

Article

A Sustainable Alternative for Cosmetic Applications: NADES Extraction of Bioactive Compounds from Hazelnut By-Products

Grazia Federica Bencresciuto ¹, Monica Carnevale ², Enrico Paris ², Francesco Gallucci ²,
Enrico Santangelo ² and Carmela Anna Migliori ^{1,*}

¹ Research Centre for Engineering and Agro-Food Processing, CREA Council for Agricultural Research and Economics, Strada delle Cacce 73, 10135 Turin, Italy; graziafederica.bencresciuto@crea.gov.it

² Research Centre for Engineering and Agro-Food Processing, CREA Council for Agricultural Research and Economics, Via della Pascolare 16, 00015 Monterotondo, Italy; monica.carnevale@crea.gov.it (M.C.); enrico.paris@crea.gov.it (E.P.); francesco.gallucci@crea.gov.it (F.G.); enrico.santangelo@crea.gov.it (E.S.)

* Correspondence: carmelaanna.migliori@crea.gov.it

Abstract: Hazelnut processing generates a variety of by-products, including skins, shells, and defatted (DFT) flour, which contain valuable bioactive compounds. These by-products are rich in polyphenols, fibers, and other molecules that are suitable for incorporation into nutraceutical and cosmetic products. The efficiency of three natural deep eutectic solvents (NADES), such as betaine/sorbitol/water (BS), fructose/lactic acid/water (FL), and fructose/glycerol/water (FG) was compared with a control (C) extractant (ethanol/water). These NADES were combined with two extraction techniques: a conventional method involving heat and magnetic stirring, and ultra-sound-assisted extraction (US). The free radical scavenging capacity (FRC), total phenolic content (TPC), and the polyphenolic profile (HPLC) were evaluated. BS NADES exhibited superior efficiency for the extraction from the skin and shell, while FL was optimal for defatted flour. Although the skin is the least abundant hazelnut processing by-product, it exhibited the highest polyphenol content and antiradical activity, indicating potential for cosmetic applications. The suitability of DFT flour, skin, and the residual panel of extracts for thermochemical and biochemical conversion processes was investigated. Some of the materials were found to be conducive to thermochemical conversion, while others were suitable for anaerobic digestion.

Keywords: NADES; circular economy; by-products; ultra-sound assisted extraction; phenolic compounds; antiradical activity; proximate analysis; ultimate analysis; biogas potential



Academic Editor: Dario Donno

Received: 10 January 2025

Revised: 31 January 2025

Accepted: 7 February 2025

Published: 12 February 2025

Citation: Bencresciuto, G.F.; Carnevale, M.; Paris, E.; Gallucci, F.; Santangelo, E.; Migliori, C.A. A Sustainable Alternative for Cosmetic Applications: NADES Extraction of Bioactive Compounds from Hazelnut By-Products. *Sustainability* **2025**, *17*, 1516. <https://doi.org/10.3390/su17041516>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Agricultural wastes are rich in important bioactive compounds, such as proteins, lignin, polyphenols, fibers, and carbohydrates, which can be used for various applications [1–3]. In the contemporary era, the principal objective is to optimize the usage of by-products, with the dual aim of minimizing the generation of residues and their reuse. Hazelnut (*Corylus avellana* L.) is a widely used product in the food industry. World production is widespread in 38 countries in the northern hemisphere, mainly in temperate climates, and world production in 2020/2021 was over 1.1 million tons [4]. Turkey has the highest hazelnut production with 765,000 tons in 2022, followed by Italy (98,670 tons) and Azerbaijan (72,104 tons) [5].

Hazelnuts are used by the confectionery industry in various forms (roasted or natural; whole or chopped; cut into flakes; ground into paste), often in combination with chocolate [6].

The fruit is formed by a hard, wooden shell enclosing an edible kernel. The kernel or seed is covered by the skin or cuticle, a brown perisperm with a bitter, astringent taste, which is usually removed by a process known as “whitening”, which consists of a roasting treatment to obtain a peeled and clean seed, the main component used in the food industry [7]. The inedible portions of hazelnuts (around 58%), such as the shells and skins, represent a substantial amount of the waste generated during harvesting and processing by the food industry [8]. Hazelnut shells represent about 50% of the total weight of hazelnuts [9], while hazelnut skins represent 2.5% of the total weight of hazelnuts [10]. The global production of hazelnut shell waste is about 429,000 tons y^{-1} [11], and about 27,000 tons of hazelnut skins are wasted every year [12]. In Italy, 3000 tons of this by-product are produced per year [7]. The residues of processing, which are typically discarded, can be valuably reintroduced as raw materials in productive cycles according to the principles of the circular economy. Hazelnut shells, for instance, are rich in lignocellulosic biomass, comprising approximately 13–32% hemicellulose, 16–27% cellulose, and 40–50% lignin [13]. The high calorific value, uniform size, and low ash content of the shells make them suitable for exploitation in biochemicals, biofuels, and pellet production, as well as thermochemical processes like pyrolysis and gasification [7,8]. They also serve as low-cost CO₂ adsorbents and activated carbon [9]. Additionally, they can produce value-added products like xylooligosaccharides, levulinic acid, furfural, and prebiotics [9,14].

Hazelnut skin contains 67.7% fiber (57.7% insoluble), 8% protein, 14.5% fat, and 1.7% ash [15]. It has a unique phenolic profile with high antioxidant activity [16]. The main phenolic compounds are flavan-3-ols (catechin, epicatechin) and gallic acid [15,17]. Due to its high polyphenol content, hazelnut skin is being explored for use in functional food ingredients [18,19].

Defatted hazelnut flour (or meal), a by-product from oil extraction, is rich in protein (35–41%), fiber (10%), lipids (25.2–48%), carbohydrates (4.97–8.64%), and essential amino acids [19,20]. It can be used as a protein source in animal and fish diets [21] and is being studied for functional food development [19]. However, more research is needed on its full potential [20].

In recent years, some studies have focused on the phenolic content of hazelnut processing by-products, owing to their antioxidant and antiradical scavenging activities [9,14,22]. For these reasons, there is a growing interest in extracting these bioactive compounds for use in nutraceuticals, dietary supplements, pharmaceuticals, and cosmetic products. Wasik et al. [23] demonstrated that hazelnut wastes are rich in active compounds with high antioxidant potential, making them very attractive for anti-aging cosmetics.

Several techniques have been explored for extracting polyphenolic compounds from agricultural waste. Commonly, the extraction is carried out with the traditional approach, consisting of maceration using organic solvents, such as ethanol, methanol, and acetone [24,25]. However, this method requires large quantities of solvents, raising concerns about the environmental sustainability, as well as the drawbacks, of the potential for residual solvents in the final product [26]. As a result, researchers are now focusing on greener alternatives that reduce solvent use and environmental impact.

Deep eutectic solvents (DESs) represent an alternative to conventional solvents due to their biocompatibility, low toxicity, and sustainability. DESs are essentially mixtures containing a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), combined in a specific molar ratio. DESs are typically regarded as environmentally friendly, and when the components of DES are derived from natural products, they are designated as natural deep eutectic solvents (NADES), which are less toxic than DESs [27]. In NADES, hydrogen bond donors are represented by alcohols, sugars, and amino acids, while bond acceptors consist of organic acids, such as lactic or citric acid [28]. NADES are showing

excellent applications in several fields, including the pharmaceutical industry, chemical synthesis, and the cosmetic industry [29]. They were reported to play an important role in enhancing the antioxidative activities of plant extracts [28] and in extracting polyphenols from plant materials and agricultural wastes [30,31]. The efficiency of their extraction is improved when they are combined with other methods, such as ultrasound [29,30,32,33].

In recent years, ultrasound-assisted extraction (USA) has arisen as a suitable greener technique to extract phenolic compounds. It relies on ultrasonic frequencies in the 20–2000 kHz range. These frequencies destroy plant tissues and pass through plant cells, whereby cycles of expansion and compression result in elevated temperatures and negative pressures within the tissues. This method has been shown to yield higher extraction efficiency than traditional techniques, offering a faster and more sustainable extraction process [22,34].

Within a circular economy context, the main objective of this research was to assess and compare different extraction methods of the polyphenolic fraction from hazelnut processing wastes for exploiting as a bioactive ingredient in the cosmetic sector. The efficiency of three NADES to extract valuable phenolic compounds from hazelnut skin, shells, and defatted flour was investigated, applying two different extraction techniques (heat and magnetic stirring and ultrasound-assisted extraction) for each NADES. The qualitative and quantitative analyses of the polyphenolic compounds present in the extracts and their free radical scavenging capacity were evaluated to choose the best extraction method. To further complete the analysis of their possible utilization, the exhausted panels resulting from the extraction of polyphenolic substances from defatted flour and skins were analyzed to determine the main parameters linked to the thermochemical (combustion) and biochemical (anaerobic digestion) conversion processes.

2. Materials and Methods

2.1. Samples Preparation

The by-products of hazelnut processing were kindly provided by the company Alta Langa sited in Alba (Turin, Italy). The by-products were shells and skins from roasted hazelnut and defatted flour (DFT-flour) from raw hazelnut. The shells were subjected to mechanical pulverization in a blender (Vorwerk blender model T5, Vorwerk & Co., Wuppertal, Germany) at the CREA-IT laboratory in Turin. The average diameter of the resulting particles was approximately 200 µm. DFT flour and skin were, respectively, micronized and pulverized (average diameter 0.5–1 mm) by the producer.

2.2. NADES Preparation and Characterization

In accordance with the methodology available in the literature, three different NADES were chosen [35,36] to optimize the extraction of phenolic compounds from the tested material (Table 1): (i) betaine/sorbitol/water in a 1:1:5 molar ratio (BS); (ii) fructose/lactic acid/water in a 1:5:5 molar ratio (FL); and (iii) fructose/glycerol/water in a 1:1:5 molar ratio (FG).

Table 1. Abbreviation and chemical composition of tested NADES. The third component is milli Q water in a molar ratio of 5 in all NADES.

NADES	HBA	HBD	Molar Ratio
BS	Betaine	Sorbitol	1:1
FL	Fructose	Lactic acid	1:5
FG	Fructose	Glycerol	1:1

HBA: hydrogen bond acceptor; HBD: hydrogen bond donor.

The right amount of milli-Q water (based on the molar ratio) was added in a 200 mL beaker, covered with an aluminum foil, and placed on a heating magnetic stirrer (Velp mod. ARE, Usmate Velate (MB)—Italy) at a 310 rpm stirring speed and a temperature exceeding 60 °C. The remaining components were subsequently added in accordance with the specified quantities as specified in Table 1 and the mixture was left to stir until the temperature exceeded 60 °C and the solution became transparent.

A solution of ethanol/water (60:40 V:V) was used as a conventional solvent (C), based on Benoit et al. (2021) [35] with slight modifications. For each mixture, the following parameters were recorded: pH by a Crison pHmeter Basic 20 (Crison Instruments, Barcelona, Spain), density, and refractive index with an accuracy of ± 0.0002 nD by an Abbe Refractometer (Giorgio Bormac srl, Modena, Italy).

