mainly inorganic, an X-ray fluorescence test was carried out. This chemical test provides the elemental composition of the sample analysed, as well as the proportion in which each element is found. The X-ray fluorescence test was performed with the commercial equipment ADVANT'XP+ (ADVANT'XP+, Thermo Fisher, Waltham, MA, USA).

However, the chemical elements have more or less activity, cementitious capacity, or even contamination depending on the chemical compound in which they are combined. In order to determine the main chemical compounds present in the biomass bottom ash, an X-ray diffraction test was carried out. This test was carried out with the equipment model X'Pert PRO of the commercial brand PANalytical (X'Pert PRO, PANalytical, Malvern, UK).

Once the chemical characteristics of the biomass bottom ash had been analysed, the different existing main physical tests were carried out to determine the feasibility of using the ash as a filler in bituminous mixtures. For this purpose, the biomass bottom ash, taken directly from the producing industry and dried, was subjected to a particle reduction process similar to that which would be carried out in industry. This milling process is completely similar to the one used to obtain a limestone filler, lime, or cement, taking into account that the mechanical resistance of biomass bottom ash is lower, so the energy cost and the wear and tear of the equipment is also lower. The ash sample prepared in this way was used for all physical tests.

The first of the physical tests carried out was the laser particle size test due to the fact that the fillers must have a small particle size. With this test, the particle size distribution of the processed biomass bottom ash can be determined from the size of 1 micrometre to 2000 micrometres.

Once the grading curve of the biomass bottom ashes was evaluated, the particles were analysed with a scanning electron microscope. This test provides important qualitative information on the biomass bottom ash, more specifically on the surface of the biomass bottom ash, due to the high magnifications that can be performed. The sample prepared according to the detailed methods was coated with carbon so the surface of the biomass bottom ash could be observed clearly. The scanning electron microscope used was a high resolution (FESEM) MERLIN (Carl Zeiss, Oberkochen, Germany) with EDX and WDX (Oxford Analytical, High Wycombe, UK) capabilities.

In addition, there are three physical tests that provide very important information about the filler and its suitability for use. These tests are particle density, bulk density in Kerosene, and plasticity index. The particle density test (standard UNE-EN 1097-7) shows the density of biomass bottom ash without taking into account air voids. It is therefore an essential test to assess whether it is necessary to make volumetric corrections in the conformation of bituminous mixtures, as some wastes, such as those from the steel industry, have a higher density than commercial fillers and must be suitably dosed. The bulk density in Kerosene test (standard UNE-EN 1097-3) evaluates whether the material is very powdery. A powdery filler presents problems in its proportioning in industry, as it produces a high percentage of dust. In addition, a very powdery filler, i.e., with a small particle size, has a high specific surface area, so its use in bituminous mixtures will result in a higher percentage of bitumen absorption to form the mastic. This fact should be monitored and special attention should be paid to it, as it can be a critical point. Finally, the plasticity index test (UNE-EN ISO 17892-12) evaluates the presence of clayey particles that will provide a higher plasticity index and can also cause undesirable later expansivity problems in contact with water.

Most of the wastes produced in different industries have very varied chemical compositions due to their production processes. Therefore, there may be certain chemical elements that produce contaminating leachates that are environmentally harmful, even if they are found in low proportions. To quantify this fact, the analysis of biomass bottom ash leachates was carried out according to the UNE-EN 12457-3 standard. The results of this test were compared with the limits established by Spanish-European regulations. For the analysis of the leachate, the commercial equipment Agilent 7900 (7900, Agilent, Santa Clara, CA, USA) was used.

2.2.2. Life Cycle Assessment of Biomass Bottom Ash Compared to Commercial Filler

The purpose of this part is to determine the environmental benefit of treating biomass bottom ash for use in bituminous mixtures compared to commercial fillers.

This environmental assessment is carried out with the software SimaPro, version 8.3.0.0, from PRé Consultants (Amersfoort, the Netherlands). To compare the results, the environmental cost of the treatment of a limestone filler, a lime, and a cement were also evaluated. The comparison of the environmental impacts of processing biomass bottom ash with the commercial fillers discussed above is due to different reasons. On the one hand, they are the most commonly used fillers in bituminous mixtures and construction materials. On the other hand, they have similar physical characteristics to biomass bottom ash, i.e., they have a small particle size. And finally, biomass bottom ash has cementitious characteristics, as has been stated by several researchers, so the environmental cost of its treatment has been compared with that of an inert filler and limestone filler, and with other cementitious fillers, cement, and lime. Therefore, the environmental benefits of biomass bottom ash can be compared with common materials and with different properties, establishing a variety of cases.

