Energy Recovery from Spent Coffee Ground and Brewery Spent Grains: a Circular Economy Approach to Waste Valorization

I.A. Idowu[1,2], L.J.R. Nunes[3] , K.S Hashim[1] and A. Shaw[1]

1.   Built Environment and Sustainable Technologies (BEST) Research Institute, Faculty of Engineering and Technology, Liverpool John Moores University, United Kingdom. i.a.idowu@ljmu.ac.uk, K.S.Hashim@ljmu.ac.uk, A.Shaw@ljmu.ac.uk

2.   Low Carbon Eco Innovatory Unit, Liverpool John Moores University, United Kingdom i.a.idowu@ljmu.ac.uk

3.   PROMETHEUS, Unidade de Investigação em Materiais, Energia e Ambiente para a Sustentabilidade, Escola Superior Agrária, Instituto Politécnico de Viana do Castelo, Rua da Escola Industrial e Comercial de Nun'Alvares, 4900-347 Viana do Castelo, Portugal leonelnunes@esa.ipvc.pt

Correspondence: leonelnunes@esa.ipvc.pt

Abstract

The circular economy assumes an increasingly important role towards the journey to net zero carbon emissions. While the UK is the first major economy to commit in law to net zero by 2050, through the set out landmark strategy and a vision for a decarbonised economy in 2050. Harnessing the waste resource for energy is crucial for a decarbonised economy. The present work addresses the management of brewery spent grains and coffee spent ground residues through incorporating of both material in the production of biomass pellets and their direct recovery, in an autonomous way, by combustion. It is also intended to evaluate its potential in comparison to other fuels derived from biomass using different conversion and recovery technologies. The results from incorporating these residues in processes such as the production of biomass pellets and other more conventional biomasses already presents more promising results. However, recovery through thermochemical conversion processes, such as pyrolysis, seems to be the scenario with the highest probability of success.

Keywords: brewery spent grains; spent coffee ground; circular economy; energy recovery; waste management; biomass energy.

1. Introduction

The circular economy assumes an increasingly important role in the daily lives of societies [1]. The recovery of waste generated in different industrial processes and the daily activities of populations contributes significantly to solving problems related to

waste management, at the same time contributing to the creation of new value chains and reintroducing these material flows in new production chains [2]. These flows actively contribute to saving resources, both from the perspective of replacing virgin raw materials and the replacement of energy products, when circularization is done through energy recovery [3].

Agro-industrial waste constitutes a very significant percentage of waste generated in Europe. According to information on the European Parliament's official website (https://www.europarl.europa.eu/, accessed on 1 June 2022), 2.5 billion tonnes of waste are produced in Europe annually, from which 20 million tons correspond to waste generated in sectors associated with agriculture, forestry and fisheries. The use of this waste is a priority, justified by the inherent potential of this type of waste, which traditionally, over time, has been incorporated into the very processes where they were generated, as is the case of its use as fertilizer or introduced in animal feed, or still energetically valued [4].

Waste such as brewery-spent grains and coffee spent ground are two widespread types of waste generated in increasing amounts, given the increase in consumption associated with both beer and coffee [5]. The first type essentially results from the brewing industry, which can vary in scale, depending on whether it is a mass production process or a production unit of the so-called craft beer [6]. Both one type of product and the other generate the same type of waste, only varying in quantity. On the other hand, the second type of waste is generated at coffee consumption points and may also be associated with food industries in which coffee is part of the composition of any product. In the catering and hospitality sector, the waste generated will appear smaller than in the industry and even smaller in the domestic sector.

The management of the quantities produced is particularly important since, from the point of view of their collection, the process can be more or less efficient and, therefore, more or less viable [7]. Traditionally, this type of residue, mainly brewery spent grains, will be used for animal feed or incorporation in soil fertilization processes. In the case of coffee spent ground from industrial processes, the destination given to waste will be similar to that of brewery-spent grains [8]. However, coffee spent ground generated in the catering and hospitality sector is usually disposed of together with other organic waste, while coffee spent ground from domestic use is disposed of together with other urban solid waste, in which case it is also it is common for the waste to be surrounded by a plastic capsule [9]. These issues associated with how waste is deposited and stored while

awaiting its management make it difficult to recover it autonomously. In the case of coffee spent ground from the agri-food industry, its recovery is now more accessible since the quantities are more significant, and its storage is usually carried out independently. Its use as a substrate to grow crops, such as mushrooms, has been identified as a solution with interest and the potential to serve as a destination for significant amounts of waste [10].

However, as mentioned above, the increasing amounts of waste require alternatives that can handle all the waste generated, so there are several options found in recent literature. For example, for coffee spent ground, Campos-Vega et al. [11] analysed the different organic compounds found in coffee, such as fatty acids, amino acids, polyphenols, minerals and polysaccharides, which, because they are found in significant amounts, justify their appreciation. Ciesielczuk et al. [12] valued coffee spent ground as a slow-action organo-fertilizer. Kovalcik et al. [13] analysed the methods available in coffee spent ground, namely bioactive compounds, carbohydrates and oil fraction.

A similar situation is found for brewery-spent grains, with many studies also available and addressing different perspectives. The potential for use as a fertilizer was one of the first approaches to be considered, as demonstrated by the study by Mbagwu and Ekwealor [14]. These authors confirmed the improvements in the productivity of two fragile soils induced by the brewery spent grains due to the high contents of N, P, K, Ca, Mg and carbon and the low C:N ratio. Other less conservative approaches, such as the immobilization of kefir and Lactobacillus casei on brewery spent grains for use in sourdough wheat bread-making, were presented, for example, by Plessas et al. [15], or as the new support for brewing yeast immobilization, as presented by Brányik et al. [16].