2.3. Extraction of the Polyphenolic Fraction from Hazelnut Skin, Shells, and Defatted Flour

Phenolic compounds were extracted using two distinct extraction procedures. The first was the traditional extraction method (t), which combined high temperature with magnetic stirring. The second used ultrasound-assisted extraction (us). These procedures were combined with the conventional solvent and NADES. All extractions were conducted in triplicate.

2.3.1. Traditional Extraction

The matrix, comprising either 5 g of DFT flour or 2.5 g of skins or shells, was incorporated into the extracting mixture (80 mL). The mixture was heated at 70 °C for three hours on a magnetic stirrer (Velp mod. ARE, Usmate Velate (MB)—Italy) set at 310 rpm [35]. Thereafter, the solution was cooled, coarsely filtered, and then centrifuged at $13,636 \times g$ for five minutes ($T = 20$ °C). The values of pH, density, and the final volume of the supernatant were measured. The supernatant was then aliquoted and stored at -20 °C until further analysis. This temperature was selected as optimal to extract efficiently avoiding the degradation of phenolic compounds, which occurs at 80 °C [37].

2.3.2. Ultrasound-Assisted Extraction

A mixture of 5 g of hazelnut DFT flour or 2.5 g of skins or shells was prepared by mixing the respective materials with the solvent (80 mL) in 100 mL glass bottles closed with screw cap. This mixture was shaken and then positioned for one hour in a sonicator (Elmasonic S 100, Elma, Singen, Germany) operating at a frequency of 37 kHz [38]. After the completion of the ultrasound treatment, the cooled mixture was centrifuged at $13,636 \times g$ for five minutes at 20 °C. The pH and density of the extracts was then measured, and the volume of the supernatant was recorded. The supernatant was subsequently aliquoted and stored at a temperature of -20 °C.

2.4. Physical and Chemical Characterization of the Extracts

2.4.1. pH and Density of Extracts

For each extract, the final volumes were recorded and the same determinations described in paragraph 2.2 were carried out in triplicate for each extract.

2.4.2. Free Radical Scavenging Capacity (FRC) Assay

The ability of the extracts to scavenge the DPPH* radical was monitored in accordance with the methodology described by Deepa et al. [39]. An aliquot (100 μ L) of the extract was mixed with 3.9 mL of methanolic solution of DPPH* (0.025 g L^{-1}) in a test tube. The mixture was then incubated in the dark for 30 min. The absorbance was determined by reading the sample at 515 nm against methanol in a double beam spectrophotometer (VWR mod. P9, Milan, Italy) and expressed as the mg of catechin equivalent (CE) g^{-1} of sample.

2.4.3. Total Phenols Content

The total phenol content of the sample extracts from the three matrices was determined by the Folin–Ciocalteu phenol reagent method [40], as modified by Slatnar et al. [41]. Briefly, 100 µL of the samples were combined with 6 mL of water and 500 µL of Folin–Ciocalteu's reagent. After a six-minute interval, 1.5 mL of a sodium carbonate solution (20% *w/v*) and 1.9 mL of milli-Q water were added. The reaction mixtures were vortexed and incubated in the dark at 40 °C for 30 min. The absorbance of the reaction mixtures was read at 765 nm by spectrophotometry using a double beam spectrometer (VWR mod. P9, Milan, Italy). A solution of ethanol and water (60/40) was used as a control. The total phenol content of each extract was determined by constructing a standard curve with gallic acid as the standard, at concentrations of 0.2, 0.8, 2, and 4 mg mL^{−1}. The polyphenol content was expressed as the mg of gallic acid equivalent (GAE) g^{−1} of the sample. Absorption measurements were conducted in triplicate.

2.4.4. Chromatographic Characterization of Phenolic Compounds

The samples extracted with the conventional solvent (ethanol/water, 60:40 V:V) and the t or us technique were analyzed by HPLC to identify the most representative phenolic compounds. The ethanolic extracts were filtered through a 45 µm polyamide filter, 2-fold diluted with methanol, and transferred to a vial prior to injection into the HPLC system. The analysis of phenolic compounds was conducted on a Jasco BS-997 HPLC system, equipped with Thermo scientific Accucore 250 C18 column (Sunnyvale, CA, USA) length: 150 mm; internal diameter: 4.6 mm; particle size: 2.6 µm) operated at 25 °C and a UV–Vis detector (Jasco FP-2020 PLUS, Tokyo, Japan), in accordance with the methodology described by Slatnar et al. [41]. The spectra of the compounds were recorded at wavelengths of 280 nm and 350 nm. The mobile phase consisted of an aqueous solution of 0.1% formic acid in milli-Q water (A) and a 0.1% formic acid solution in acetonitrile (B). Samples were eluted according to the linear gradient from 5% to 20% B in the first 15 min, followed by a linear gradient from 20% to 30% B for 5 min, then an isocratic elution for 5 min, followed by a linear gradient from 30% to 90% B for 5 min, and then an isocratic mixture for 15 min, before returning to the initial conditions. An injection volume of 20 µL was employed, with a flow rate maintained at 0.6 mL min^{−1}. The standards employed for the identification and quantification of the phenolic compounds in samples were: (−)-epicatechin; (+)-catechin; phloridzin; quercetin-3-O-rhamnoside; myricetin-3-O-rhamnoside.

2.5. Chemical–Physical Characterization of Exhausted Panel

The characterization of the exhausted panels was carried out at LASER-B (Laboratory of Experimental Activities and Renewable Energy from Biomass) of CREA-IT in Monterotondo (Rome). The experimental layout included four substrates:

- Raw DFT flour;
- Raw skin;
- The residue (panel) of DFT flour extraction by FL (FL-DFT-Flour);
- The residue (panel) of skin extraction by BS (BS-Skin).

All the determinations were repeated in triplicate.

2.5.1. Proximate Analysis

The moisture content was determined following the UNI EN ISO 18134–2:2024 [42]. For each substrate, about 300 g were dried at 105 ± 2 °C in a drying oven (Memmert UFP800, Schwabach, Germany) for 24 h, until reaching a constant weight. The ash content was measured by drying 1 g of sample in a muffle furnace (Lenton EF11/8B, Hope Valley, UK) set at two steps. During the first step, the temperature rose to 250 °C with a heating rate

of $6.5\text{ }^{\circ}\text{C min}^{-1}$, and remained at $250\text{ }^{\circ}\text{C}$ for 1 h. During the second step, the temperature rose to $550\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, remaining at $550\text{ }^{\circ}\text{C}$ for 2 h (UNI EN ISO 18122:2022) [43].

The volatile solids (VS) were determined on a dry basis. For each sample, 1 g of the dried sample was put in a crucible and inserted into a muffle furnace at $925 \pm 10\text{ }^{\circ}\text{C}$ for 7 min. After heating, the crucible was removed and cooled in a desiccator. The difference in weight loss before and after heating gave the volatile content, according to ASTM D 3175-89 [44]. The percentage of fixed carbon (FC) of the biochar derived from the difference between 100% and the sum of moisture content, ash content, and volatile matter.

To determine the higher heating value (HHV), peel samples were sequentially ground with a cutting mill (Retsch SM 100, Haan, Germany), and thereafter with a rotor mill (Retsch ZM 200, Haan, Germany). Each sample was reduced to a pellet of about 1 g through a pellet press (Pellet Press 2810, Parr Instruments, Moline, Illinois, USA) and then analyzed using an isoperibol calorimeter (6400 Parr Instruments, Moline, Illinois, USA) according to the UNI EN ISO 18125:2017 [45]. Before the analysis, the instrument was calibrated with benzoic acid. The analysis was performed in triplicate. The lower heating value (LHV) was calculated starting from the HHV and the hydrogen content.

The pH was measured employing the Eutech Instruments pH700 pH/mV/ $^{\circ}\text{C}/^{\circ}\text{F}$ Bench Meter with a glass electrode, according to the UNI EN 13037 (2012) standard [46]. The pH value was detected in a solution of deionized water (50 mL), in which about 5 g of the sample was added.

2.5.2. Ultimate Analysis

The elemental composition (C, H, N, S, O) of peels was determined by using a Costech ECS 4010 CHNS-O (Valencia, CA, USA) elemental analyzer. The limit of quantification (LOQ) allowed by the instrument was 0.05% for each element. The oxygen content (O) was calculated by the difference on a dry basis (UNI EN ISO 16948:2015) [47].

For determining the content of macro, micro, and trace elements, the samples were homogenized to have a uniform distribution of the elements. Then, after weighing about 0.5 g, each sample was added to $6 \pm 0.1\text{ mL}$ of HNO_3 65% and $3 \pm 0.1\text{ mL}$ of H_2O_2 30% for the mineralization into a microwave Milestone START D, according to the U.S. EPA Method 3051A. The digestion occurred at $180\text{ }^{\circ}\text{C}$, 650 W for 42 min. Then, the samples were filtered and diluted with deionized water. The content of macro- and microelements (mg kg^{-1} dry weight) was determined with an ICP-MS (Agilent 7700, Agilent, Santa Clara, CA, USA), as provided by the ISO 16967:2015 [48] and ISO 16968:2015 [49].

2.5.3. Biogas Potential

Starting with the elementary composition, we estimated the theoretical biochemical methane potential (TBMP) through a stoichiometric method (Buswell's formula). This estimation was based on the amount of organic matter (expressed by the formula $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$) to be subjected to biodegradation and on the products derived from anaerobic biodegradation [50–53].

2.6. Statistical Analysis

The data of phenolic characterization, as well as those linked to conversion processes, were checked for normality and then subjected to analysis of variance (one-way) with the PAST software [54], version 3.22 (2018, Oyvind Hammer, University of Oslo, Norway, <https://www.nhm.uio.no/english/research/resources/past/>, accessed on 6 December 2024). Significantly different means were separated via Tukey's HSD test. For data deviating from normality, the Kruskal–Wallis test for non-parametric ANOVA and the Dunn's test for mean separation were used. Principal component analysis (PCA) [55] was performed

using the same software to analyze the behavior of the exhausted panels in relation to the energy parameters.

3. Results and Discussion

3.1. NADES Characterization

The pH of the pure solvents exhibited a notable decline in FL with lactic acid, as expected, while the highest value was observed in BS (Table 2). This outcome was likely due to betaine, which possesses the capacity to bind hydrogen ions (increasing the pH of the medium) due to the presence of a negatively charged functional group (carboxylate ion) spaced from the cationic site [56]. The lowest density was observed in the control sample, while the highest values were observed in the BS and FL samples, followed by the FG samples. The refractive index (IR) and °Brix values of the solvents were significantly different: the control had the lowest value and BS had the highest, while FG and FL had intermediate values between the control and BS.

