



Article Evaluation of the Thermal Energy Potential of Waste Products from Fruit Preparation and Processing Industry

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Abstract: In the context of a changing climate and increasing efforts to use renewable energy sources and waste materials and to green the environment, new sources and technologies for energy recovery from waste are being sought. This study evaluates the possibilities of energy generation potential from waste products of fruit species used in the food processing industry. The results indicate good potential for energy use of materials from fruit processing due to low input moisture content of around 15 wt. %, an average energy lower heating value (LHV) of 16.5 MJ·kg⁻¹, an average low ash content of 4.9% and meeting most of the emission limits of similar biofuels. Elemental analysis and combustion residue studies indicate safe operation within existing standards. The results of our analyses and experience from similar studies allow us to recommend most of the studied waste materials for energy generation use directly in processing plants at the local level.

Keywords: circular economy; energy mix; heating value; fruit stone; nut shell; pomace

1. Introduction

The current EU policy and legislative framework, including the energy market, is increasingly moving towards sustainable development, energy self-sufficiency, zero emission and circular production. These objectives are being followed up by the policies of individual institutions and countries by adopting the necessary measures, including subsidies or regulations, which affect all areas of the economy [1–4].

Biomass is an energy source composed of organic materials and natural resources [5]. After traditional fossil fuels such as oil (32%), coal (27%) and natural gas (22%), biomass (9.8%) is the next most important energy source [6,7].

Compared to traditional fossil fuels, biomass has a number of beneficial characteristics that predispose it to wider use. It is a hydrocarbon fuel with a high oxygen content that has a zero carbon balance. This means that the carbon consumed in the energy generating process was generated entirely during relatively recent short period of time [8]. Utilization of biofuel energy is relatively weather-independent compared to solar, wind and hydro power, and can be produced and consumed locally and adequately sized or managed. However, it is still seasonal and dependent on local agricultural activity. The boiler combustion technology is relatively simple, easily adapting to greater variability in feedstock and use conditions. For these reasons, the combustion of biofuels, and especially those using waste feedstock, is increasingly in demand within the energy mix. A further benefit is that the possibility of using biomass has relatively low cost associated with its conversion into biofuel form [9].



Citation: Bača, P.; Mašán, V.; Vanýsek, P.; Burg, P.; Binar, T.; Suchý, P.; Vaňková, L. Evaluation of the Thermal Energy Potential of Waste Products from Fruit Preparation and Processing Industry. *Appl. Sci.* **2024**, *14*, 1080. https://doi.org/10.3390/app14031080

Academic Editors: Tomohiro Tabata and Francesca Scargiali

Received: 13 December 2023 Revised: 19 January 2024 Accepted: 25 January 2024 Published: 26 January 2024



Copyright: © 2024 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/). The ongoing structural changes of the energy systems require better use of regional energy resources [10]. For these reasons, it is necessary to carry out a detailed analysis of all regional raw materials that may represent a promising source of energy [11]. Increasingly, therefore, attention is being paid to the use of various types of biomass that, until now, have been considered less suitable for energy use because of their characteristics or lack of availability [12].

There is a growing global trend towards more efficient use of agricultural and food by-products [13]. However, it should be true that only biomass otherwise unsuitable for further efficient use is burned and that it is indeed a true waste material [14]. This article focuses on waste from the food processing industry processing of fruit, grapes and nuts, which are relatively biologically active. This waste cannot be stored for long periods of time or transported over long distances for further use [15]. Improper collection and disposal of this waste, in particular that from the fruit processing industry, can cause serious environmental and ecological problems as well as significant loss of biomass [16]. EU Member States produce approximately 100 million tonnes of biowaste and by-products per year. Of this amount, fruit processing accounts for 14.8% and the distilling industry for approximately 4% [17]. A closer examination of the different types of fruit processed reveals significant species variation in terms of the amount of waste produced. Moreover, waste production for each species is influenced by seasonality, the concentration of cultivation areas in a given area and climatic factors. Depending on the commodity, the type of fruit and its processed parts (seed, pericarp, skin, etc.) and the processing technology chosen, the amount of waste materials can vary significantly. The largest proportion of waste products is generated during the processing of stone fruit (35%), followed by grapes (30%), nuts (30%), pome fruit (12%) and small fruit (3%) [18,19]. The waste products produced may vary in their characteristics, such as moisture, consistency or even chemical composition, which may have an impact on their overall energy potential [20]. The energy recovery from this waste biomass appears to be the simplest and most efficient if performed directly in processing plants or the regions in which the plants are located. The biomass in the form of stones, shells and seeds has the greatest potential. However, waste biomass with higher moisture content in the form of pomace, husk, pericarp, etc. may also be used. The moisture content of these raw materials can be lowered through drying, which can be done advantageously by using existing waste heat available in processing plants.