The life cycle analysis methodology was carried out for the detailed materials according to ISO 14040 and ISO 14044. As a result, various stages were defined within the processing of the materials that are essential for obtaining a filler for bituminous mixtures. These stages or processes are as follows:

- Raw material extraction. Obtaining raw materials for the production of filler for bituminous mixtures has a series of significant impacts that must be taken into account. Firstly, there is an alteration of the landscape, causing significant effects on fauna and flora and, in turn, influencing groundwater flows. Once the surface has been prepared for the extraction of the material, different processes must be developed to extract the raw material. It is usual at this stage to use explosives to fragment the rock and then collect it with mechanical equipment. This collection equipment loads the transport vehicles that will be taken into account in the subsequent stage. Therefore, the explosives produce a series of environmental effects such as seismic and airborne

waves and even dust clouds. In addition, the mechanical equipment used for drilling or loading usually consumes fossil fuels. Consequently, there are a series of emissions into the environment and a significant environmental impact.
- Freight transport. Loading equipment from the previous stage provides the materials to vehicles for transport. This transport, usually carried out by vehicles that consume fossil fuels, takes the material from the deposit to the processing plant. In this research, 100 kilometres was taken as the transport distance, as this is the maximum distance allowed for filler processing to be economically viable.
- Milling. Once the material has been received from the quarry, the aggregates are treated in the industry to obtain the filler for bituminous mixtures. This type of installation has crushing equipment arranged in series or in parallel of enormous dimensions. In most cases, this equipment is powered by electric currents, producing significant emissions. At the same time, in order to obtain aggregate circuits that produce a quality filler, there are different conveyor belts with high energy consumption. These types of conveyor belts take up a considerable amount of space and produce various negative environmental aspects, such as water consumption, noise, dust, etc.
- Material processing. In the case of cement or lime, a subsequent high-temperature calcination stage is necessary to form the cementitious compounds. This stage is carried out in furnaces usually fuelled by fossil fuels or biomass, producing significant greenhouse gas emissions. This stage also includes the final packaging operations, thus obtaining a marketable material that can be used in bituminous mixtures.

Once the stages have been defined, the methodology followed is determined. It should be noted that the stages contemplated for the environmental analysis are sufficient to obtain a quality filler for use in bituminous mixtures, whether from biomass bottom ash, cement, lime, or limestone. Subsequently, there will be the transport and shaping of the bituminous mixes, as well as the transport, paving, and compaction of the mixes. These stages are not included in the study, as it is considered that the environmental difference between the two materials would be negligible. The biggest environmental difference is in the processes of obtaining the material.

The methodology followed for the environmental calculation is CML 2000 version 2.05 (Centre for Environmental Studies, Leiden, The Netherlands). This methodology was used for different reasons.

- It has a high versatility and is able to quantify different impacts adequately.
- The data it uses are based on European and even global databases so that the extrapolation of the results to different countries is immediate.
- In addition, several studies have used this methodology and have been successful in calculating the environmental impact.

In order to carry out this methodology of environmental impact analysis, it was necessary to use different real databases in which the impact of each stage is directly measured. The data used for this purpose correspond to different sources. These sources are detailed below:

- Data from reputable databases, Ecoinvent v.3.2 (Ecoinvent, Zurich, Switzerland).
- Empirical data measured directly from the different stages.
- Bibliographic data published in various research studies related to the field of study.

On the basis of the above premises, the environmental effects of processing biomass bottom ash as a filler for bituminous mixtures in comparison with commercial materials were obtained. In this way, the results could be objectively compared and a series of partial conclusions could be drawn that determine the benefits of using this by-product in comparison with traditional materials.

3. Results

This section describes the results of the tests detailed in the methodology. These tests correspond to the chemical and physical characterisation of the biomass bottom ash and the evaluation of the environmental effects produced in the treatment of the ash to obtain a marketable filler in comparison with other commercial materials. Therefore, the results that technically and environmentally evaluate the usefulness of biomass bottom ash as a filler in bituminous mixtures are shown.

3.1. Chemical and Physical Analysis of Biomass Bottom Ash

For the characterisation of the biomass bottom ash, different physical and chemical tests were carried out. The first of the chemical tests was the elemental analysis test. The results of this test are shown in Table 1.

Table 1. Elemental analysis of biomass bottom ash.