Table 2. Characterization of pure solvents. The reported values of pH and density consist of the average value of three distinct measurements. For each column, the values followed by a different letter differ according to Tukey's HSD test ($p \leq 0.05$).

	pH	Density (g cm ⁻³)	°Brix	IR(nD)
C	5.20 ^b	0.88 ^c	18.75 ^d	1.3615 ^d
BS	6.56 ^a	1.24 ^a	72.75 ^a	1.4723 ^a
FL	1.18 ^c	1.24 ^a	57.73 ^c	1.4360 ^c
FG	5.30 ^b	1.19 ^b	63.00 ^b	1.4485 ^b

C: ethanol/water; BS: betaine/sorbitol/water, FL: fructose/lactic acid/water, FG: fructose/glycerol/water.

3.2. pH and Density of the Extracts

As observed in the pure extractant, the pH values of FL extracts were lower than those of the other samples, which is attributable to the presence of lactic acid (Table 3). In general, the type of matrix influenced the final pH in comparison to the pure extracting medium, while the extraction technique did not influence the pH in the case of DFT flour, except in BS, where the traditional technique resulted in a higher pH than the US technique. In the case of skin and shell, control is lower in the traditional technique. The addition of DFT flour appeared to enhance the pH values of all the extracts obtained through the conventional technique. A distinctive trend was observed in the case of FL NADES, whereby the inclusion of all the tested matrices resulted in a reduction in the pH values of the extracts obtained through both techniques, in comparison with the values of the pure NADES reported in Table 3.

As expected, based on the data obtained for pure extractives (Table 2), the density is lower in the control for both techniques and for all matrices, except in DFT flour where the NADES FG showed significant differences between the two techniques.

3.3. Total Phenols Content, Extraction Efficiency, and Free Radical Scavenging Capacity

As shown in Figure 1, C-t and C-us extracts showed the lowest content of total polyphenols (2.30 mg GAE g⁻¹ for C and 3.44 mg GAE g⁻¹ for C-us) for DFT flour. Higher values were found in FL-t and FL-us (17.65 mg GAE g⁻¹ for FL and 13.76 mg GAE g⁻¹ for FL-us), followed by BS and FG with and without ultrasound, ranging between 9 and 10 mg GAE g⁻¹. In the literature, few data are available about the chemical composition of hazelnut DFT flour. Xu et al. [21] found that the DFT flour of hybrid hazelnuts from Nebraska contains total phenolics ranging from 8.71 to 12.9 mg TA (tannic acid) g⁻¹, while in Simsek et al. [57], values ranged from 0.5 to 10 mg GAE g⁻¹ for flour of different varieties

of Turkish hazelnut. These results demonstrate that the content of phenolic compounds is deeply influenced by the variety of different geographic origins.

Table 3. pH and density (d) of NADES and control extracts obtained from hazelnut DFT flour, skin, and shell with traditional and ultrasound-assisted extraction. The reported values of pH and density consist of the average value of three distinct measurements. For each column, the values followed by a different letter differ according to Tukey's HSD test ($p \leq 0.05$).

	DFT Flour		Skin		Shell	
	pH	Density (g cm ⁻³)	pH	Density (g cm ⁻³)	pH	Density (g cm ⁻³)
C-t	6.74 cd	0.92 c	5.69 b	0.90 b	5.47 c	0.94 b
BS-t	7.64 a	1.25 b	6.58 a	1.25 a	7.25 a	1.24 a
FL-t	0.78 e	1.24 b	0.27 c	1.24 a	0.20 d	1.28 a
FG-t	6.50 d	1.22 b	5.87 b	1.25 a	5.99 b	1.28 a
C-us	6.77 c	0.91 c	7.07 a	0.90 b	6.21 b	0.92 b
BS-us	7.37 b	1.24 b	6.78 a	1.24 a	7.48 a	1.27 a
FL-us	0.93 e	1.25 b	0.62 c	1.19 a	0.45 d	1.28 a
FG-us	6.68 cd	1.43 a	5.92 b	1.19 a	6.32 b	1.25 a

t = traditional method; us = ultrasound; C = control (ethanol/water); BS = betaine/sorbitol/water; FL = fructose/lactic acid/water; FG = fructose/glycerol/water.

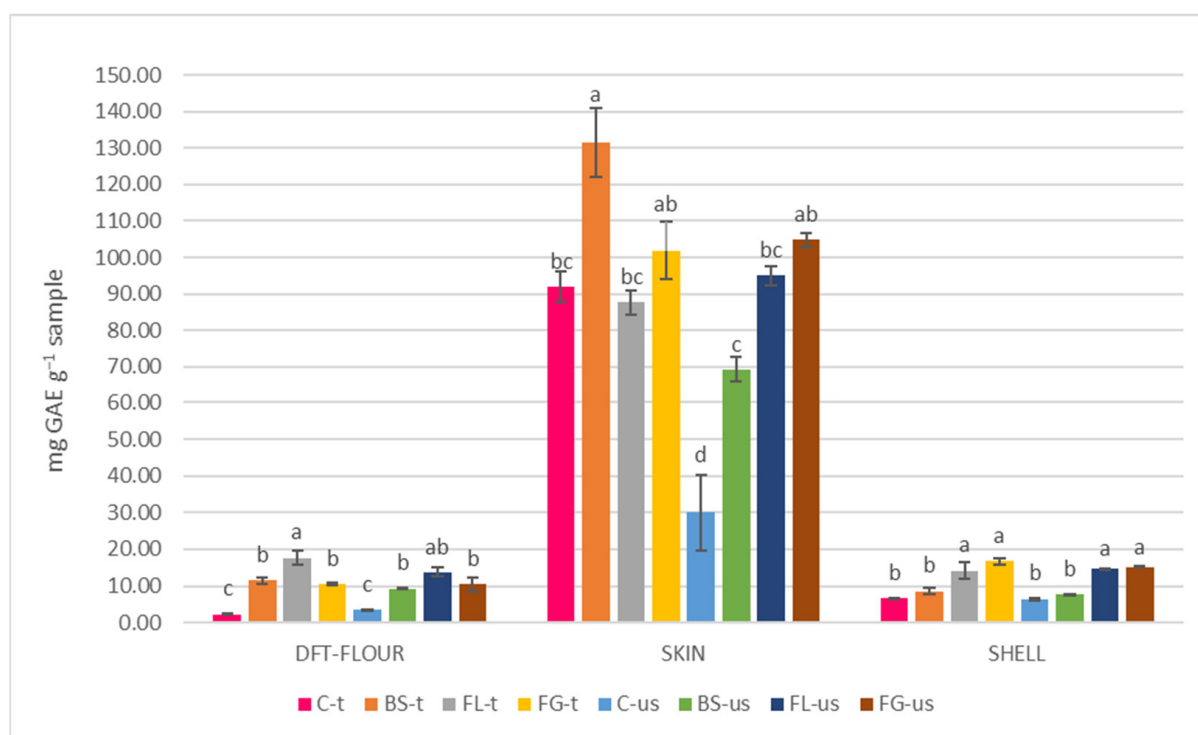


Figure 1. Total phenolic compounds of C and NADES extracts from hazelnut DFT flour, skin, and shells, obtained by heating magnetic stirrer (t) and ultrasound-assisted extraction (us). The values are expressed as mg of the gallic acid equivalent (GAE) g⁻¹ of DFT flour, skin, and shells. Different letters indicate significant differences among the extracts ($p \leq 0.05$). t = traditional method; us = ultrasound; C = control (ethanol/water); BS = betaine/sorbitol/water; FL = fructose/lactic acid/water; FG = fructose/glycerol/water.

The total polyphenol content of the skin was significantly higher (about ten-fold) than that of DFT flour and shells for all these. The highest total phenols content was shown by BS-t (131.62 mg GAE g⁻¹), followed by FG, where the content was 101.86 and 104.77 mg GAE g⁻¹, without and with ultrasound treatment, respectively. Interestingly, the total polyphenols increased progressively from C to FG, with a statistically significant

difference when ultrasound-assisted extraction was used. The lowest content, as for DFT flour, was found in C-us (29.95 mg GAE g⁻¹), while the same extractant combined with the traditional technique (C-t) showed an efficiency comparable to the FL-t and FL-us treatment (91.83 mg GAE g⁻¹). These data are in good agreement with other authors, particularly Zeppa et al. [58], who found values of total phenolic compounds of 160 mg GAE g⁻¹ for roasted skins obtained from 'Tonda Gentile Trilobata', the same variety used in this research. The total phenolic compounds content in hazelnut skins are influenced by various factors, as evidenced by the variable values ranging from 51 to 232 mg GAE g⁻¹ found by other authors [15,16].

In the shells extracts, C-t and C-us, together with BS-t and BS-us, showed the lowest values (between 6.45 and 8.53 mg GAE g⁻¹). The NADES FL and FG, with both extraction methods, were the most efficient in terms of total polyphenol content (between 14.18 and 16.69 mg GAE g⁻¹). The polyphenols content found in the C-t and C-us extracts was very similar to the data found in the literature [59,60]. Benoit et al. [35] investigated the extraction efficiency of polyphenols from marigold flowers using NADES and conventional solvents. The efficiency trend was highly comparable to that observed in the present study. Indeed, the NADES containing betaine demonstrated a markedly higher extraction efficiency than the control (ethanol/water 50:50). Notably, the NADES betaine/sorbitol/water in 1:1:5 molar ratio also exhibited the highest efficiency. Moreover, the solvent containing fructose and glycerol demonstrated higher efficiency compared to the control, as observed in the present study in the case of hazelnut shell.

Fructose was found to be an effective hydrogen acceptor, regardless of the type of donor (in FL, represented by lactic acid and in FG, represented by glycerol) in the case of the shell. In DFT flour, fructose was found to be more efficient in combination with lactic acid, while in the skin, it was found to be more efficient in combination with glycerol. Betaine, as a hydrogen acceptor, only yielded superior results in the case of the skin. The efficiency of NADES was found to be strongly influenced by the phenolic profile of the matrices studied. As reported in the review by Rente et al. [61], flavonoids are mostly extracted using HBDs based on organic acids, alcohols, and sugars, while phenolic acids are mostly extracted using alcohol and organic acid-based HBDs. The potential interactions that have resulted in the observed variations are challenging to comprehend, given the current knowledge of only the phenolic profile of the hydroalcoholic extracts.

The extraction efficiency of the ultrasound technique was either lower or equal to that of the traditional technique for all matrices tested, with the exception of skin, where the efficiency of the ultrasound-assisted extraction combined with C and BS extractants was higher than that of the traditional technique.

Concerning the anti-radical activity (Figure 2), DFT flour exhibited higher levels in the C-us (3.41 mg CE g⁻¹) and lower levels in FL-t (2.04 mg CE g⁻¹). The remaining treatment yielded intermediate values, falling between 2.57 mg CE g⁻¹ of BS-t and 3.26 mg CE g⁻¹ of FG-us, with no notable differences among them. Thus, despite the differences observed for the total phenolic compounds, the scavenging capacity was similar regardless of the extractant or the extraction method used. Therefore, in the case of DFT flour, other compounds may operate to level the scavenging capacity.