Concerning energy recovery from both brewery-spent grains and coffee spent ground, perhaps because the amounts available until recently were easily manageable with the available processes, the focus was given more to more experimental processes, still underdeveloped and very focused on the recovery of waste as a means of increasing the efficiency of their production processes. For example, Géczi et al. [17] examined the technical and economic feasibility of energy recovery from brewery spent grains by aerobic and anaerobic digestion in the industrial unit itself to increase the efficiency and yield of the process. Byrne et al. [18] analysed the potential of various organic residues, including brewery spent grains. Coffee spent ground has also been studied with some persistence concerning energy recovery and more or less following the paths traced for brewery spent grains. In the case of coffee spent ground, the focus seems to be on biogas

production, as shown, for example, by Vítěz et al. [19]. Other approaches also emerge, namely the analysis of the recovery potential using thermochemical conversion processes, such as pyrolysis, as presented by Kwon et al. [20], or by hydrothermal carbonization, as presented by Afolabi et al. [21].

The present work addresses the management of brewery spent grains and coffee spent ground residues through the possibility of incorporation in the production of biomass pellets and their direct recovery, in an autonomous way, by combustion. It is also intended to evaluate its potential compared to other fuels derived from biomass using different conversion and recovery technologies.

2. Materials and methods

2.1. Sampling and materials preparation

The biomass materials; Brewery Spent Grains (BSG) and Spent Coffee Grounds (SCG), were supplied by Love Lane Brewery Liverpool and Coffee Bean Shop Liverpool, UK, respectively. The brewery samples were provided in the form of a shaft, while the Coffee waste was provided in the form of particulate powder. The appearance of the samples as received is shown in Figure 1. The samples, when collected, were immediately stored in a freezer box to prevent microbial growth prior to analysis.
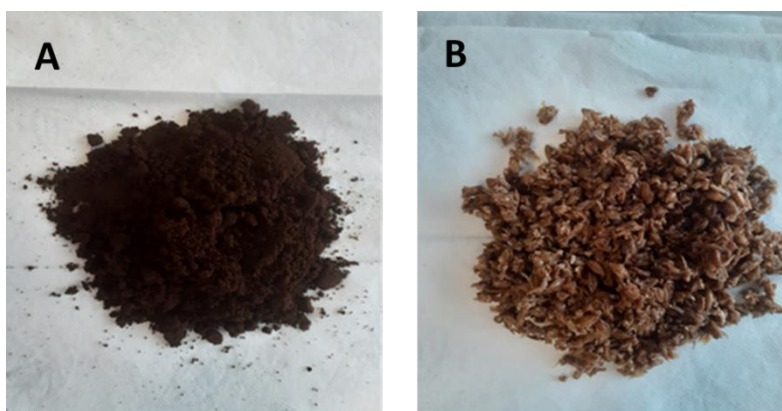

Figure 1: Digital photographs of (a) as received BSG (b) as received SCG.

2.1.1. Material preparation

The moisture content for biomass materials was determined using British Standard BS EN 14774-3:2009, both samples prepared were dried at a temperature of $105 \pm 2\ °C$ in an air atmosphere until a constant mass was achieved and the percentage moisture is

calculated from the loss in mass of the sample in previous research (Idowu et al 2021). Initial moisture content for BSG and SCG was determined as 81.8 wt. % and 57.1 wt. % respectively (Idowu et al. 2021). 200g of BSG and SCG samples were measured in a 200 micron aperture mesh sieve and air dried in the laboratory at room temperature for five days. Samples were weighed after five days, and the moisture content for each sample measured was <10 wt.%. Prepared samples were placed in airtight paper bags prior to shipment to xxx laboratory in Portugal for combustion analysis.

2.1.2 Laboratory characterization

The objective was to analyze the properties of the materials from a perspective of energy recovery. Therefore, the laboratory characterization of the collected materials was carried out according to the sequence presented in the standard ENPlus ®, enabling a direct comparison with other solid fuels derived from biomass. Table 1 presents the list of standards referred to in the standard ENPlus ® and where the laboratory procedures used are described.

Table 1. Standards used in the laboratory characterization tests.

Standard	Description
ISO 17225-1: 2014	Solid biofuels—Fuel specifications and classes—Part 1: General requirements.
ISO 16948: 2015	Solid biofuels—Determination of total content of CHNO.
ISO 16967: 2015	Solid biofuels—Determination of major elements—Al, Ca, Fe, Mg, P, K, Si, Na and Ti.
ISO 16968: 2015	Solid biofuels—Determination of minor elements—Ar, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn.
ISO 16994: 2016	Solid biofuels—Determination of total content of S and Cl.
ISO 18125: 2017	Solid biofuels—Determination of calorific value.
ISO 21404: 2020 (en)	Solid biofuels—Determination of ash melting behavior.

Elemental analysis (CHNO) was performed in the LECO CHN628 apparatus, in which the operating principle consists of weighing a sample in a tin foil that is later placed in the autoloader and then introduced into the furnace containing pure oxygen, with carbon, hydrogen, and nitrogen being completely oxidized and the CHN contents calculated. Oxygen content on a dry basis is calculated by difference. Thermogravimetric analysis (TGA) was performed using ELTRA THERMOSTEP equipment. One gram of each sample was introduced into crucibles and placed inside an oven, along with an empty

reference crucible. As the temperature increased, crucibles were weighed on a precision scale. Moisture, volatile, and fixed carbon contents were determined throughout the heating process. Lastly, the final residue represented the ash content. A TITROLINE 7000 titrator from SI Analytics was used to determine the chlorine content. For this procedure, sample preparation involves previous digestion of the sample, performed in a SINEO MDS-6G microwave since titration requires a liquid sample. Chlorine content determination is achieved by potentiometric titration. The lower and higher heating values were determined using an adiabatic bomb calorimeter, model 6400 Automatic Isoperibol Calorimeter, by PARR INSTRUMENT. After each procedure, the equipment provides the corrected temperature increase that is later used to determine the heating value. The determination of ash fusibility consists of monitoring the behavior of ash melting along a temperature ramp. The samples, converted to ashes, were subsequently placed in a plastic dish, where two drops of ethyl alcohol were added and homogenized. Then, this paste was transferred to a mold, where a cylinder was compacted. Subsequently, the cylinders were placed on a zirconia lamella and then placed inside the chamber of the ash fusibility furnace, which in this specific case was an SYLAB IF 2000 g device. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine trace elements and sulphur. The equipment used was a THERMO SCIENTIFIC (iCAP 6000 series). A peristaltic pump delivered the digested samples to an analytical nebulizer and introduced them into the plasma flame that broke down the samples into charged ions, releasing radiation with specific wavelengths.