Sample	Nitrogen, %	Carbon, %	Hydrogen, %	Sulfur, %
BBA	0.400 ± 0.008	4.410 ± 0.090	0.540 ± 0.001	0.000 ± 0.001

The elemental analysis test shows low percentages of nitrogen and sulphur. This fact benefits the incorporation of ashes as a filler in bituminous mixtures, since if this were not the case, tests would have to be carried out to quantify the leaching of these elements to avoid environmental pollution due to their use. It is also worth noting the low percentage of carbon and hydrogen, so these values represent the existence of a mainly inorganic material.

In order to evaluate the loss of volatile elements at high temperatures, as well as the presence of transformed chemical compounds, a loss on ignition test was carried out. This test showed a mass loss on ignition value, under the conditions detailed in the methodology, of $14.55 \pm 0.52\%$. This value represents several factors. On the one hand, there may be organic particles that were not properly combusted and, on the other hand, it also reflects the transformation and formation of chemical compounds different from those existing in the sample, either by oxidation, hydration, or carbonation. Based on the results of the elemental analysis tests and compared to the loss on ignition results, there seems to be a low proportion of organic matter, i.e., unburned. However, there were some chemical compounds that were transformed by calcination processing, usually into oxides. In other words, the high temperatures and the speed of the industrial process did not develop the complete transformation of the chemical compounds in the sample.

As detailed above, the composition of biomass bottom ash is mainly inorganic, according to the values obtained in the previous tests. Therefore, an X-ray fluorescence test was performed to determine the chemical elements with the highest atomic weight present in the sample. The results of the X-ray fluorescence test of the biomass bottom ash are listed in Table 2.

It should be recalled that the X-ray fluorescence test is an elemental test. That is, it provides information on the chemical elements present in the sample and the proportion in which they are present. On this basis, it can be seen that the main element present in the sample is potassium. This is to be expected if we take into account that the ash comes from the combustion of almond shells and alpeorujo. On a second level, other chemical elements usually found in biomass bottom ashes are calcium, silicon, magnesium, phosphorus, and aluminium. These chemical elements, depending on the chemical compound in which they are combined, can provide very interesting characteristics to the bituminous mixture that incorporates biomass bottom ash as a filler. At the same time, the existence of sulphur and chlorine—non-volatile in the sample—should be mentioned, so it is necessary to carry out a subsequent ash leaching test to assess that the concentrations of these elements in the leachate are lower than those set by the regulations.

Table 2. X-ray fluorescence of biomass bottom ash.

Compound	Wt.%	Est.Error
K_2O	45.2	0.25
CaO	8.98	0.14
SiO_2	8.96	0.14
SO_3	6.43	0.12
Cl	4.72	0.11
MgO	4.04	0.10
P_2O_5	3.56	0.09
Al_2O_3	1.64	0.06
Fe_2O_3	0.864	0.0430
Na_2O	0.623	0.0310
ZnO	0.197	0.0098
TiO_2	0.0728	0.0036
SrO	0.0533	0.0027
MnO	0.0312	0.0020
Rb_2O	0.0237	0.0037
NiO	0.0221	0.0016
CuO	0.0207	0.0021
Cr_2O_3	0.0105	0.0020

As mentioned above, the activity, cementitious properties, or leaching does not only depend on the chemical elements present, but also on the way they are combined. Therefore, an X-ray diffraction test is essential to determine which main chemical compounds are present in the ashes. The diffractogram of biomass bottom ash is shown in Figure 1.

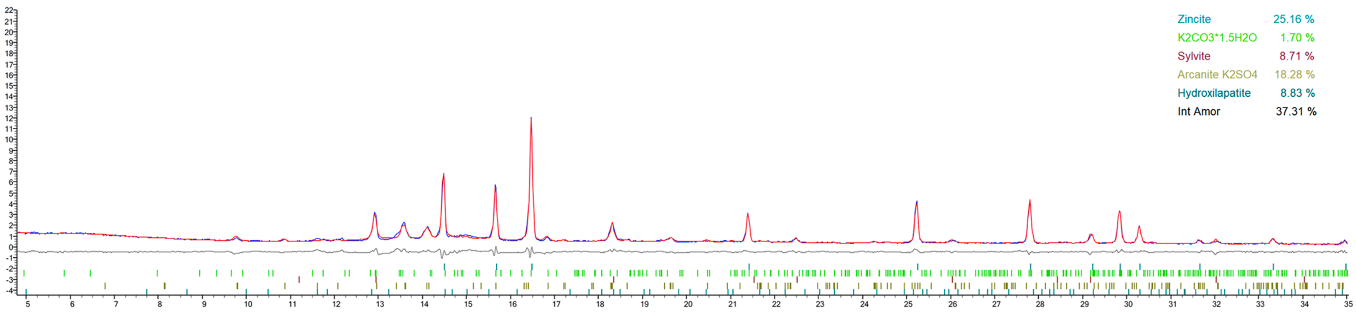

Figure 1. Results of X-ray diffraction of biomass bottom ash.