For the skin, a general pattern showed the highest values for the control (12.73 mg CE g⁻¹ of sample in C-us and 9.10 mg CE g⁻¹ of sample C-t). The scavenging capacity of both controls was statistically higher than the capacity of the NADES within the same extraction method (traditional or ultrasound-assisted). However, the use of ultrasounds allowed for an increment of scavenging capacity with respect to the traditional method. In shell extracts, the lowest antiradical activity was found in C-t (1.75 mg CE g⁻¹ of sample), while the highest was found in BS-t (7.19 mg CE g⁻¹ of sample), FL-us, and FG-us (6.50 and

6.68 mg CE g⁻¹ of sample, respectively). Intermediate values were found in the other theses, including C-us, which gave significantly higher values compared to its counterpart without ultrasound (C-t).

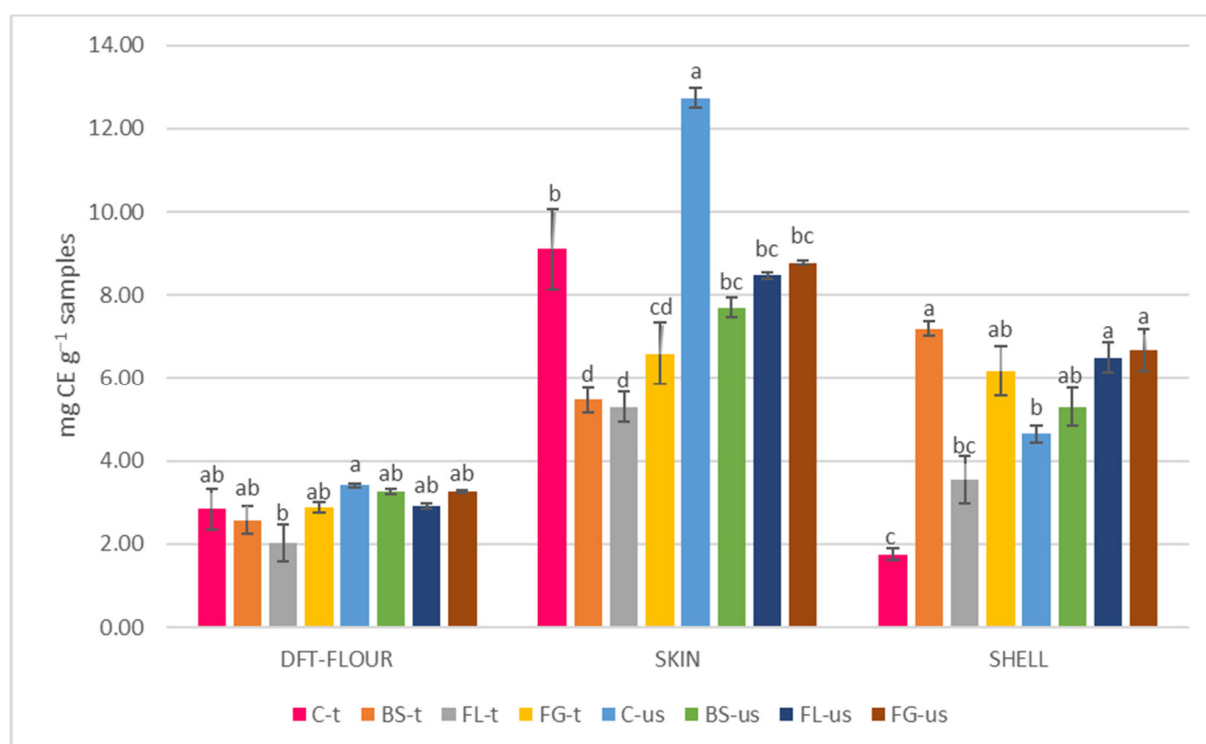


Figure 2. Free radical scavenging capacity of C and NADES extracts from hazelnut DFT flour, skin, and shells, obtained by heat and magnetic stirring (t) and ultrasound-assisted extraction (us). The values are expressed as the catechin equivalent (CE) g⁻¹ of defatted flour, skin, and shells. Different letters indicate significant differences among the extracts ($p \leq 0.05$). t = traditional method; us = ultrasound; C = control (ethanol/water); BS = betaine/sorbitol/water; FL = fructose/lactic acid/water; FG = fructose/glycerol/water.

A common trait of such a feature is the lowering of scavenging capacity when the BS is used coupled with the traditional method of extraction. The anti-radical activity values of the extracts with ethanol using the ultrasound technique align with those described by Di Michele et al. [51] for the hazelnut shell, yielding a mean value of 1.86 ± 0.13 mg TE g⁻¹. In the study by Benoit et al. [35], The extractant betaine/sorbitol was the only one to demonstrate significant anti-radical activity in comparison to the control. In comparison with the matrices tested in this study, the results reported by Benoit [35] are contradictory for flour and cuticle, where C-us demonstrated the highest values. Conversely, the results of the same study are consistent for the shell, where NADES BS-t exhibited the highest anti-radical activity.

3.4. Chromatographic Characterization of Phenolic

The polyphenolic profile of the NADES extracts was not analyzed due to the high viscosity of the extracts, which hindered injection into the HPLC system, despite attempts to dilute the extracts and heat the column. Therefore, the profile was studied just for the DFT flour, skins, and shells extracts obtained by the traditional method (heat and magnetic stirring) and ultrasound-assisted extraction. The following phenolic compounds were identified and quantified by HPLC (Table 4): gallic acid, (+)-catechin, (–)-epicatechin, myricetin-3-O-rhamnoside, quercetin-3-O-rhamnoside, and phloridzin (or phloretin-2'-O-

glucoside). Such compounds are recognized as the most abundant polyphenols in hazelnut by-products [41,62].

Table 4. Quantitative analysis of phenolic compounds ($\mu\text{g g}^{-1}$) identified in hazelnut DFT flour, skins, and shells extracts in ethanol/water 60:40, with heating magnetic stirrer (C-t) and ultrasound-assisted extraction (C-us). The values are expressed in $\mu\text{g g}^{-1}$ of DFT-flour, skins, and shells. For each column, the values followed by a different letter differ according to Tukey's HSD test ($p \leq 0.05$).

		Phenolic Acid		Flavan-3-ols				Flavonols				Flavonoid	
		Gallic Acid		(+) -Catechin		(−) -Epicatechin		Myricetin-3-O-Rhamnoside		Quercetin-3-O-Rhamnoside		Phloridzin	
DFT flour	C-t	135.74	bc	49.87	b	10.77	ns	0.18	b	1.78	c	3.12	b
	C-us	248.82	b	185.45	a	21.27	ns	0.62	b	2.50	c	2.38	b
Skin	C-t	1136.47	a	183.91	a	34.55	ns	13.00	a	49.67	a	88.76	a
	C-us	990.89	a	125.49	ab	15.82	ns	13.03	a	56.09	a	84.92	a
Shell	C-t	5.87	c	36.30	b	28.81	ns	0.40	b	5.09	c	0.00	c
	C-us	8.27	c	24.19	b	21.59	ns	0.00	c	20.12	b	10.51	b

ns = not significant.

Gallic acid was the most abundant phenolic compound in DFT flour and skin, ranging from $5.88 \mu\text{g g}^{-1}$ of the shell C-t extract to $1136.47 \mu\text{g g}^{-1}$ of the skin C-t extract and $990.89 \mu\text{g g}^{-1}$ in C-us skin. With regard to the flavan-3-ols class, for (−)-epicatechin, no significant differences among the extracts were found, while the content of (+)-catechin was significantly higher in the C-us extract of DFT-flour and the extract of skin, both C-t and C-us.

Also, myricetin-3-O-rhamnoside and quercetin-3-O-rhamnoside, two flavonols, showed the highest content in C-t and C-us skin extracts. In the other extracts, myricetin-3-O-rhamnoside was present only in traces, while quercetin-3-O-rhamnoside ranged between $1.78 \mu\text{g g}^{-1}$ (C-t DFT-flour) and $20.13 \mu\text{g g}^{-1}$ (C-us shells).

The maximum concentration of phloridzin, belonging to the dihydrochalcones class, was found in both types of skin extracts ($84.92 \mu\text{g g}^{-1}$ of the sample for C-us and $88.77 \mu\text{g g}^{-1}$ of the sample for C-t). In the case of the shell, the extraction method had a crucial role, because in C-us shells, the extract was measured as $10.51 \mu\text{g g}^{-1}$ of phloridzin, while the C-t shells extract was completely absent. The amount of phloridzin in DFT flour varied between 3.13 (C-t) and 2.39 (C-us) $\mu\text{g g}^{-1}$, with no discernible differences among the extraction techniques.

The correlation value between the antiradical activity of the extracts and the total polyphenol content was 0.62, indicating that there was no straightforward relationship between the two variables. Specifically, extracts with the highest polyphenol content did not always correspond to high antiradical activity values. In contrast, the highest levels of antiradical activity were observed in extracts with a higher content of myricetin-3-O-rhamnoside, quercetin-3-O-rhamnoside, and phloridzin, as evidenced by correlation values exceeding 0.9.

A limited number of data are available in the existing literature regarding the quantitative analysis of the individual polyphenolic compounds in hazelnut DFT flour and shell. Bener et al. [36] reported values lower than those in the present research for gallic acid, (+)-catechin and (−)-epicatechin in DFT-flour. In contrast, the values reported for quercetin-3-O-rhamnoside were higher (6.38 – 10.23 mg kg^{-1}). In their study, Di Michele et al. [59] reported values of $1.70 \pm 0.06 \mu\text{g g}^{-1}$ for gallic acid and $318.5 \mu\text{g g}^{-1}$ for (+)-catechin, which is considerably higher than the levels observed in the materials examined in the present study. The reported values for quercetin-3-O-rhamnoside were found to be consistent with the findings of the present research.

The phenolic fraction of skin has been investigated in several published works. The values reported by Goncuoglu et al. [16] are in accordance with those obtained in the present study for gallic acid. In contrast, Ozdemir et al. [15] observed higher values for catechin and epicatechin (678 and 104 $\mu\text{g g}^{-1}$), while the value for gallic acid was very close to that found in the present work (786 $\mu\text{g g}^{-1}$).

As evidenced in the scientific literature, the identified phenolic compounds, with their distinctive properties, give specific characteristics to the resulting extracts, making them suitable for use in the production of cosmetics with defined functional properties. As demonstrated by Alonso et al. [63], gallic acid has been shown to prevent lipid peroxidation, which damages the skin barrier and accelerates the photo-aging process. In their review, Bae and colleagues [64] reported that catechins enhance the photo stability and protection of the skin from UV rays, thereby slowing the skin-aging process. Furthermore, they inhibit UVA- and UVB-induced inflammatory pathways and demonstrate anti-microbial activities. Finally, they activate skin barrier passage, enhancing the effect of cosmetics.

Elloumi et al. [65] reported beneficial effects on the swift healing of skin injuries for the flavonols quercetin-3-O-rhamnoside and myricetin-3-O-rhamnoside.