3. Results

3.1. Laboratory characterization
3.1.1. Spent coffee grains

The results obtained for the elemental analysis are shown in Figure 2.
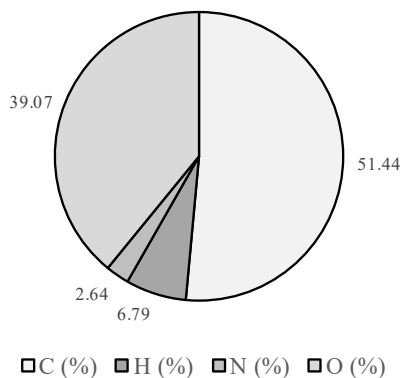
Figure 2. Obtained results from the elemental analysis (CHNO) of spent coffee ground samples.

As shown, the C content reached a mean value of 51.44 ± 0.005%, with a standard deviation of 0.12%. The H content reached a mean value of 6.79 ± 0.002%, with a standard deviation of 0.04%. The N content reached a mean value of 2.64 ± 0.01%, with a standard deviation of 0.02%. The O content reached a mean value of 39.07 ± 0.15%. In the elemental analysis, the levels of S and Cl were also determined, reaching, respectively, a mean value of 0.053 ± 0.0003%, with a standard deviation of 0.0006%, and of 0.0039 ± 0.0002%, with a standard deviation of 0.0006%.

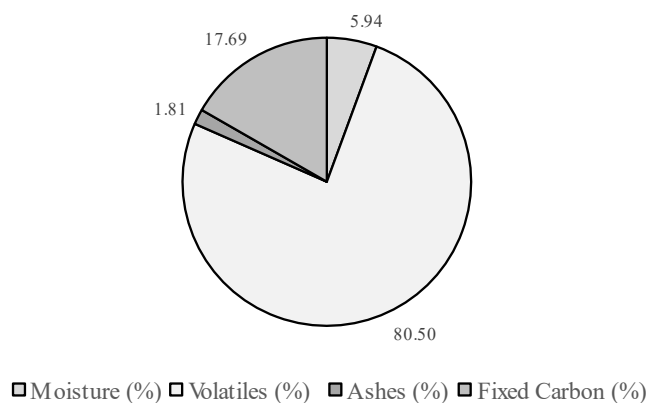The results obtained in the thermogravimetric analysis are shown in Figure 3.

Figure 3. Thermogravimetric analysis of spent coffee ground samples.

The moisture content verified in the results, which is 5.94 ± 0.06%, with a standard deviation of 0.14%, corresponds to the moisture remaining after the material has dried for 24 hours in the laboratory oven, so it should not be taken into account for analysis in comparative processes and assessment of the energy recovery potential. The mean volatile content measured was 80.50 ± 0.22%, with a standard deviation of 0.53%. The

ash content was $1.81 \pm 0.02\%$, with a standard deviation of 0.06%. The mean fixed carbon content measured was $17.69 \pm 0.20\%$, with a standard deviation of 0.49%.

The calorimetric analysis showed a mean value for the low heating value (LHV) of 20.78 ± 0.02 MJ·kg^{-1}, with a standard deviation of 0.06 MJ·kg^{-1}, and a mean value for the high heating value (HHV) of 22.25 ± 0.03 MJ·kg^{-1}, with a standard deviation of 0.07 MJ·kg^{-1}. These higher results for high heating value presented by spent coffee ground seem to be influenced differently by the different elements detected in the elemental analysis. This influence was analyzed by performing a Pearson correlation, which returned a value of 0.46 for C and 0.70 for H. On the other hand, N, with -0.85, O, with -0.44, and S, with -0.54, present a negative correlation with the heating value. Cl does not show any correlation with calorific value. Thus, the high levels of C and H positively influence the growth of calorific value, while the levels of N, O and S negatively influence the calorific value. On the other hand, Cl does not influence the final value of the calorific value.

The results obtained for the chemical analysis of the major elements by ICP-OES are shown in Figure 4.
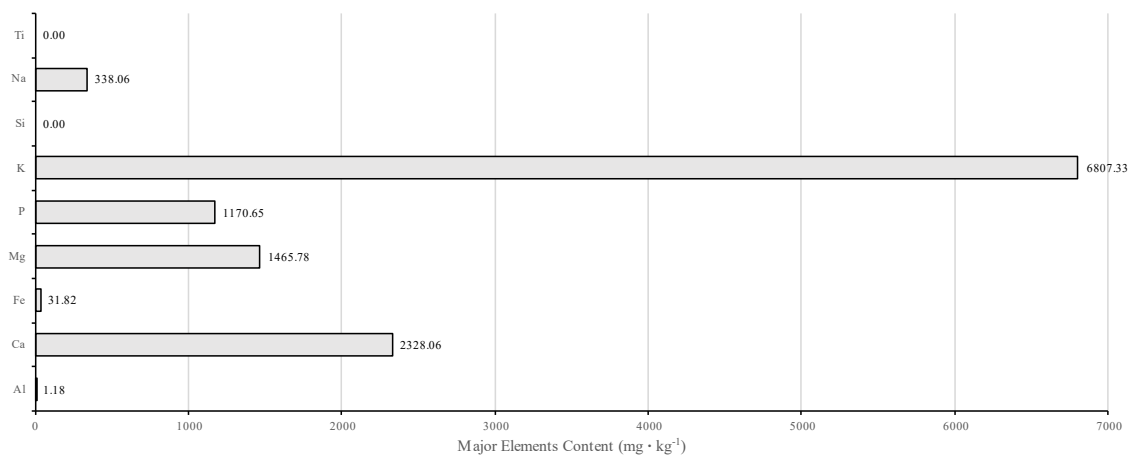

Figure 4. Chemical analysis by ICP-OES for the major elements (mg·kg^{-1}).