The aim of this study was to analyse physical and chemical characteristics and carry out determination of energy generation potential of waste products from processing of selected fruit species in the processing industry in the conditions of the Czech Republic and the EU. A partial goal is to expand the level of knowledge about the possibilities of energy utilization of this waste biomass, and at the same time to eliminate problems associated with waste handling and disposal.

2. Materials and Methods

The research described herein used a methodology of qualitative research based on laboratory analysis, statistical and empirical data of waste materials. The data were obtained from study of ten different types of waste products from the fruit and nuts processing industry. The combustion heat capacity as well as ash residues and possible unwelcome contaminants were rigorously analysed. The assessment of viability of calorific use is illuminated on the data of waste materials produced in a particular country (the Czech Republic), where in some sense the data are more qualitative, which enters into the methodology as well.

2.1. Characteristics of the Samples

Chosen samples of the raw material from the processing plants were acquired directly from producers in the region of South Moravia in the Czech Republic according to ISO 18135 [21]. Table 1 has been obtained from Situation and outlook reports—Fruit and Grape vine and wine [22,23] and it shows the available waste material in the Czech Republic for the year 2022, showing the amount of potential waste material that could be treated and burned to generate heat. The volume of the material shown reflects material harvested and processed, with the exception of almonds, dates and pistachio nuts, which are imported and only processed in the country. These materials represent commonly occurring waste materials in the processing industry and have so far been used for energy production only to a limited extent. These materials (Figure 1) are, however, produced in relatively large quantities during the processing season.

Table 1. Volume of waste materials production in the Czech Republic or imported to the country in one calendar year.

Fruit	Processed Waste Product	Amount of Harvest or Import in the Czech Republic (Tonnes)	Content of Waste Products in the Fruit (g·kg ⁻¹)	Potential Amount of Waste Material (Tonnes)	
Raspberries (<i>Rubus idaeus</i>)	pomace	8753	421	3685	
Sea-buckthorn (Hippophae rhamnoides)	pomace	783	323	253	
Grape vine (<i>Vitis vinifera</i>)	pomace	92,000	352	32,384	
Grape vine (Vitis vinifera)	seed cake	92,000	85	7820	
Almond (Prunus dulcis)	shell	4440	315	1399	
Pistachio (Pistacia vera)	shell	1008	124	125	
Almond (Prunus dulcis)	seed coat	4740	28	133	
Peach (Prunus persica)	stone	5731	124	711	
Plum (Prunus domestica)	stone	28,269	78	2205	
Date (Phoenix	stone	1421	89	126	
Sum		239,145		48,840	

Note: The data source is the report on fruit production in the Czech Republic 2022 [22,23].

The pomace of raspberries, sea-buckthorn and grapes is the result of pressing the fruit to produce juice. The pomace consists of seeds, pulp, skins and minimally the stems. It also contains residual water. The applied pressure of the press governs the residual moisture content (the higher the pressure, the more compact the pomace and the lower the moisture content).

Processing of raw almonds yields, as a by-product, shells and sometimes seed coats when the seeds (nuts) are treated. The almond shell is dry, relatively hard material, and prior to consumption is always removed. On the other hand, the seed coat is thin and does not need to be removed when producing raw almonds. For use in confectionery, it is removed by blanching. The blanching process produces waste that is quite moist.

The stones of peach, plum and date are obtained from the raw fruit and are separated relatively easily from the fruit without adhering pulp. The stones are relatively dry and also contain inside approximately 30% oil, which can potentially add to the calorific value of the waste. This waste material is encountered in the canning and distilling industries or in the press production of juices.