The diffractogram of the biomass bottom ash shows a high content of amorphous or non-diffracting material. Silicate, potassium carbonate, sylvite, and arcanite are identified as main phases. Therefore, the silicates are directly responsible for the cementitious properties of the biomass bottom ash. In turn, the existence of potassium carbonates ensures the dimensional stability of the ashes, i.e., the carbonation process has taken place and, consequently, there will be no expansivity problems. Furthermore, sulphur and chlorine, as evaluated in the X-ray fluorescence test, are found in the chemical compounds arcanite and sylvite, respectively. These chemical compounds are more stable than other sulphur or chlorine compounds, so they should not present problems of leaching of these chemical elements. However, as detailed above, a leachate test was subsequently carried out to corroborate that the concentrations of sulphur and chlorine were below the limits established by the regulations.

Once the chemical characterisation of the biomass bottom ash had been carried out and its composition determined, as well as the critical points to be taken into account, the ashes were milled to obtain a filler material similar to that which would be obtained in industry.

Firstly, the particle size distribution was analysed, thanks to the use of the laser particle size technique. The grading curve of biomass bottom ash can be seen in Figure 2.

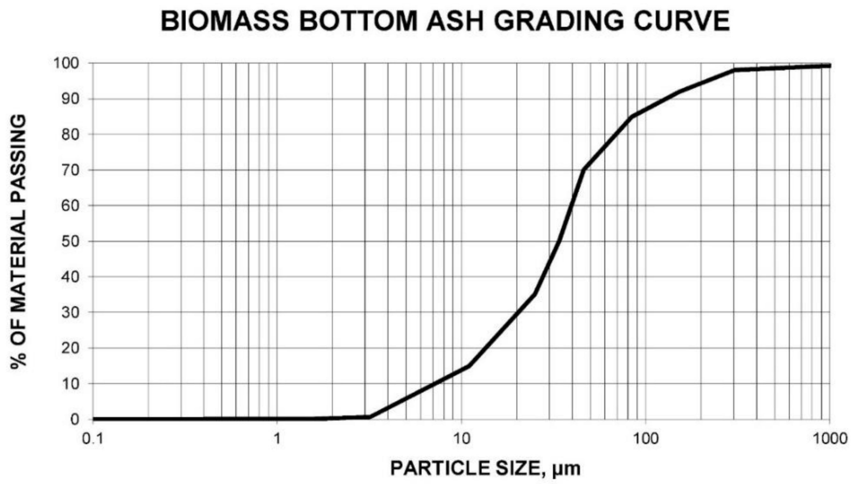

Figure 2. Biomass bottom ash grading curve.

The grading curve of the analysed biomass bottom ashes shows a higher proportion of particles smaller than 0.063 mm. This fact is essential for the use of the ashes as a filler in bituminous mixtures, as regulations limit the percentage of particles smaller than 0.063 mm to 70%. Consequently, it can be stated that the particle size of the biomass bottom ash after processing is adequate.

On the other hand, the scanning electron microscope provides very interesting qualitative information about the biomass bottom ashes, as it is possible to perform high magnification and to observe the surface of the ashes in detail. The images of the biomass bottom ash at different magnifications with the scanning electron microscope are shown in Figure 3.