From the results, it is possible to highlight the low levels of Al and Fe, which present, respectively, mean values of 1.18 ± 0.64 mg·kg^{-1}, with a standard deviation of 1.57 mg·kg^{-1}, 31.82 ± 0.61 mg·kg^{-1}, with a standard deviation of 1.50 mg·kg-1. The Si and Ti elements presented values below the lower detection limit of the equipment, which is < 0.001 mg·kg^{-1}, so these elements are considered not present in the spent coffee ground samples. The elements Ca, Mg, P, K and Na, present values that can be considered high,

with mean values of, respectively, 2328.06 ± 33.65 mg·kg^{-1}, with a standard deviation of 82.44 mg·kg^{-1}, 1465.78 ± 7.21 mg·kg^{-1}, with a standard deviation of 17.66 mg·kg^{-1}, 1170.65 ± 6.70 mg·kg^{-1}, with a standard deviation of 16.42 mg·kg-1, 6807.33 ± 32.81 mg·kg^{-1}, with a standard deviation of 80.37 mg·kg^{-1}, and 338.06 ± 57.85 mg·kg^{-1}, with a standard deviation of 141.71 mg·kg^{-1}.

The chemical analysis of the minor elements is shown in Figure 5.

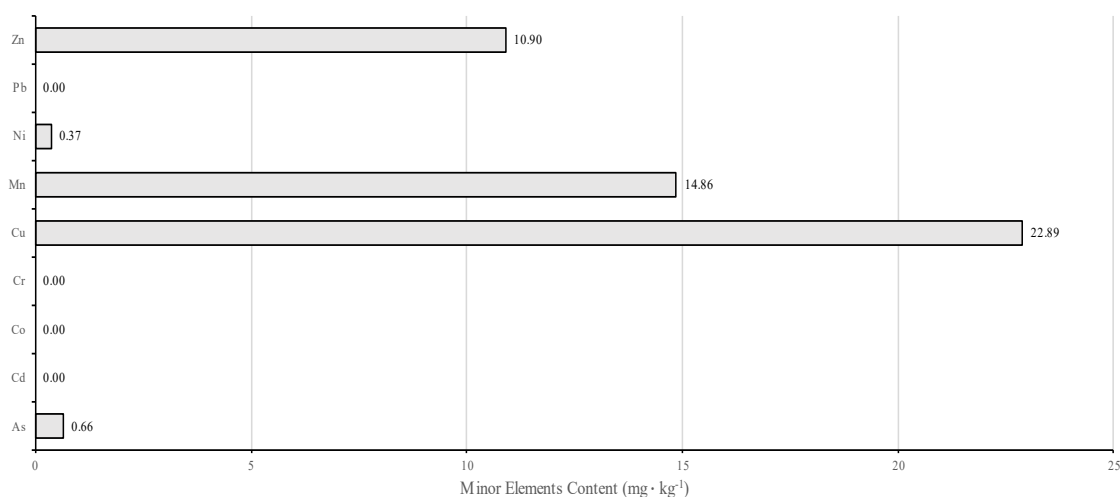**Figure 5** Chemical analysis by ICP-OES for minor elements (mg·kg^{-1}).

In this group of chemical elements, Cu, Mn and Zn presented values with some significance, with mean values of, respectively, 22.89 ± 0.12 mg·kg^{-1}, with a standard deviation of 0.29 mg·kg^{-1}, 14.86 ± 0.32 mg·kg^{-1}, with a standard deviation of 0.79 mg·kg^{-1} and 10.90 ± 0.09 mg·kg^{-1}, with a standard deviation of 0.22 mg·kg^{-1}. As for the elements As and Ni, they presented mean values of, respectively, 0.66 ± 0.35 mg·kg^{-1}, with a standard deviation of 0.86 mg·kg^{-1}, and 0.37 ± 0.04 mg·kg^{-1}, with a standard deviation of 0.09 mg·kg^{-1}. The elements Cd, Co, Cr and Pb presented values below the lower detection limit of the equipment used in the chemical characterization tests (< 0.001 mg.kg^{-1}).

These metallic elements will contribute to the higher ash content since they will convert into oxides during the combustion process, which will constitute the mineral fraction of the ash. However, given the difference in content between the different elements, not all of them will contribute in the same way to the final content of the ash resulting from the combustion of spent coffee ground. By applying a Pearson correlation between the ash content and the different major elements, significant positive correlations were obtained for Ca, Mg, P and K, with coefficients of 0.59, 0.64, 0.32 and 0.33. On the

other hand, Na presented a significant negative correlation, with a Pearson correlation coefficient of -0.59. The Na content occurs in inverse proportion to the ash content. This situation may be related to the fact that this element from the alkali metals group tends to be found more frequently in fly ash than in bottom ashes and is therefore often associated with fouling and slagging phenomena in the ducts of thermal conversion equipment. On the other hand, minor elements have no impact on ash production as the amount found in the spent coffee ground is small.

Regarding the fusibility of the ashes resulting from the combustion of spent coffee ground, they present the results that can be seen in Table 2.

Table 2. Spent coffee ground ash fusibility temperatures (IDT – Initial Deformation Temperature; ST – Softening Temperature; HT – Hemispherical Temperature; and FT – Flow Temperature).

	IDT (ºC)	ST (ºC)	HT (ºC)	FT (ºC)
Mean	873	1011	1061	1167
Standard Deviation	12	3	3	4
Measurement Uncertainty	5	1	1	2

As can be seen, this material produces ash, which, despite not being in very high quantities, has low melting temperatures, especially at IDT, with 873 ± 5 ºC. This situation must be related to the presence of a significant content of Ca, which works as a flux, lowering the melting temperature of the ash. The presence of K, an element of the alkali metals group, also contributed to the easy sintering of the spent coffee ground ash.