Pistachio shells are produced by shelling the kernel; the shells are hard and dry and are therefore suitable for incineration.

Grape seed cakes are produced when grape seeds are pressed to produce oil. The solid residue, the cakes, still contains a portion of residual oil that can increase calorific value of the waste material.

Characterised waste products:

The materials were collected separately for the individual experiment variants (approximately 50 kg per variant) directly from producers in the South Moravia region of the Czech Republic. First half part of the sample for analysis was immediately crushed on a Retsch SM 100 cutting mill (Retsch GmbH, Haan, Germany), with the required fractions of sieves according to the individual standards and analyses (most often 0.5 mm). The crushed materials were analysed in a biofuel laboratory to determine the moisture content at collection. The materials were then stored in a climate box to keep the moisture at 10% and then were characterised in terms of physical and chemical properties. The second half part was dried and processed on an analytical sieve shaker Retsch AS 200 Control (Retsch GmbH, Haan, Germany) to determine the average particle size.



Figure 1. Some materials used in this study: (A)—Raspberry pomace; (B)—Sea-buckthorn pomace;
(C)—Almond shell; (D)—Almond seed coat; (E)—Peach stone; (F)—Plum stone; (G)—Pistachio shell;
(H)—Grape seed cake.

2.2. Physical Properties

Chemical and physical analyses were conducted following relevant ISO standards. Samples for analysis were weighed on an OHAUS PX224 laboratory balance (OHAUS Europe GmbH, Nänikon, Switzerland). The bulk density of samples was measured according to the standard ISO 17828 [24] and a standardized five-litre container designed for this analysis was used. The moisture content of the samples was measured following the standard ISO 18134-2 [25]. Samples were placed in a laboratory dryer oven Memmert UF 30 (Memmert GmbH & Co. KG—Schwabach, Germany) at 105 ± 2 °C and dried in air until a constant mass was attained. The moisture content was calculated from the loss in the mass of the test portion using the formula described in the used standard. The ash content was

measured according to the standard ISO 18122 [26] in a LAC LMH muffle furnace (LAC, s.r.o., Židlochovice, the Czech Republic). The ash content is determined by calculating the mass of the residue remaining after the sample is heated and combusted in air under rigidly controlled conditions. Samples of chips (minimum 1 g each) were weighed before and after their complete combustion, conducted at 550 ± 10 °C. The higher heating value (HHV) of the samples was analysed using a Parr 6400 automatic isoperibol calorimeter (Parr Instruments, Moline, IL, USA) according to ISO 18125 [27]. The lower heating value (LHV) was calculated by the instrument software from the HHV in accordance with the equations in ISO 1928 [28]:

$$Q_i^r = Q_s^r - \gamma \cdot (W_t^r + 8.94 \cdot H_t^r) \tag{1}$$

where

- Q_i^r —LHV of the evaluated sample, MJ·kg⁻¹;
- Q_s^r —HHV of the original sample, MJ·kg⁻¹;
- γ —heat of vaporization of 1% of H₂O, MJ·kg⁻¹, at 25 °C, γ = 0.02442 MJ·kg⁻¹;
- 8.94—hydrogen to water mass conversion ratio;
- *W*^{*r*}_{*t*}—total water content in the original sample, %;
- H_t^r —total hydrogen content in the original sample, %.

2.3. Experimental Methods

2.3.1. Determination of Carbon, Hydrogen and Oxygen

All C, H and O measurements were performed using a FLASH 2000 (Thermo Fisher Scientific Inc., Waltham, MA, USA) organic elemental analyser according to the standard ISO 16948 [29]. The standards used for measurement were purchased from Thermo Fisher Scientific Inc. For C and H measurement, 1–3 mg of measured sample were placed in a "soft" small tin container and introduced into a quartz reactor filled with copper oxide and electrolytic copper. The reactor was heated to 950 °C and a small volume of oxygen was injected along with the sample. For O measurement, 1–1.5 mg of measured sample was placed in a "soft" silver container and introduced into a quartz reactor filled with nickel-plated carbon. The reactor was heated to 1050 °C. The gases released by the combustion of the sample were measured by the machine built-in thermal conductivity detector (TCD). The relative C, H and O content was determined by comparing the resulting spectra to a sulphanilamide standard.