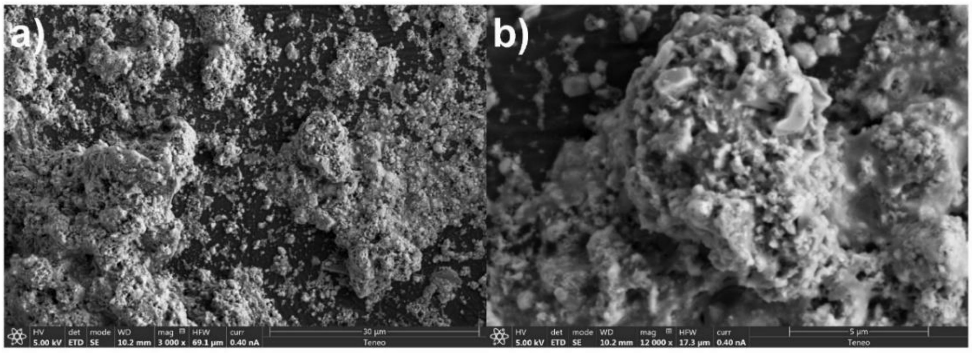

Figure 3. Scanning electron microscope images of biomass bottom ashes at different magnifications in the secondary option. (**a**) 3000×. (**b**) 12000×.

Scanning electron microscope images of biomass bottom ashes show a very irregular ash surface. Micropores and cavities are abundant on the surface of the ashes, which has a significant influence on the higher specific surface area. The higher specific surface area results in higher bitumen absorption in bituminous mixes. As a result, a higher quality mastic is formed, capable of enveloping the aggregates and enabling the bituminous mix to achieve tensile strength. In turn, a higher percentage of bitumen also leads to a longer working life, as there is a higher proportion of mastic capable of withstanding the repeated traffic loads.

On the other hand, it is essential to determine the particle density, the bulk density in Kerosene, and the plasticity index of the biomass bottom ash, as these properties determine the feasibility of using the residue as a filler. The results of these tests are shown in Table 3.

Table 3. Density and plasticity tests for the fine portion of biomass bottom ash.

Test	Standard	Value/Unit
Particle density	UNE-EN 1097-7	2.54 ± 0.07 t/m^3
Bulk density	UNE-EN 1097-3	0.45 ± 0.01 t/m^3
Plasticity index	UNE-EN ISO 17892-12	No plasticity

The particle density of biomass bottom ash is similar to that of a commercial filler. Therefore, no volumetric corrections in proportioning are necessary. At the same time, the bulk density in Kerosene is low, although acceptable by regulation. This fact reflects the higher specific surface area visualised in the images obtained with the scanning electron microscope. This lower bulk density will result in higher bitumen absorption, resulting in the creation of a higher quality mastic to withstand traffic loads, as mentioned above. Finally, the null plasticity index value reflects the cementitious properties of the chemical compounds mentioned in the X-ray diffraction test. Consequently, this null value shows the non-existence of a clayey particle that could cause subsequent expansivity problems.

Finally, the leachate test carried out on the biomass bottom ash evaluates the presence of contaminating elements in the leachate, conditioning the use of the ash without the production of environmental problems. The results of the leachate test are shown in Table 4.

Table 4. Concentration of chemical elements in the biomass bottom ash leachate compared to regulatory limits.

Element	BBA, mg/kg	Maximum Limits, mg/kg
Ba	0.182 ± 0.005	17
Cd	0.002 ± 0.001	0.009
Cr	0.002 ± 0.001	0.5
Mo	0.001 ± 0.001	0.5
Ni	0.009 ± 0.001	0.4
Pb	0.001 ± 0.001	0.5
Se	0.002 ± 0.001	0.007
V	0.003 ± 0.001	1.3
Zn	0.012 ± 0.001	1.2
As	0.002 ± 0.001	0.5
Cu	0.009 ± 0.001	2
Hg		0.01
Sb	0.001 ± 0.001	0.06
Chloride	134 ± 3	800
Sulphates	86 ± 3	377

The concentrations of pollutant elements present in the biomass bottom ash leachate are lower than the maximum values allowed by Spanish–European regulations [36]. Furthermore, it should be noted that the precoating of the ashes by bitumen and the formation of mastic will drastically reduce the leaching of these chemical elements.

Based on the results of the physical and chemical characterisation of the ashes, it can be stated that the biomass bottom ash has suitable properties for use as a filler in bituminous mixtures.

3.2. Life Cycle Assessment of Biomass Bottom Ash Compared to Commercial Filler

Once the physical and chemical properties of the biomass bottom ash had been evaluated and its suitability for use as a filler in bituminous mixtures had been determined, the environmental impacts of processing the ash to obtain a marketable filler were determined. These environmental impacts were compared with those caused by the processing of cement, lime, or limestone filler.

It should be noted that one of the most commonly used factors to evaluate the environmental cost of a process is global warming. This factor is measured in kilograms of carbon dioxide equivalent. Therefore, Figure 4 shows the equivalent CO_2 emissions produced by the processing of the four materials detailed.