3.2.2. Brewery Spent Grains

The results obtained from the elemental analysis of brewery spent grains are shown in Figure 6.
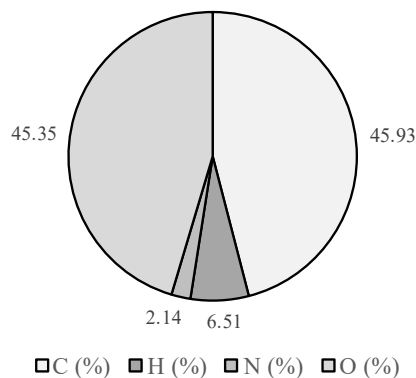
45.35

45.93

2.14 6.51

☐C (%) ■H (%) ■N (%) ☐O (%)

Figure 6. Results from elemental analysis (CHNO) of brewery spent grains samples.

As can be seen, the C content has a mean value of 45.93 ± 0.07%, with a standard deviation of 0.17%. H has a mean content of 6.51 ± 0.01%, with a standard deviation of 0.02%. N has a mean content of 2.14 ± 0.02%, with a standard deviation of 0.06%. O has a mean content of 45.35 ± 0.09%, with a standard deviation of 0.22%. The mean contents of S and Cl are, respectively, 0.0512 ± 0.0004%, with a standard deviation of 0.0009%, and 0.0116 ± 0.0007%, with a standard deviation of 0.0016%. Compared to the spent coffee ground analyzed in Section 3.1, there is a difference that can be considered significant in the levels of C and O. In other words, in the case of C, a higher content was found in the spent coffee ground, with 51.44 ± 0.05%, which means a carbon content 12% higher than that found in brewery spent grains. The O content of brewery spent grains, which is 45.35 ± 0.09%, is higher than that observed for spent coffee ground, which was 39.07 ± 0.06%, which means an O content of 16% higher. This difference in C and O contents is justified by the torrefaction process applied to coffee in its production process. Although this torrefaction process takes place at low temperature and in a controlled manner, some volatile organic compounds are eliminated, mainly oxygenated compounds, which contribute to the concentration of, on the one hand, C and, on the other hand, to the decrease of the O content. There were no significant differences for the remaining elements, namely for N, H, S and Cl. However, this fact impacts the heating value since it appears that, in this case, the O content will negatively influence the observed result. The mean low calorific value determined was 17.88 ± 0.02 MJ·kg^{-1}, with a standard deviation of 0.05 MJ·kg^{-1}, and the mean high heating value presented a value of 19.30 ± 0.02 MJ·kg^{-1}, with a standard deviation of 0.05 MJ·kg^{-1}. In other words, there is a difference of 16% in the heating value of the brewery spent grains, which is in line

with the difference recorded in the O content, which was found to exist between the two materials.

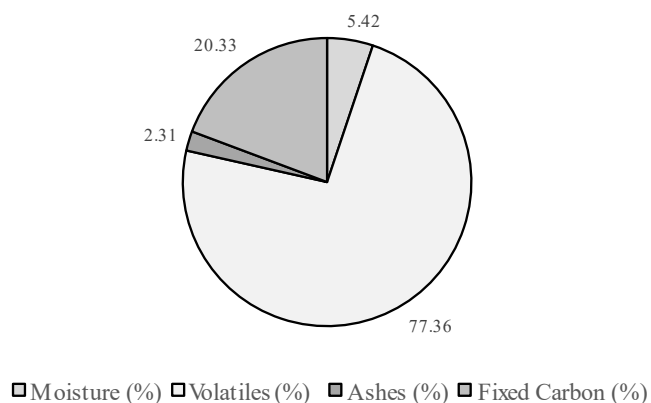Concerning the thermogravimetric analysis, were obtained the results are summarized in Figure 7.

Figure 7. Thermogravimetric analysis of brewery spent grains.

As mentioned in Section 3.1, the measured humidity, it should not be taken into account for a combustibility analysis, since the mean value of $5.42 \pm 0.14\%$, with a standard deviation of 0.34%, results from the drying process in a laboratory oven before carrying out the chemical, thermogravimetric and calorimetric characterization tests. The volatile content presented a mean value of $77.36 \pm 0.09\%$, with a standard deviation of 0.21%. The ash content presented a mean value of $2.31 \pm 0.04\%$, with a standard deviation of 0.11%. Fixed carbon had a mean content of $20.33 \pm 0.09\%$, with a standard deviation of 0.22%. In these results, the value that seems to draw the most attention is the fixed carbon content, higher than observed in the spent coffee ground. This fact seems, at first sight, to contradict what typically occurs with torrefied materials, where there is an increase in the fixed carbon content due to the concentration of C that occurs. However, the coffee torrefaction process is controlled to avoid the loss of all volatile compounds, namely caffeine. Thus, given the higher carbohydrate content of cereals, this higher fixed carbon content of brewery spent grains compared to the spent coffee ground is understandable.

The results obtained for the chemical analysis of the major elements by ICP-OES are shown in Figure 8.
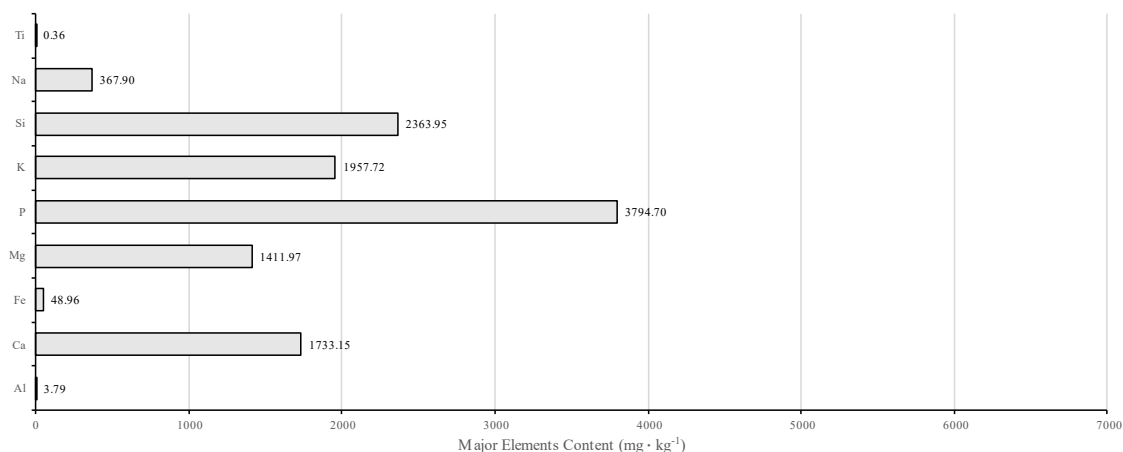
Figure 8. Chemical analysis by ICP-OES for major elements.