2.3.2. Determination of Major and Minor Elements, Total Sulphur and Total Chlorine

The elemental composition of the samples was determined by X-ray fluorescence spectrometry (XRF). The analysis was performed using a Niton XL3t GOLDD+ (Thermo Fisher Scientific, Waltham, MA, USA), with static and cuvettes based on the standards ISO 16967 [30], ISO 16968 [31] and ISO 16994 [32]. Prior to the analysis of elemental composition, the samples were dehydrated by drying them in a laboratory oven Memmert UF 30 (Memmert GmbH & Co. KG—Schwabach, Germany) at 105 °C for 24 h. After drying, the samples were homogenized by gently rubbing them in a porcelain friction pan. The homogenized samples were then placed in standard Mylar foil cuvettes, with three grams of each sample weighed into individual cuvettes. The "All Geo" test mode was used. The accuracy of the determinations was checked using reference materials (IRM 5718, Metranal 6, Metranal 13, Metranal 22, NIST 2781, NIST 2702; ANALYTIKA, spol. s r.o., Prague, the Czech Republic). The results were evaluated in percent and calculated in milligrams per kilogram.

2.4. Methods of Statistical Analysis

All analyses were performed in triplicate. The one factor analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) tests were conducted to determine the differences among averages at a significance level of $\alpha = 0.05$. The results are reported as

averages and standard deviations. Averages with different letters within the column are significantly different from each other. The Statistica 14.0 (TIBCO Software Inc., Palo Alto, CA, USA) software package was used.

3. Results and Discussion

3.1. Characterization of Raw Materials for Energy Utilization

Table 2 shows the most important parameters of the tested materials in terms of their energy generation potential. According to the assumptions and results of similar studies [15,33–38] the materials containing seeds with oils (Sea-buckthorn, grape vine pomace and grape vine seed cake) have the highest LHV. Almond seed coat also has a statistically similar high LHV, although it does not contain seeds. According to the results of the statistical comparison, materials such as fruit shells and stones achieve similar HHV. These materials have LHV comparable to wood pellets and higher than lump wood, and in this respect meet the ISO 17225-6 [39] standard (minimal 14.5 $MJ \cdot kg^{-1}$). Interestingly, the almond seed coat material is very specific according to our results. While it has high ash content, it still achieves a very good O:C ratio, and a high LHV, which is unexpected, perhaps due to high contents of lignin. In addition, the calorific value will increase even more by pelletizing these materials.

Table 2. The physical and energy properties of materials.

Fruit Species and Characteristics	Moisture at Collection (wt. %)	Average Particle Size (mm)	Ash (wt. %)	HHV (MJ∙kg ⁻¹)	LHV (MJ·kg ⁻¹)	Bulk Density (kg∙m ^{−3})
Raspberry pomace	19.6	0.8	4.8 ± 0.2 ^d	$18.8\pm0.1~^{\rm c}$	$15.79\pm0.07~^{\rm cd}$	486
Sea-buckthorn pomace	21.7	1.9	2.78 ± 0.05 $^{\mathrm{ab}}$	$21.0\pm0.1~^{\rm a}$	$17.82\pm0.17~^{\rm a}$	437
Grape vine pomace	36.2	2.7	$2.8\pm0.6~^{ m ab}$	$20.4\pm0.5~^{\rm a}$	18.0 ± 0.8 $^{\rm a}$	496
Grape vine seed cake	8.0	67.4	3.5 ± 0.6 ^{bd}	$20.84\pm0.15~^{a}$	$17.85\pm0.24~^{\rm a}$	1163
Almond shell	6.7	43.9	$10.0\pm0.8~^{\rm e}$	$17.51\pm0.04~^{\rm b}$	$14.83\pm0.05~^{\rm b}$	362
Pistachio shell	4.7	19.3	$2.07\pm0.12~^{ m ab}$	$17.23\pm0.03~^{\rm b}$	$14.9\pm0.1~^{ m bc}$	467
Almond seed coat	18.2	50.5	$19\pm1~^{ m f}$	$20.49\pm0.04~^{\rm a}$	17.9 ± 0.2 a	512
Peach stone	9.7	39.4	$0.51\pm0.01~^{ m c}$	19.57 ± 0.06 ^d	$17.14\pm0.15~^{\rm f}$	523
Plum stone	7.9	27.6	$1.9\pm0.6~^{\mathrm{ac}}$	$18.9\pm0.1~^{\rm c}$	16.05 ± 0.24 ^{de}	547
Date stone	17.4	30.7	$1.47\pm0.04~^{\rm ac}$	$17.75\pm0.04~^{\rm b}$	15.1 ± 0.3 ^{bc}	503