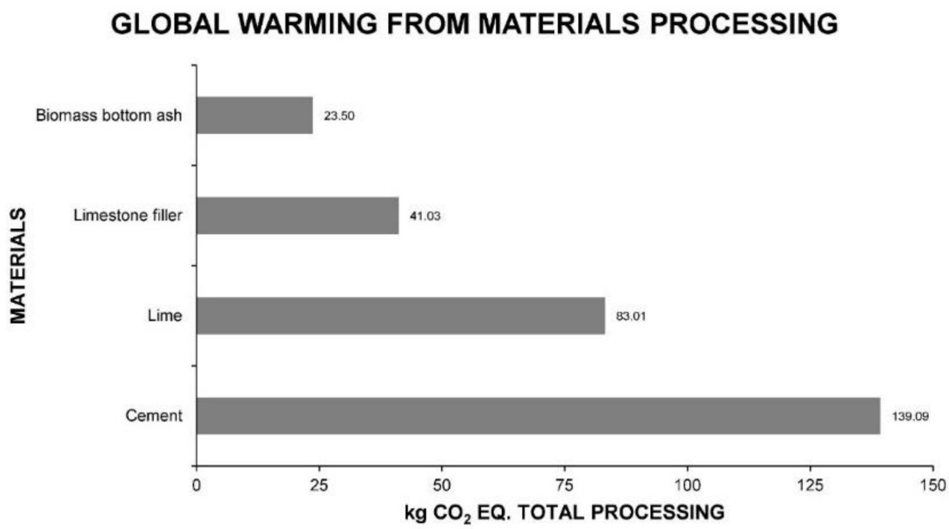

Figure 4. Global warming emissions in kilograms of CO_2 equivalent from the processing of cement, lime, limestone filler, and biomass bottom ash.

As expected, CO_2 emissions from cement production are much higher than those produced by the processing of other materials. Lime, in turn, produces significant CO_2 emissions, much higher than those produced by limestone filler or biomass bottom ash. The higher CO_2 emissions from lime and cement are mainly due to the use of high temperatures to obtain the final material and the need for an adequate milling process after this process. The furnaces in which the detailed material is obtained are fuelled in most cases by fossil fuels, producing significant CO_2 emissions. In turn, the processing of biomass bottom ash is the process that produces the lowest CO_2 emissions, since, unlike the processing of limestone filler, no extraction stage of the material is necessary.

To better understand the differences in CO_2 emissions produced by the processing of the four materials, the CO_2 emissions per stage of the processes discussed are shown in Figure 5.

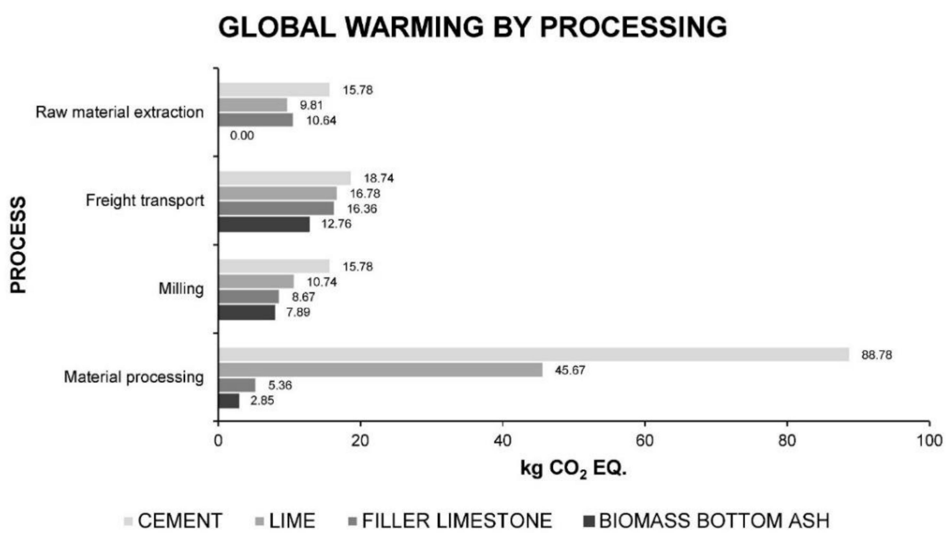

Figure 5. Global warming emissions in kilograms of CO_2 equivalent per stage of cement, lime, limestone filler, and biomass bottom ash processing.