From the chemical analysis of the major elements, it can be seen that Al, Ti and Fe occur in small amounts, with mean contents of, respectively, 3.79 ± 1.46 mg·kg^{-1}, with a standard deviation of 3.57 mg·kg^{-1}, and 0.36 ± 0.14 mg·kg^{-1}, with a standard deviation of 0.33 mg·kg^{-1}, and 48.96 ± 1.22 mg·kg^{-1}, with a standard deviation of 2.98 mg·kg-1. On the other hand, Ca, with a mean content of 1733.15 ± 27.29 mg·kg^{-1}, with a standard deviation of 66.84 mg·kg-1, the Mg, with a mean content of 1411.97 ± 13.79 mg·kg^{-1}, with a standard deviation of 33.78 mg·kg^{-1}, the P, with a mean content of 3794.70 ± 19.77 mg·kg^{-1}, with a standard deviation of 48.42 mg·kg^{-1}, the K, with a mean content of 1957.12 ± 15.89 mg·kg^{-1}, with a standard deviation of 224.68 mg·kg^{-1}, and Na, with a mean content of 367.90 ± 13.15 mg·kg^{-1}, with a standard deviation of 32.22 mg·kg^{-1}, present high values, contributing to the also higher ash content observed in the brewery spent grains. With correlation analysis, it was verified that the major elements that contribute the most to the ash content are Ca, Fe, Mg, P, K and Si, with correlation coefficients of, respectively, 0.24, 0.29, 0.65, 0.52, 0.57 and 0.49. Also, in these materials, the Ca content seems to negatively influence the melting temperature of the ashes, which in this case presents the values shown in Table 7. Although higher, they still do not present high values, mainly for IDT, with a mean value of 1159 ± 1 ℃ and a standard deviation of 3 ℃.

Table 3. Brewery spent grains ash fusibility temperatures (IDT – Initial Deformation Temperature; ST – Softening Temperature; HT – Hemispherical Temperature; and FT – Flow Temperature).

	IDT (ºC)	ST (ºC)	HT (ºC)	FT (ºC)
Mean	1159	1351	1498	1519

Standard Deviation	3	6	4	7
Measurement Uncertainty	1	2	2	3

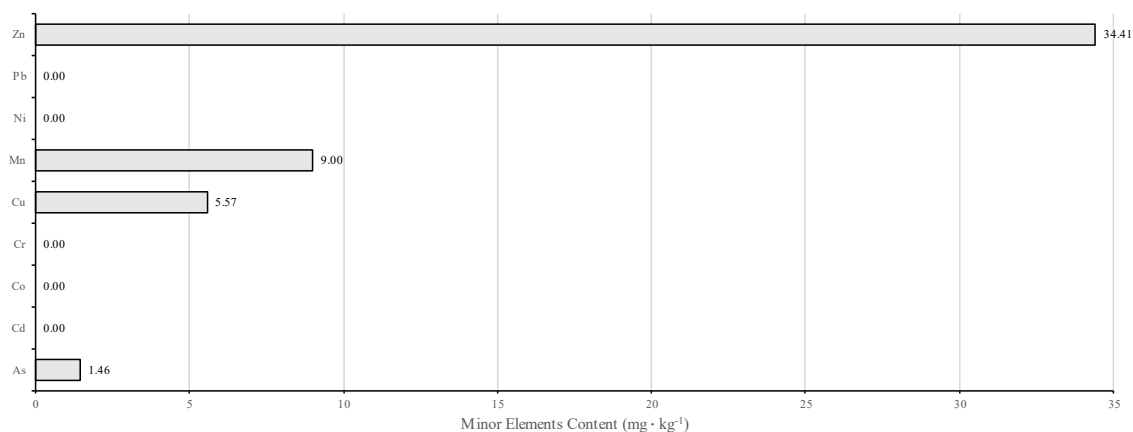The results obtained in the analysis of minor elements are shown in Figure 9.

Figure 9. Chemical analysis by ICP-OES of minor elements from brewery spent grains.

As can be seen, the elements Pb, Ni, Cr, Co and Cd presented values below the lower limit of detection, so it is considered that they present a null result and are not present in the analyzed material. On the other hand, As, with a mean content of 1.46 ± 0.25 mg·kg^{-1}, with a standard deviation of 0.62 mg·kg^{-1}, Cu, with a mean content of 5.57 ± 0.09 mg·kg^{-1}, with a standard deviation of 0.23 mg·kg^{-1}, Mn, with a mean content of 9.00 ± 0.62 mg·kg^{-1}, with a standard deviation of 1.52 mg·kg^{-1}, and Zn, with a mean content of 34.41 ± 0.71 mg·kg^{-1}, with a standard deviation of 1.73 mg·kg^{-1}, present values with some relevance. However, concerning the contribution these elements may have in the formation of ash, only Zn, as it is the most abundant, presents a positive correlation (0.43) and may have some significance.