Phloridzin-rich polyphenolic fractions are under investigation for their free-radical scavenging mediated and their anti-ultraviolet protective role. These effects, based on antioxidant activity, are very interesting for dermo-cosmetic applications in view of their potential ability in reducing solar DNA-induced damages of the skin [66].

3.5. Chemical–Physical Characterization for Energy Conversion of Exhausted Panel

Considering the chemical–physical parameters analyzed, the substrates proved to be very different, as can be seen from the dispersion of the PCA plot (Figure 3). There was a clear separation between (i) the starting substrates (skin vs. DFT flour), (ii) the extraction residues relative to the corresponding starting substrates (skin vs. BS skin; DFT flour vs. FL-DFT flour) and (iii) the extraction residues (BS skin vs. FL-DFT flour).

The moisture content of the extraction residues was higher than the initial substrates, reaching 20.18% for the FL-DFT flour (Table 5). This substrate showed some peculiarities. All the substrates (except the DFT flour) had high volatile solids content, which together with the fixed carbon represents the combustible fraction in the material. The LHW of FL-DFT flour was statistically higher than the starting substrate (DFT flour) as well as the other substrates. Such data were in contrast with the general indication of an inverse relationship between moisture content and calorific value [67].

Table 5. Proximate analysis of the substrates. For each row, the values followed by a different letter differ according to Tukey’s HSD test ($p < 0.01$).

	DFT-Flour	FL-DFT Flour	Skin	BS Skin
Moisture (% tq)	7.60 c	20.18 a	8.76 bc	10.40 b
Volatile solids (% tq)	86.28 b	78.46 c	88.70 a	88.62 a
Fixed carbon (% tq)	1.89 a	0.72 b	0.26 b	0.62 b
Ashes (% ss)	4.23 a	0.64 c	2.28 b	0.36 c
Low heating value (MJ kg^{-1})	20.75 b	23.78 a	19.58 c	17.46 d
pH	6.10 a	2.22 d	4.88 b	4.05 c

The same substrate (FL-DFT flour) also has the highest oxygen content (Table 6), a factor considered unfavorable for obtaining a high LHV. From all this, it can be assumed that the extraction solution is not “neutral” from the point of view of the energetic properties, which could be improved (calorific value of FL-DFT Flour), even in the presence of contrasting behavior.

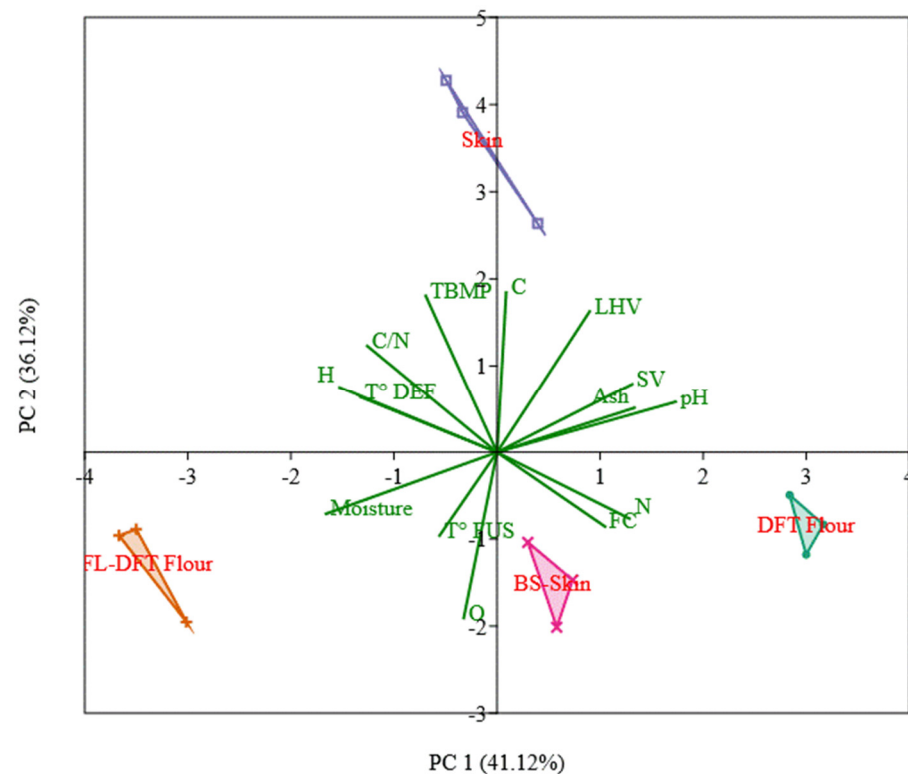


Figure 3. Biplot showing the PCA results of skin (violet triangle), BS skin (pink triangle), DFT flour (green triangle) and FL-DFT flour (orange triangle) separation based on the main the chemical-physical traits (green lines). Ash (ash content), C, H, N, O (carbon, hydrogen, nitrogen, and oxygen content), SV (volatile solids), FC (fixed carbon), LHV (low heating value), T° DEF (deformation temperature), T° FUS (fusion temperature), TBMP (theoretical biochemical methane production).

Table 6. Ultimate analysis of the substrates. For each row, the values followed by a different letter differ according to Tukey's HSD test ($p < 0.01$).

	Raw Material		Exhausted Panel			
	DFT Flour		FL-DFT Flour		BS Skin	
C (% ss)	31.72	b	41.26	a	30.65	b
H (% ss)	1.61	b	3.88	a	4.63	a
N (% ss)	3.50	b	2.47	c	1.87	c
O (% ss)	58.94	ab	50.11	b	62.21	a
C/N	9.10	b	17.04	a	16.46	a

Ashes, a non-combustible component along with moisture, were statistically higher in the starting materials than in the extraction residues, with the highest value recorded for DFT flour (Table 5). However, the deformation and melting temperatures were higher in the other substrates (Figure 4), with the highest significant values for skin (deformation temperature) and BS skin (melting temperature). Both the ash content and its behavior at high temperatures are important factors affecting power plants' efficiency through slagging, corrosion, and fouling [68]. The use of biomasses of different origins in plants based on direct combustion can cause agglomeration in the furnace and the deposition of ashes on the surfaces of the heat exchangers. In the absence of controls and chemical characterization (ash content) on the type and nature of not lignocellulosic biomass, the phenomena of deposition of material in the internal parts of the plants, as well as in corrosion of the walls and a decrease in energy efficiency, may occur [69]. Low ash melting temperatures are a critical issue, often associated with high concentrations of alkali metals in biomass ash. Even if the ash fusibility values observed in this work were high, the nature and shape

of the original sample's matrix at lower temperatures could cause fouling and abrasion phenomena in the conversion plant.

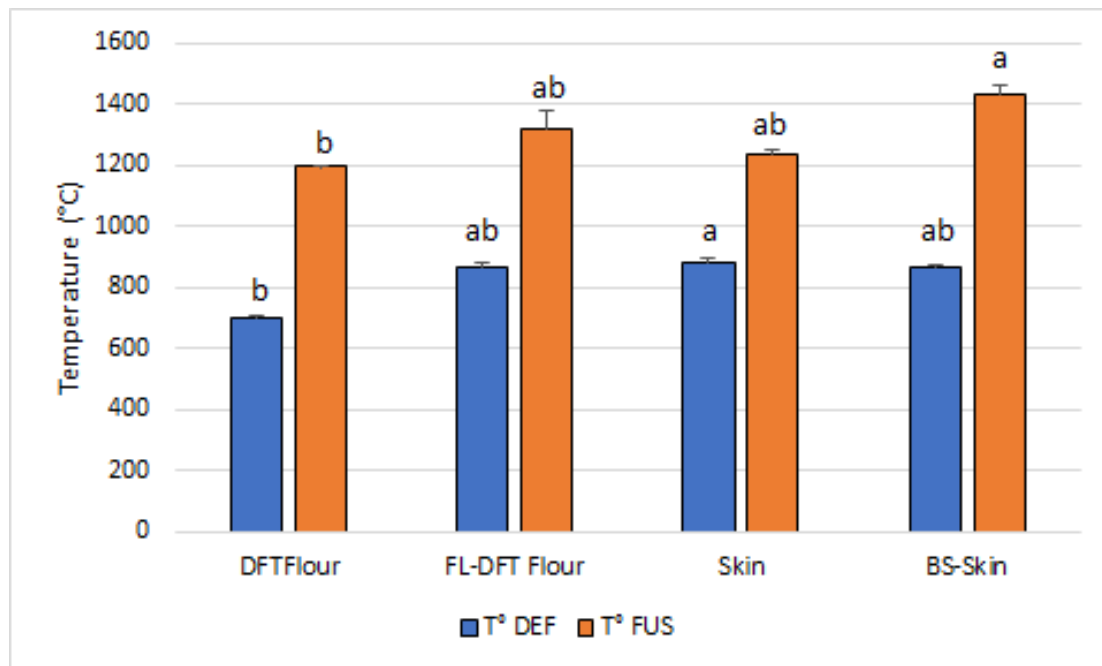


Figure 4. Temperature of deformation (T° DEF) and fusion (T° FUS). For each trait, different letter indicates a statistical difference ($p < 0.05$) after Kruskal–Wallis analysis and mean separation through Dunn's test.

When assessing the suitability of the substrates for use in anaerobic digestion, we observed different behaviors (Figure 5). Hazelnut skin showed a statistically higher TBMP and methane content in the biogas than all other substrates, but there was a reduction in the TBMP and methane content in the corresponding extraction residue. The opposite behavior was observed for DFT flour, although the improvement in TBMP after extraction was not statistically significant. The values obtained for biogas production were within the range observed for a large number of waste materials; Lesteur et al. (2010) [70] reported bibliographic data varying from 148 (cattle manure) to 473 (citrus waste) $\text{ml CH}_4 \text{ g}^{-1} \text{VS}$; while Labatut et al. [71] provided a larger range from corn leachate ($106.5 \text{ mL CH}_4 \text{ g}^{-1} \text{VS}$) to used vegetable oil ($648.5 \text{ mL CH}_4 \text{ g}^{-1} \text{VS}$). The percentage of methane ranged between 19 (DFT flour and BS skin) and 38% (skin), deemed, instead, rather low compared with the values reported in the literature. For instance, Dinuccio et al. [72], studying different agro-industrial biomasses, observed a percentage of methane in biogas ranging from 56.0 to 76.3%, while in Fiore et al. [73] the methane content exceeded 55% in all cases of agro-industrial waste. Interestingly, Fiore et al. [73] also analyzed a hazelnut mix composed of raw hazelnut skin (removed with hazelnut shell), fine hazelnut skin (removed after roasting process), and large hazelnut skin (removed after the roasting process). The methane content of the mix (62%) measured experimentally was higher than the values estimated in the present work.