As can be seen in Figure 5, the first stage of material extraction is nil for biomass bottom ash, as it is a by-product of the industry and no operations are necessary to obtain the raw material. In turn, the emissions produced at this stage by limestone filler and lime are very similar, as the starting raw material is practically the same and the same pollution is produced. Emissions from cement at the raw material extraction stage are higher than those of the other materials, due to the fact that the strength of the siliceous rocks used is greater and a greater energy input is necessary for their extraction.

Something similar occurs in the freight transport stage, where the lower CO_2 emissions in the transport of biomass bottom ash from the quarry to the processing plant should be highlighted. This is due to the fact that the other materials (cement, lime, and limestone filler) are transported in large blocks of material, unlike biomass bottom ash, which already has a smaller particle size. Consequently, it is possible to transport more ash than raw materials for lime, cement, or limestone filler in the same volume, reducing the CO_2 emissions produced by vehicles.

In the milling stage, the emissions produced by lime and limestone filler are similar, since, as mentioned above, the raw material is the same. On the other hand, the mechanical strength of the biomass bottom ash evaluated is lower, so the energy required for the process is lower and, consequently, so are the emissions. Similarly, for cement, the siliceous rocks used have a higher strength and therefore the CO_2 emissions are higher.

Finally, the processing stage is where the biggest differences occur between the four materials. At this stage, the emissions of biomass bottom ash and limestone filler are similar, as only final treatments and packaging are carried out. On the other hand, lime and cement, once the raw materials have been ground and mixed in the exact proportion, must undergo a high temperature process, hence the substantial increase in CO_2 emissions. Cement is the material that produces the highest emissions at this stage, mainly due to the greater complexity of the process and the higher temperatures that must be reached.

The SimaPro software, in addition to the CO_2 emissions influencing global warming, also allows the measurement of a number of other environmental effects that are of interest for assessing the environmental benefits of processing biomass bottom ash. These environmental conditions for the four materials under study are described in Table 5.

Table 5. Environmental impacts associated with the processing of cement, lime, and limestone filler compared to the processing of biomass bottom ash for use as a filler.

Impact Category	Unit	Cement	Lime	Limestone Filler	BBA
Abiotic depletion	kg Sb eq.	1.923	0.424	0.182	0.148
Acidification	kg SO_2 eq.	1.737	0.319	0.124	0.086
Eutrophication	kg PO_4 eq.	0.529	0.187	0.032	0.022
Human toxicity	kg 1.4-DB eq.	125.631	224.628	13.462	10.886
Fresh water aquatic ecotox.	kg 1.4-DB eq.	68.846	20.821	3.342	2.798
Marine aquatic ecotoxicity	kg 1.4-DB eq.	148752.881	42767.815	7079.377	5979.543
Terrestrial ecotoxicity	kg 1.4-DB eq.	1.361	0.324	0.049	0.043
Photochemical oxidation	kg C_2H_4 eq.	0.065	0.020	0.006	0.005

The units of the different environmental impacts correspond to kilogram equivalents of the element or chemical compound indicated, where DB is equal to dichlorobenzene. As can be seen in Table 5, in all cases—i.e., for all environmental effects—the emissions studied are lower for the processing of biomass bottom ash. Therefore, these data together with the CO_2 emissions corroborate the environmental advantages of ash processing compared to commercial materials.

However, for a better graphical understanding of the results, Figure 6 shows the emissions as a percentage of the total for each of the materials according to the conditions shown in Table 5.

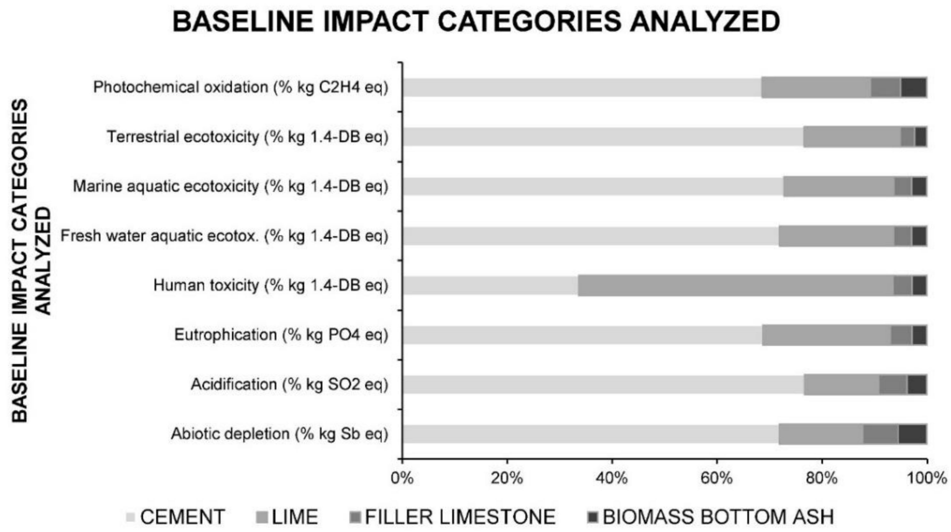

Figure 6. Emission percentages of various impacts for cement, lime, limestone filler, and biomass bottom ash.