4. Discussion

Several works refer to the valorisation of brewery spent grains, mainly, as mentioned, through the extraction, concentration, and production of compounds present in the residue. For example, Carvalheiro et al. [22] addressed the issue of oligosaccharide production by autohydrolysis of brewery spent grains. This perspective of processing in a biorefinery system, which in this specific case was used to produce xylooligosaccharides (XOS), seems to have been the preferred path for a wide range of works. An example of this is the work presented by Terrasan et al. [23], who addressed

the production of xylanolytic enzymes, or by López-Linares et al. [24], who addressed microwave-assisted hydrothermal as greener pre-treatment of brewery spent grains for biobutanol production, or by Niemi et al. [25], who found that pre-hydrolysis with carbohydrases facilitates the release of protein from brewery spent grains, or by Montusiewicz et al. [26], who addressed the hydrodynamic cavitation of brewery spent grains diluted by wastewater, or the effect of a milling pre-treatment on the enzymatic hydrolysis of carbohydrates in brewery spent grains, presented by Niemi et al. [27], or by Nigam [28]. From the perspective of energy recovery, Chou et al. [29] conducted a pilot study on the influence of stirring and pH on anaerobes converting high-solid organic wastes to hydrogen. In other words, a more advanced approach and already thinking about a state-of-the-art fuel, which is also the path suggested by Poladyanet al. [30], who addressed hydrogen production by Escherichia coli using brewery waste. However, other approaches have tried to find solutions for the residues by adapting technologies and methodologies already applied to other residues of agro-industrial origin, such as through fermentation processes, aerobic and anaerobic digestion, or even by the application of technologies thermochemical conversion. Examples of this are the works presented by Čater et al. [31], Panjičko et al. [32], Bochmann et al. [33], Jones and Ingledew [34], Goldfarb and Ceylan [35], Balogun et al. [36] or Lorente et al. [37]. This wide range of energy recovery processes supports the idea that, preferably, this will be the path that may have the most potential, without forgetting, however, other forms of recovery, such as the use of these wastes in bioremediation processes [38-46]. From the point of view of energy recovery processes by direct combustion, only one relevant work was found, presented by Celaya et al. [47], who analyzed the co-combustion of brewery spent grains and coal.

In the case of coffee spent ground, the existing works, in a significantly smaller number, approach practically the same perspectives as the works presented for brewery spent grains, with processing in a biorefinery system also showing some relevance here. For example, Zuorro and Lavecchia [48] refer to coffee spent ground as a valuable source of phenolic compounds and bioenergy, or Mussato et al. [49], who analyzed sugar metabolism and ethanol production by different yeast strains from the coffee industry wastes hydrolysates, or Kwon et al. [50]. They analyzed the sequential co-production of biodiesel and bioethanol with coffee spent ground. Also, in this case, the thermochemical conversion processes assume some prominence. For example, Zhang et al. [51] analyzed the torrefaction performance and energy usage of biomass wastes and their correlations with the severity index. However, as can be seen in the various references analyzed, the

direct conversion by combustion of these materials, similarly to what was observed for brewery spent grains, does not seem to have aroused interest. For this reason, the present work assumes an innovative character.

The results show that both spent coffee ground and brewery spent grains have some potential for energy recovery through direct combustion techniques. As can be seen from the results obtained, the calorific value measured for the two materials analyzed is high, which may indicate, from the outset, good possibilities for energy recovery. The two materials analyzed present lower and higher calorific values, which, compared to other biomass resulting from other recovery processes, such as densification, torrefaction, or hydrothermal carbonization, present good conditions that justify their energy recovery. As shown in Figure 13, spent coffee ground and brewery spent grains can present a higher value than wood pellets, a product that does not undergo any chemical change process but only physical through the densification of the constituent material by mechanical pressing. Compared to torrefied biomass, spent coffee ground has an equivalent value, while brewery spent grains have a lower value. This approximation of spent coffee ground to torrefied material is justified since the coffee production process also involves torrefying the material. The material resulting from the hydrothermal carbonization process (HTC) presents values above (~ 2 $MJ \cdot kg^{-1}$) of the torrefied materials.
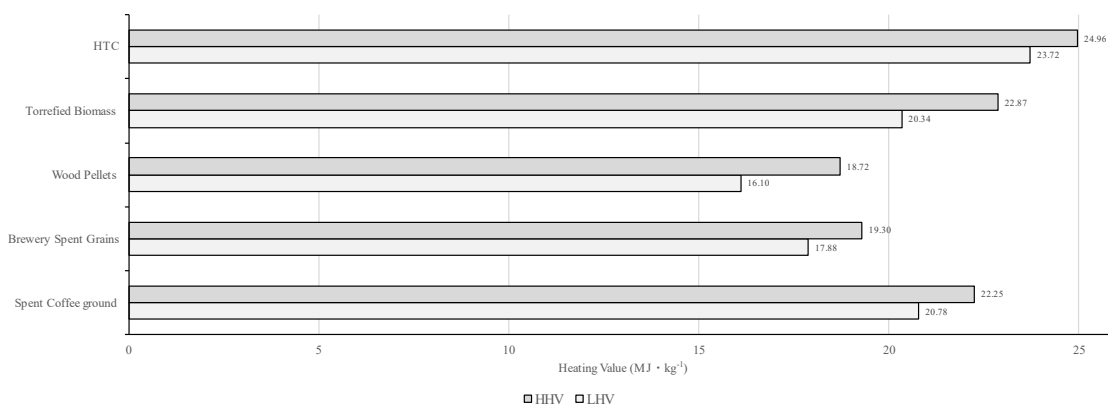
Figure 10. Comparative analysis of lower and higher calorific values of different types of biomass resulting from different conversion processes (torrefaction, densification, hydrothermal carbonization).

However, from the point of view of energy recovery, not only the calorific value is important, but as other parameters also play a decisive role in the efficiency of the thermal conversion processes, such as the ash content, the volatile content, or even the chemical composition of the ash. These parameters influence the kinetics of the oxidation reactions

of materials, the release of energy, and how the by-products resulting from these reactions react with the surface of the thermal conversion equipment, as is the case of Cl and alkali metals. These chemical elements contribute significantly to corrosive, fouling, and slagging phenomena on equipment surfaces and ducts, so fuels, where these elements are abundant, are preferred over others where these levels are present in smaller amounts. The high content of N and S can also be considered a problem since their presence in fuels can lead to NO_x and SO_x, which result in gas emissions to the atmosphere, depending on the temperatures of the combustion chamber. Table 4 presents the limit values presented by the ENPlus ® standard, which is used to characterize the biomass materials used for energy recovery, and which allows a comparison with the most common forms of biomass used in the production of wood pellets, such as softwoods species (*Pinus pinaster*, *Pinus sylvestris*, ...), or species of the genus *Eucalyptus*.