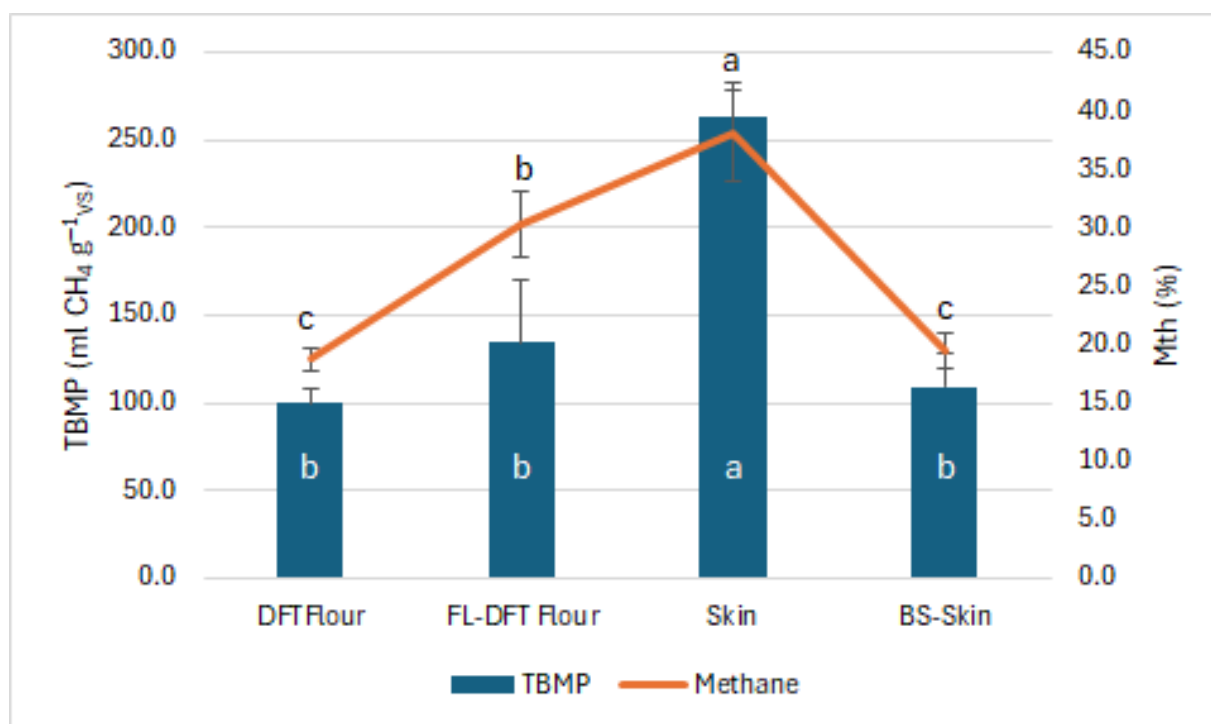


Figure 5. Theoretical biochemical methane potential (TBMP, ml CH₄ g⁻¹ vs) and theoretical percentage of methane in biogas (Mth, %), calculated according to Roati et al. [52]. The values were adjusted for the vs. content. For each variable, different letter indicates a statistical difference ($p < 0.05$) after Tukey's HSD test. Bars indicate the standard deviation.

The use of Buswell's formula to estimate the TBMP has been amply debated [51,70,71]: the method may give overestimated results, but the usefulness of the formula for informational purposes is recognized and, with corrections for substrate biodegradability, may give values closer to actual methane production [71]. As also reported by other authors [74,75], the use of residual products from extraction in anaerobic digestion could be an interesting change to be explored. However, the figure also highlights the possible variability determined by the type of feedstock available, as well as an awareness of the limitations of this type of estimation and the constraints associated with scale-up from laboratory to pilot and then to a large scale.

In general, the starting substrates have a higher (in some cases, statistically significant) content of macro and trace elements than the residues of the extractions. The only exceptions were Na for skin and Al for DFT flour. The reduction factor between DFT flour and its residue after extraction with FL was on average eight, while that between skin and the residue after extraction with BS was about 13.5, considering both macro and trace elements (Tables 7 and 8). The varying degree of reduction is probably the result of an interaction between the source material and the extraction method, and raises the question of using a mass balance to understand whether the missing quantities have been dissolved in the waste solutions. Such a check is particularly important for Ni and Sr. The former, being the cause of possible allergenic reactions, must necessarily be present at low levels in the industrial product, while Sr, although no negative effects are known, has been found to be present at significant levels in the starting materials.

Table 7. Macro element measured in each substrate (g kg^{-1}). For each element, different letters indicate a statistical difference ($p < 0.05$) after Kruskal–Wallis analysis and mean separation through Dunn’s test.

	DFT Flour		FL-DFT Flour		Skin		BS Skin
Macroelement							
Na	0.007		<LOQ		0.319		0.839
Mg	4.73	a	0.40	bc	2.04	ab	0.14
K	20.23	a	1.68	bc	7.63	ab	0.32
Ca	1.023	a	0.146	bc	0.808	ab	0.058
Mn	0.065	a	0.006	bc	0.019	ab	0.001
Fe	0.147	ab	0.015	c	0.342	a	0.020
Cu	0.057	a	0.005	bc	0.010	ab	0.001
Zn	0.061	a	0.005	bc	0.015	ab	0.001
Al	0.011	c	0.026	ab	0.252	a	0.014

Table 8. Trace element measured in each substrate (mg kg^{-1}). For each element, different letters indicate a statistical difference ($p < 0.05$) after Kruskal–Wallis analysis and mean separation through Dunn’s test.

	DFT Flour		FL-DFT Flour		Skin		BS Skin
Trace Element							
Cr	0.179	bc	0.072	c	6.411	a	0.412
Co	0.232	a	0.025	b	0.178	ab	0.013
Ni	5.850	a	1.090	bc	3.789	ab	0.253
As	0.007		<LOQ		0.057		<LOQ
Se	0.055		<LOQ		0.028		0.012
Sr	21.600	ab	2.512	bc	26.401	a	2.072
Cd	0.034		<LOQ		0.038		<LOQ
Pb	0.079	ab	0.026	b	0.097	a	0.028

By-products of hazelnut processing, such as the skin and DFT flour, are deemed suitable for food products or molecules extraction [7], while the energy option has been explored for matrices not analyzed in this work, such as the shells [76] or hazelnut pruning [77]. Therefore, comparisons with studies focused on other type of matrices appear baseless and misleading. On the other hand, the residues of extraction (FL-DFT flour and BS skin) could be approximated to the solid waste of some agro-industries, such as olive oil, wine, and tomato processing [78]. However, one should bear in mind that this is a step beyond, because we are talking about solid residues that have undergone a further extraction process.

The truth of the matter is that the type of substrates analyzed in this study are rather atypical, and have shown some contradictions in the values of the parameters associated with thermal or biochemical conversion. McKendry [79] outlined that the high content of O and H reduced the value of a fuel, but FL-DFT flour, having the highest content of O (62.21%), also showed the highest LHV (23.78 MJ kg^{-1}). Moreover, biomasses with a C/N ratio below 30 are deemed more suitable for biochemical conversion, but in the present work, although the ratio was well below this value, the estimated TBMP was rather low.

4. Conclusions

The efficiency of the different NADES was found to vary depending both on the matrix investigated and extraction technique. The NADES containing betaine, sorbitol, and

water with the traditional method exhibited superior efficiency, expressed as total phenolic compounds, for skin. In the case of the defatted flour, however, the NADES consisting of fructose, lactic acid, and water yielded the highest quantity. With respect to the shell, comparable efficiencies were observed for both extraction techniques when employed for the NADES containing fructose, lactic acid, and water, as well as fructose, glycerol, and water.

In nearly all combinations of NADES/extraction techniques, the matrix showing the greatest potential was the skin, despite its quantitative scarcity as a byproduct of hazelnut processing. The highest potential is associated with a higher content of total polyphenols and a higher anti-radical activity for the majority of extractants in comparison to the other matrices.

In contrast to the findings of previous studies, the utilization of ultrasound did not enhance the extraction efficiency, except for the C-us vs. C-t and BS-us vs. BS-t extracts of skin. It is possible that an increase in extraction time may lead to improvements in this regard.

When considering the anti-radical activity, an important property for the use of extracts in the cosmetic sector, the best performing extractant in the case of the skin is the traditional extractant (ethanol/water 60:40 V:V) combined with ultrasound, followed by the extract obtained with the same mixture using the traditional technique. Furthermore, the shell, which is produced in greater quantities than the skin during hazelnut processing, exhibits comparable values for some extracts to those of the skin, particularly for the BS, FL-us and FG-us samples. It can therefore be concluded that the most abundant, but poorest, source of functional substances can be transformed into a type of extract of interest for cosmetic applications by using the optimal combination of NADES and extraction techniques.

However, when considering the content of the individual polyphenols identified in the different matrices, the skin remains the most interesting matrix, as it contains a greater proportion than the other matrices of the main phenols studied. Owing to their biological activity, the extracts obtainable from the skin could improve the beneficial effects that cosmetics have on the swift healing of skin injuries, anti-ultraviolet protection, the reduction in solar DNA-induced damage to the skin, and the prevention of lipid peroxidation.

The tested matrices have shown the anomalous nature and behavior of the parameters associated with energy conversion for some values, i.e., LHW, ash, and moisture. For these ones, they could be comparable to biomass for thermochemical conversion processes; however, for others, such as pH and C/N, they appeared more suitable for valorization by anaerobic digestion. For this reason, it appears hazardous to give clear indications, while it might be wiser to conduct additional investigations on the matter.

Author Contributions: Conceptualization, C.A.M. and E.S.; methodology, C.A.M., G.F.B., E.S., M.C. and E.P.; validation, C.A.M. and G.F.B.; formal analysis, C.A.M., G.F.B. and E.S.; investigation, C.A.M., G.F.B., M.C., E.P., F.G. and E.S.; resources, C.A.M. and F.G.; writing—original draft preparation, C.A.M., G.F.B., E.S., M.C., E.P. and F.G.; writing—review and editing, C.A.M. and E.S.; visualization, C.A.M. and G.F.B.; supervision, C.A.M. and G.F.B.; project administration, C.A.M.; funding acquisition, C.A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fondazione CRT (Cassa di Risparmio di Torino), bando Erogazioni Ordinarie 2022, RF = 2022.0844.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

Acknowledgments: The authors acknowledge Giorgia Scandone for her precious contributions to the investigation during her Master’s thesis.