Figure 6 clearly shows the decrease in emissions, for all impacts associated with the processing, of biomass bottom ash compared to the other materials. More specifically, and because different authors have stated that biomass bottom ash has cementitious characteristics, it can be seen that the decrease in the emissions of ash with respect to cement are considerable. At the same time, it could be stated that ash emissions are similar to those of limestone filler; however, the difference between these emissions are notable, even though they are not as high as with cement. Furthermore, limestone filler is an inert filler, i.e., it does not contribute any cementitious characteristics to the bituminous mixture and, therefore, it will not achieve the strength of the final product as biomass bottom ash does.

In short, and in view of the results obtained from the comparison of emissions from the process of obtaining cement, lime, limestone filler, and biomass bottom ash, it can be stated that the use of ash produces a considerable reduction in emissions and in different impacts.

4. Conclusions

The tests carried out and the methodology followed in the present investigation led to a series of partial conclusions, which are detailed below:

- The biomass bottom ash has a low percentage of organic matter, with mainly the chemical elements potassium, calcium, silicon, magnesium, and phosphorus. There is also sulphur and chlorine, which were evaluated in the leachate test.
- The main chemical compounds in biomass bottom ash are silicates, potassium carbonate, sylvite, and arcanite. These elements seem to be responsible for the cementitious characteristics mentioned by several researchers.
- Biomass bottom ash has a particle size after processing suitable for use as a filler in bituminous mixtures, showing a particle density similar to that of a commercial material.
- The bulk density in Kerosene, which is adequate according to regulations but slightly lower than that of a commercial filler, reflects the high specific surface area of the biomass bottom ash. This higher specific surface area will result in a higher percentage of bitumen and, consequently, a higher quality mastic. At the same time, the ashes do not exhibit plasticity.
- The leachate test carried out on biomass bottom ash showed a lower concentration of the polluting chemical elements than the maximum limits set by the regulations.
- The CO_2 emissions produced by the processing of biomass bottom ash compared to a commercial limestone filler are about 40% lower. Compared to lime and cement, there is an emission reduction of about 70% and 80%, respectively.

- The other environmental effects studied in this research show how the lowest emissions are produced by the processing of biomass bottom ash compared to cement, lime, or limestone filler.

Based on these partial conclusions, it can be stated that the use of biomass bottom ash as a filler in bituminous mixtures is technically possible and that there is also a considerable reduction in the environmental impact of its processing compared to other materials such as limestone filler, lime, or cement. Therefore, this paper is essential for future researchers wishing to develop bituminous mixtures with biomass bottom ash as a filler, because it characterises in depth this waste in different areas and detects those critical points where special attention should be paid, primarily the higher specific surface area of the ashes that allow a higher percentage of bitumen absorption, as the other properties are similar to those obtained with commercial materials. In turn, it should be noted that the use of currently unused waste avoids landfilling, avoids the extraction of new raw materials, and creates sustainable materials within the circular economy.

Author Contributions: Conceptualisation, F.A.C.-I., F.J.I.-G., J.M.T.-S. and J.S.-M.; methodology, F.A.C.-I., F.J.I.-G., J.M.T.-S. and J.S.-M.; software, J.M.T.-S. and J.S.-M.; validation, F.A.C.-I. and F.J.I.-G.; formal analysis, F.A.C.-I. and F.J.I.-G.; investigation, J.M.T.-S. and J.S.-M.; resources, F.A.C.-I.; data curation, F.J.I.-G.; writing—original draft preparation, J.S.-M.; writing—review and editing, J.M.T.-S.; visualisation, J.M.T.-S.; supervision, F.A.C.-I.; project administration, J.S.-M.; funding acquisition, F.A.C.-I. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The technical and human support provided by CICT of Universidad de Jaén (UJA, MINECO, Junta de Andalucía, FEDER) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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