Table 4. Comparison of ENPlus ® parameters with spent coffee ground and brewery spent grains.

Parameter	Units	ENPlus ® reference values			Spent Coffee Ground	Brewery Spent Grains
		A1	A2	B		
Moisture	%	≤ 10.0			5.94	5.42
Ashes	%	≤ 0.7	≤ 1.2	≤ 2	1.81	2.31
LHV	MJ·kg^{-1}	≥ 16.5			20.78	17.88
N	%	≤ 0.3	≤ 0.5	≤ 1.0	2.64	2.14
S	%	≤ 0.04		≤ 0.05	0.0530	0.0512
Cl	%	≤ 0.02		≤ 0.03	0.0039	0.0116
IDT	ºC	≥ 1200		≥ 1100	873	1159
As	%	≤ 1			≤ 0.01	≤ 0.01
Cd	%	≤ 0.5			≤ 0.01	≤ 0.01
Cr	%	≤ 10			≤ 0.01	≤ 0.01
Cu	%	≤ 10			≤ 0.01	≤ 0.01
Pb	%	≤ 10			≤ 0.01	≤ 0.01
Ni	%	≤ 10			≤ 0.01	≤ 0.01
Zn	%	≤ 100			≤ 0.01	≤ 0.01

As can be seen, most of the results fall within the limit values presented by the ENPlus ® standard. For example, the minor elements presented values significantly lower than those indicated in the standard, the same happening for the Cl content. The lower calorific value also falls within the limits of the norm, as it is significantly higher in both cases. On the other hand, the ash content presented by the brewery spent grains exceeds the limits of all the categories defined by the ENPlus ® standard, which are A1, A2 and B, which allow ash content of, respectively, ≤ 0.7%, ≤ 1.2% and ≤ 2%. Spent coffee

ground could be included in Category B in ash content. However, when it comes to the N content, neither of the two products meets the limits imposed by the ENPlus ® standard since the limits imposed for each category are, respectively, $\leq 0.3\%$, $\leq 0.5\%$, and ≤ 1.0 %. Thus, spent coffee ground and brewery spent grains, with 2.64% and 2.14%, respectively, exceeded the permitted values by a large margin.

In this way, the use or even inclusion of these residues in the production process of wood pellets does not seem to be at all viable, especially from a conventional use perspective. The recovery of these residues in thermochemical conversion processes, such as torrefaction, pyrolysis, gasification, liquefaction, or others, could be possible since the fuels derived are not subject to the ENPlus ® standard and will be potentially used in industrial-type recovery processes. For example, torrefied products may follow the assumptions presented by ISO/TS 17225-8:2016 – Solid Biofuels – Fuel Specifications and Classes – Part 8: Graded thermally treated and densified biomass fuels. This standard includes different classes specifically for pellets produced by thermal processing of non-woody biomass, which is summarized in Table 5.

Table 5. Specifications of graded pellets produced by thermal processing of non-woody biomass presented in ISO/TS 17225-8:2016.

Property	Units	TA1	TA2	TA3
LHV	MJ·kg^{-1}	≥ 18.0	≥ 17.0	Not specified
Ashes	%	≤ 5.0	≤ 10.0	Not specified
N	%	≤ 1.5	≤ 2.0	≤ 2.5
S	%	≤ 0.1	≤ 0.2	≤ 0.3
Cl	%	≤ 0.1	≤ 0.2	≤ 0.3

From the calorific value point of view, either of the two residues meets the requirements presented in the ISO/TS 17225-8:2016 standard. For the S and Cl contents, compliance is also verified. However, for the N contents, the two residues under analysis could only be included in the TA3 category, which refers to the processing of herbaceous biomass, fruit biomass and aquatic biomass. Most likely, these materials could not be used exclusively or even in combinations with each other but must be used in combination with other materials that allow a dilution of the less favorable parameters, as is the case of N.

5. Conclusions

The circular economy presents itself as the new paradigm of sustainable development, as it effectively contributes to the strengthening of two essential pillars of sustainability: the environmental and economic factors. Waste management has been a growing challenge, as current societies, eager for consumption, produce an increasing amount of waste that needs to be somehow disposed. The prospect of reintroducing this waste back into production cycles is, therefore, the best way to resolve the problem, as, on the one hand, it resolves the issue of the volume of waste to be managed, while on the other hand, it allows the saving of virgin resources. It also has the advantage of creating new value chains for products that were considered end-of-life materials when analysed from the perspective of the linear economy. Both because of its diversity and the amount generated, agro-industrial waste presents challenges to its management and the prospect of recovery. Brewery spent grains and coffee spent ground fall within this group of abundant waste that needs solutions for their recovery. As seen in the literature review, much emphasis has been given to the recovery of these residues through bioremediation, use as a fertilizer, or as a substrate for crop growth. Concerning energy recovery, emphasis has been placed on fermentation and aerobic and anaerobic digestion. However, not much importance has been given to energy recovery through combustion, either directly or indirectly, through the incorporation of these materials in biomass densification processes, such as the production of biomass pellets, or even by valorisation through thermochemical conversion processes. In this work, the physicochemical properties of brewery spent grains and coffee spent ground were analysed, verifying that their direct combustion may present some difficulties due to some chemical compounds that accelerate the corrosive processes of thermal conversion equipment. (alkali metals and Cl), also associated with the state in which the waste is, mainly due to the high moisture content of the production process, which would require pre-treatment through drying. On the other hand, incorporating these residues in processes such as the production of biomass pellets and other more conventional biomasses already presents more promising results. However, recovery through thermochemical conversion processes, such as pyrolysis, seems to be the scenario with the highest probability of success, given the ability of materials to homogenize, the elimination of the high content of volatile compounds and the concentration of fixed carbon that occurs in these processes, and which allow greater viability of products for applications of energy recovery by combustion, to be used as raw material in biorefinery processes, to be used

as pre-treatment for gasification processes, for soil bioremediation, or to be used as a substrate for growing crops.

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