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

References

1. Ufitikirezi, J.d.D.M.; Filip, M.; Ghorbani, M.; Zoubek, T.; Olšan, P.; Bumbálek, R.; Strob, M.; Bartoš, P.; Umurungi, S.N.; Murindangabo, Y.T.; et al. Agricultural Waste Valorization: Exploring Environmentally Friendly Approaches to Bioenergy Conversion. *Sustainability* **2024**, *16*, 3617. [\[CrossRef\]](#)
2. Riseh, R.S.; Vazvani, M.G.; Hassanisaadi, M.; Thakur, V.K. Agricultural Wastes: A Practical and Potential Source for the Isolation and Preparation of Cellulose and Application in Agriculture and Different Industries. *Ind. Crops Prod.* **2024**, *208*, 117904. [\[CrossRef\]](#)
3. Ravindran, R.; Jaiswal, A.K. Exploitation of Food Industry Waste for High-Value Products. *Trends Biotechnol.* **2016**, *34*, 58–69. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Manterola-Barroso, C.; Padilla, D.; Ondrasek, G.; Horvatinec, J.; Gavilán-Cuicui, G.; Meriño-Gergichevich, C. Hazelnut and Walnut Nutshell Features, as Emerging Added Value by-Products of the Nut Industry: A Review. *Plants* **2024**, *13*, 1034. [\[CrossRef\]](#)
5. FAOSTAT. Available online: <https://www.fao.org/faostat/es/#data/QCL> (accessed on 17 December 2024).
6. Athar, M.; Nasir, S.M. Taxonomic Perspective of Plant Species Yielding Vegetable Oils Used in Cosmetics and Skin Care Products. *African J. Biotechnol.* **2005**, *4*, 36–44.
7. Ollani, S.; Peano, C.; Sottile, F. Recent Innovations on the Reuse of Almond and Hazelnut By-Products: A Review. *Sustainability* **2024**, *16*, 2577. [\[CrossRef\]](#)
8. Licursi, D.; Antonetti, C.; Fulignati, S.; Vitolo, S.; Puccini, M.; Ribechini, E.; Bernazzani, L.; Raspolli Galletti, A.M. In-Depth Characterization of Valuable Char Obtained from Hydrothermal Conversion of Hazelnut Shells to Levulinic Acid. *Bioresour. Technol.* **2017**, *244*, 880–888. [\[CrossRef\]](#)
9. Allegrini, A.; Salvaneschi, P.; Schirone, B.; Cianfaglione, K.; Michele, A. Di Multipurpose Plant Species and Circular Economy: *Corylus avellana* L. as a Study Case. *Front. Biosci.-Landmark* **2022**, *27*, 11. [\[CrossRef\]](#)
10. Bertolino, M.; Belviso, S.; Dal Bello, B.; Ghirardello, D.; Giordano, M.; Rolle, L.; Gerbi, V.; Zeppa, G. Influence of the Addition of Different Hazelnut Skins on the Physicochemical, Antioxidant, Polyphenol and Sensory Properties Of yogurt. *LWT* **2015**, *63*, 1145–1154. [\[CrossRef\]](#)
11. Bellomo, M.; Margiotta, V.R.; Saeli, M.; Colajanni, S.; Campisi, T. Dried-Fruit Shell Reuse in Green Construction and Building Materials. In *Mediterranean Architecture and the Green-Digital Transition*; Springer: Cham, Switzerland, 2023; pp. 467–478. [\[CrossRef\]](#)
12. Costantini, L.; Frangipane, M.T.; Molinari, R.; Garzoli, S.; Massantini, R.; Merendino, N. Hazelnut Skin Waste as a Functional Ingredient to Nutritionally Improve a Classic Shortbread Cookie Recipe. *Foods* **2023**, *12*, 2774. [\[CrossRef\]](#)
13. Zhao, J.; Wang, X.; Lin, H.; Lin, Z. Hazelnut and Its By-Products: A Comprehensive Review of Nutrition, Phytochemical Profile, Extraction, Bioactivities and Applications. *Food Chem.* **2023**, *413*, 135576. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Rivas, S.; Moure, A.; Parajó, J.C. Pretreatment of Hazelnut Shells as a Key Strategy for the Solubilization and Valorization of Hemicelluloses into Bioactive Compounds. *Agronomy* **2020**, *10*, 760. [\[CrossRef\]](#)
15. Özdemir, K.S.; Yilmaz, C.; Durmaz, G.; Gokmen, V. Hazelnut Skin Powder: A New Brown Colored Functional Ingredient. *Food Res. Int.* **2014**, *65*, 291–297. [\[CrossRef\]](#)
16. Taş, N.G.; Gökmen, V. Bioactive Compounds in Different Hazelnut Varieties and Their Skins. *J. Food Compos. Anal.* **2015**, *43*, 203–208. [\[CrossRef\]](#)
17. Shahidi, F.; Varatharajan, V.; Oh, W.Y.; Peng, H. Phenolic Compounds in Agri-Food by-Products, Their Bioavailability and Health Effects. *J. Food Bioact.* **2019**, *5*, 57–119. [\[CrossRef\]](#)
18. Cikrikci, S.; Demirkesen, I.; Mert, B. Production of Hazelnut Skin Fibres and Utilisation in a Model Bakery Product. *Qual. Assur. Saf. Crops Foods* **2016**, *8*, 195–206. [\[CrossRef\]](#)
19. ÖZTÜRK, G. A Waste Material Rich in Bioactive Compounds: Hazelnut Waste. *Eur. Food Sci. Eng.* **2023**, *4*, 15–25. [\[CrossRef\]](#)
20. Turan, D.; Capanoglu, E.; Altay, F. Investigating the Effect of Roasting on Functional Properties of Defatted Hazelnut Flour by Response Surface Methodology (RSM). *LWT* **2015**, *63*, 758–765. [\[CrossRef\]](#)
21. Xu, Y.; Hanna, M.A. Nutritional and Anti-Nutritional Compositions of Defatted Nebraska Hybrid Hazelnut Meal. *Int. J. Food Sci. Technol.* **2011**, *46*, 2022–2029. [\[CrossRef\]](#)
22. Pérez-Armada, L.; Rivas, S.; González, B.; Moure, A. Extraction of Phenolic Compounds from Hazelnut Shells by Green Processes. *J. Food Eng.* **2019**, *255*, 1–8. [\[CrossRef\]](#)
23. Waśik, A.; Klimowicz, A. Extracts from *Corylus avellana* as a Source of Antioxidants Useful in Cosmetic Preparations*. *Pomeranian J. Life Sci.* **2022**, *68*, 56–66. [\[CrossRef\]](#)

24. Bertino, A.; Mazzeo, L.; Gallo, V.; Posta, S.D.; Fanali, C.; Piemonte, V. Polyphenols Extraction from Hazelnut Skin Using Water as Solvent: Equilibrium Studies and Quantification of the Total Extractable Polyphenols. *Chem. Eng. Trans.* **2023**, *102*, 55–60. [\[CrossRef\]](#)
25. Kaoui, S.; Chebli, B.; Zaidouni, S.; Basaid, K.; Mir, Y. Deep Eutectic Solvents as Sustainable Extraction Media for Plants and Food Samples: A Review. *Sustain. Chem. Pharm.* **2023**, *31*, 100937. [\[CrossRef\]](#)
26. Panja, P. Green Extraction Methods of Food Polyphenols from Vegetable Materials. *Curr. Opin. Food Sci.* **2018**, *23*, 173–182. [\[CrossRef\]](#)
27. Fanali, C.; Gallo, V.; Posta, S.D.; Dugo, L.; Mazzeo, L.; Cocchi, M.; Piemonte, V.; De Gara, L. Choline Chloride–Lactic Acid–Based NADES as an Extraction Medium in a Response Surface Methodology–Optimized Method for the Extraction of Phenolic Compounds from Hazelnut Skin. *Molecules* **2021**, *26*, 2652. [\[CrossRef\]](#)
28. Dabetić, N.; Todorović, V.; Panić, M.; Redovniković, I.R.; Šobajić, S. Impact of Deep Eutectic Solvents on Extraction of Polyphenols from Grape Seeds and Skin. *Appl. Sci.* **2020**, *10*, 4830. [\[CrossRef\]](#)
29. Szopa, D.; Wróbel, P.; Witek-Krowiak, A. Enhancing Polyphenol Extraction Efficiency: A Systematic Review on the Optimization Strategies with Natural Deep Eutectic Solvents. *J. Mol. Liq.* **2024**, *404*, 124902. [\[CrossRef\]](#)
30. Wang, W.; Pan, Y.; Zhao, J.; Wang, Y.; Yao, Q.; Li, S. Development and Optimization of Green Extraction of Polyphenols in *Michelia Alba* Using Natural Deep Eutectic Solvents (NADES) and Evaluation of Bioactivity. *Sustain. Chem. Pharm.* **2024**, *37*, 101425. [\[CrossRef\]](#)
31. Pavlić, B.; Mrkonjić, Ž.; Teslić, N.; Kljakić, A.C.; Pojić, M.; Mandić, A.; Stupar, A.; Santos, F.; Duarte, A.R.C.; Mišan, A. Natural Deep Eutectic Solvent (NADES) Extraction Improves Polyphenol Yield and Antioxidant Activity of Wild Thyme (*Thymus serpyllum* L.) Extracts. *Molecules* **2022**, *27*, 1508. [\[CrossRef\]](#)
32. Khadhraoui, B.; Ummat, V.; Tiwari, B.K.; Fabiano-Tixier, A.S.; Chemat, F. Review of Ultrasound Combinations with Hybrid and Innovative Techniques for Extraction and Processing of Food and Natural Products. *Ultrason. Sonochem.* **2021**, *76*, 105625. [\[CrossRef\]](#)
33. Rosarina, D.; Narawangsa, D.R.; Chandra, N.S.R.; Sari, E.; Hermansyah, H. Optimization of Ultrasonic—Assisted Extraction (UAE) Method Using Natural Deep Eutectic Solvent (NADES) to Increase Curcuminoid Yield from *Curcuma longa* L., *Curcuma xanthorrhiza*, and *Curcuma mangga* Val. *Molecules* **2022**, *27*, 6080. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Khan, M.K.; Paniwnyk, L.; Hassan, S. *Polyphenols as Natural Antioxidants: Sources, Extraction and Applications in Food, Cosmetics and Drugs*; Springer: Singapore, 2019; ISBN 9789811338106.
35. Benoit, C.; Virginie, C.; Boris, V. *The Use of NADES to Support Innovation in the Cosmetic Industry*, 1st ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2021; Volume 97, ISBN 9780128216910.
36. Bener, M.; Şen, F.B.; Önem, A.N.; Bekdeşer, B.; Çelik, S.E.; Lalikoglu, M.; Aşçı, Y.S.; Capanoglu, E.; Apak, R. Microwave-Assisted Extraction of Antioxidant Compounds from by-Products of Turkish Hazelnut (*Corylus avellana* L.) Using Natural Deep Eutectic Solvents: Modeling, Optimization and Phenolic Characterization. *Food Chem.* **2022**, *385*, 132633. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Antony, A.; Farid, M. Effect of Temperatures on Polyphenols during Extraction. *Appl. Sci.* **2022**, *12*, 2107. [\[CrossRef\]](#)
38. Özdemir, M.; Torun, M. Ultrasound-Assisted Extraction of Natural Antioxidants From the Hazelnut Skin: Optimization and Comparison With Conventional Method. *Gıda* **2024**, *49*, 326–341. [\[CrossRef\]](#)
39. Deepa, N.; Kaur, C.; Singh, B.; Kapoor, H.C. Antioxidant Activity in Some Red Sweet Pepper Cultivars. *J. Food Compos. Anal.* **2006**, *19*, 572–578. [\[CrossRef\]](#)
40. Singleton, V.L.; Rossi, J.A. Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents. *Am. J. Enol. Vitic.* **1965**, *16*, 144–158. [\[CrossRef\]](#)
41. Slatnar, A.; Mikulic-Petkovsek, M.; Stampar, F.; Veberic, R.; Solar, A. HPLC–MSn Identification and Quantification of Phenolic Compounds in Hazelnut Kernels, Oil and Bagasse Pellets. *Food Res. Int.* **2014**, *64*, 783–789. [\[CrossRef\]](#)
42. *ISO 18134-2:2024*; Solid Biofuels—Determination of Moisture Content—Part 2: Simplified Method. International Organization for Standardization: Vernier, Switzerland, 2024.
43. *ISO 18122:2022*; Solid Biofuels—Determination of Ash Content. International Organization for Standardization: Vernier, Switzerland, 2022.
44. *ASTM D 3175-89*; Standards Test Method for Volatile Matter in the Analysis Sample of Coal and Coke, in Gaseous Fuels; Coal and Coke, 1989, p. 305. ASTM International: West Conshohocken, PA, USA, 1989.
45. *ISO 18125:2017*; Solid Biofuels—Determination of Calorific Value. International Organization for Standardization: Vernier, Switzerland, 2017.
46. *UNI EN 13037:2012*; Ammendanti e Substrati Di Coltivazione—Determinazione Del PH. Ente Italiano Di Normazione: Roma, Italy, 2012.
47. *ISO 16948:2015*; Solid Biofuels—Determination of Total Content of Carbon, Hydrogen and Nitrogen. International Organization for Standardization: Vernier, Switzerland, 2015.

48. ISO 16967:2015; Solid Biofuels—Determination of Major Elements—Al, Ca, Fe, Mg, P, K, Si, Na and Ti. International Organization for Standardization: Vernier, Switzerland, 2015.
49. ISO 16968:2015; Solid Biofuels—Determination of Minor Elements. International Organization for Standardization: Vernier, Switzerland, 2015.
50. ABuswell, M.; Hatfield, W.D. Bulletin No. 32, Anaerobic Fermentations, State of Illinois, Department of Registration and Education, Division of the State Water Survey, Urbana, Illinois. 1936. Available online: <http://www.isws.illinois.edu/pubdoc/B/ISWSB-32.pdf> (accessed on 9 January 2025).
51. Achinas, S.; Euverink, G.J.W. Theoretical Analysis of Biogas Potential Prediction from Agricultural Waste. *Resour. Technol.* **2016**, *2*, 143–147. [\[CrossRef\]](#)
52. Roati, C.; Fiore, S.; Ruffino, B.; Marchese, F.; Novarino, D.; Zanetti, M.C. Preliminary Evaluation of the Potential Biogas Production of Food-Processing Industrial Wastes. *Am. J. Environ. Sci.* **2012**, *8*, 291–296. [\[CrossRef\]](#)
53. Santangelo, E.; Carnevale, M.; Migliori, C.A.; Picarella, M.E.; Dono, G.; Mazzucato, A.; Gallucci, F. Evaluation of Tomato Introgression Lines Diversified for Peel Color as a Source of Functional Biocompounds and Biomass for Energy Recovery. *Biomass Bioenergy* **2020**, *141*, 105735. [\[CrossRef\]](#)
54. Hammer, Ø.; Harper, D.A.T.; Ryan, P.D. PAST: Paleontological Statistics Software Package for Education and Data Analysis. *Palaeontol. Electron.* **2001**, *4*, 1–9.
55. Montanari, M. *Statistica Ambientale. Analisi Multivariata—Metodologie Di Ordinamento*; SISSAD Snc: Trieste, Italy, 2012.
56. Fedotova, M.V.; Kruchinin, S.E. Hydration and Ion-Binding of Glycine Betaine: How They May Be Involved into Protection of Proteins under Abiotic Stresses. *J. Mol. Liq.* **2017**, *244*, 489–498. [\[CrossRef\]](#)
57. Simsek, A.; Artik, N.; Konar, N. Phenolic Profile of Meals Obtained from Defatted Hazelnut (*Corylus avellana* L.) Varieties. *Int. J. Life Sci. Biotechnol. Pharma Res.* **2017**, *6*, 12–17. [\[CrossRef\]](#)
58. Zeppa, G.; Belviso, S.; Bertolino, M.; Cavallero, M.C.; Dal Bello, B.; Ghirardello, D.; Giordano, M.; Giorgis, M.; Grosso, A.; Rolle, L.; et al. The Effect of Hazelnut Roasted Skin from Different Cultivars on the Quality Attributes, Polyphenol Content and Texture of Fresh Egg Pasta. *J. Sci. Food Agric.* **2015**, *95*, 1678–1688. [\[CrossRef\]](#) [\[PubMed\]](#)
59. Di Michele, A.; Pagano, C.; Allegrini, A.; Blasi, F.; Cossignani, L.; Di Raimo, E.; Faieta, M.; Oliva, E.; Pittia, P.; Primavilla, S.; et al. Hazelnut Shells as Source of Active Ingredients: Extracts Preparation and Characterization. *Molecules* **2021**, *26*, 6607. [\[CrossRef\]](#)
60. Stévigny, C.; Rolle, L.; Valentini, N.; Zeppa, G. Optimization of Extraction of Phenolic Content from Hazelnut Shell Using Response Surface Methodology. *J. Sci. Food Agric.* **2007**, *87*, 2817–2822. [\[CrossRef\]](#)
61. Rente, D.; Paiva, A.; Duarte, A.R. The Role of Hydrogen Bond Donor on the Extraction of Phenolic Compounds from Natural Matrices Using Deep Eutectic Systems. *Molecules* **2021**, *26*, 2336. [\[CrossRef\]](#)
62. Jakopic, J.; Petkovsek, M.M.; Likozar, A.; Solar, A.; Stampar, F.; Veberic, R. HPLC-MS Identification of Phenols in Hazelnut (*Corylus avellana* L.) Kernels. *Food Chem.* **2011**, *124*, 1100–1106. [\[CrossRef\]](#)
63. Alonso, C.; Martí, M.; Barba, C.; Lis, M.; Rubio, L.; Coderch, L. Skin Penetration and Antioxidant Effect of Cosmeo-Textiles with Gallic Acid. *J. Photochem. Photobiol. B Biol.* **2016**, *156*, 50–55. [\[CrossRef\]](#)
64. Bae, J.; Kim, N.; Shin, Y.; Kim, S.-Y.; Kim, Y.-J. Activity of Catechins and Their Applications. *Biomed. Dermatol.* **2020**, *4*, 8. [\[CrossRef\]](#)
65. Elloumi, W.; Mahmoudi, A.; Ortiz, S.; Boutefnouchet, S.; Chamkha, M.; Sayadi, S. Wound Healing Potential of Quercetin-3-O-Rhamnoside and Myricetin-3-O-Rhamnoside Isolated from Pistacia Lentiscus Distilled Leaves in Rats Model. *Biomed. Pharmacother.* **2022**, *146*, 112574. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Baldisserotto, A.; Malisardi, G.; Scalambra, E.; Andreotti, E.; Romagnoli, C.; Vicentini, C.B.; Manfredini, S.; Vertuani, S. Synthesis, Antioxidant and Antimicrobial Activity of a New Phloridzin Derivative for Dermo-Cosmetic Applications. *Molecules* **2012**, *17*, 13275–13289. [\[CrossRef\]](#) [\[PubMed\]](#)
67. Telmo, C.; Lousada, J. Heating Values of Wood Pellets from Different Species. *Biomass Bioenergy* **2011**, *35*, 2634–2639. [\[CrossRef\]](#)
68. Monti, A.; Di Virgilio, N.; Venturi, G. Mineral Composition and Ash Content of Six Major Energy Crops. *Biomass Bioenergy* **2008**, *32*, 216–223. [\[CrossRef\]](#)
69. Riva, G.; Pedretti, E.F.; Toscano, G.; Corinaldesi, F. Model for the Forecasting of the Fusion Temperature of Biomass Ashes. In Proceedings of the XXXIII CIOSTA-CIGR V Conference, Reggio Calabria, Italy, 17–19 June 2009.
70. Lesteur, M.; Bellon-Maurel, V.; Gonzalez, C.; Latrille, E.; Roger, J.M.; Junqua, G.; Steyer, J.P. Alternative Methods for Determining Anaerobic Biodegradability: A Review. *Process Biochem.* **2010**, *45*, 431–440. [\[CrossRef\]](#)
71. Labatut, R.A.; Angenent, L.T.; Scott, N.R. Biochemical Methane Potential and Biodegradability of Complex Organic Substrates. *Bioresour. Technol.* **2011**, *102*, 2255–2264. [\[CrossRef\]](#)
72. Dinuccio, E.; Balsari, P.; Gioelli, F.; Menardo, S. Evaluation of the Biogas Productivity Potential of Some Italian Agro-Industrial Biomasses. *Bioresour. Technol.* **2010**, *101*, 3780–3783. [\[CrossRef\]](#)
73. Fiore, S.; Ruffino, B.; Campo, G.; Roati, C.; Zanetti, M.C. Scale-up Evaluation of the Anaerobic Digestion of Food-Processing Industrial Wastes. *Renew. Energy* **2016**, *96*, 949–959. [\[CrossRef\]](#)

74. Santangelo, E.; Migliori, C.A.; Carnevale, M.; Vincenti, B.; Gallucci, F., M.A. Bioactive Compounds in Tomato Peels of New Breeding Lines. In Proceedings of the 30th European Biomass Conference and Exhibition Proceedings, Online, 9–12 May 2022; pp. 244–248.
75. Scaglia, B.; D’Incecco, P.; Squillace, P.; Dell’Orto, M.; De Nisi, P.; Pellegrino, L.; Botto, A.; Cavicchi, C.; Adani, F. Development of a Tomato Pomace Biorefinery Based on a CO₂-Supercritical Extraction Process for the Production of a High Value Lycopene Product, Bioenergy and Digestate. *J. Clean. Prod.* **2020**, *243*, 118650. [[CrossRef](#)]
76. Borkowska, A.; Klimek, K.; Maj, G.; Kaplan, M. Analysis of the Energy Potential of Hazelnut Husk Depending on the Variety. *Energies* **2024**, *17*, 3933. [[CrossRef](#)]
77. Picchi, G.; Lombardini, C.; Pari, L.; Spinelli, R. Physical and Chemical Characteristics of Renewable Fuel Obtained from Pruning Residues. *J. Clean. Prod.* **2018**, *171*, 457–463. [[CrossRef](#)]
78. Scoma, A.; Rebecchi, S.; Bertin, L.; Fava, F. High Impact Biowastes from South European Agro-Industries as Feedstock for Second-Generation Biorefineries. *Crit. Rev. Biotechnol.* **2016**, *36*, 175–189. [[CrossRef](#)] [[PubMed](#)]
79. McKendry, P. Energy Production from Biomass (Part 1): Overview of Biomass. *Bioresour. Technol.* **2002**, *83*, 37–46. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.