Note: Data are expressed as an average \pm standard deviation. Averages with different letters within the column are significantly different, according to Tukey's test ($p \le 0.05$).

Madadian et al. [35] report an HHV for grape seeds at $18.28 \text{ MJ} \cdot \text{kg}^{-1}$ and for grape pomace at $18.76 \text{ MJ} \cdot \text{kg}^{-1}$, values very similar to those that we obtained. Our higher HHV for grape seed cake can be explained by the oil pressing process, during which excess moisture is removed. The value of grape pomace depends very strongly on the grape variety. Also, the reported ash content of 2.8% is consistent with our results.

Osman et al. [40] report an HHV for berry pomace of $21.36 \text{ MJ} \cdot \text{kg}^{-1}$ compared to our value of 18.8 MJ·kg⁻¹. However, the ash content is again very similar at 3.73%. Atimtay and Kaynak [41] report a similar HHV value for peach stone (20.65 MJ·kg⁻¹ compared to our 19.57 MJ·kg⁻¹) and a slightly higher ash content of 1.5%. Lahboubi et al. [42] report an HHV of 14.1 MJ·kg⁻¹, which is, however, for the empty fruit bunch (EFB) of the date palm, whereas we analysed only date stone, as only the separated fruit is imported for further processing. The lower stone value is due to the higher moisture content and lower calorific value of the material. The waste material used also differs in terms of elemental composition. Ozturk and Bascetincelik [43] have made an extensive comparison of several fruit and nut materials in Turkey for energy purposes. Their findings fairly replicate our results in terms of HHV, or ash content. A minor difference can be found, e.g., in pistachio shells, where they report a higher value of 19.26 MJ·kg⁻¹. The authors also confirmed that the oil contained in the seeds increases the calorific value.

Most materials also meet the standard in terms of ash content, which is below 6% and belong to class A (family home use) [44]. Almond shell material is close to this limit but does not meet it, and thus and would be classified in the lower category B for industrial applications. The almond seed coat materials, on the other hand, have a significantly higher ash content and from this perspective are more suitable for co-firing with other materials [45]. The results confirmed that materials with lower ash content achieve higher HHV due to a higher calorific value.

The combustion temperature in the boilers is also important for reducing ash and fuel emissions. The standard used for testing biofuels, ISO 18122 [26], defines a test temperature of only 550 ± 10 °C, but the boiler combustion temperature is normally higher. Significant ash mass loss may occur at temperatures above $550 \,^{\circ}$ C, and inorganic compounds decompose at temperatures above $750 \,^{\circ}$ C [46]. Thus, even such materials as almond shells and seed coat can, in the end, produce lower ash content. In addition, higher ash content in itself may not be a problem, as it can be addressed by adjusting the combustion process and more frequent clearing of the fire grate in the boilers [47].

The materials evaluated in this work can be mostly processed very well for energy generation. A number of them (pistachio shell, peach, plum and date pits and grape seed cake) are suitable for incineration directly as they leave the processing lines. For the use of direct combustion, they are of sufficient particle size (Table 2) as not to clog the hopper or the feed to the boiler. Sufficient hardness of the material also gives a good expectation of minimal abrasion or breakage into a smaller fraction. Moisture and pulp residues are also kept to a minimum [48]. Together with the relatively higher calorific value, they are well suited for energy generation.

Other materials (grape vine, raspberry and sea-buckthorn pomace) are characterized by high moisture content, unsuitable for direct combustion. The small fraction and small particles that are produced during drying and their transport can cause considerable problems in direct combustion. Therefore, they can be recommended as an admixture for other fuels and for the production of compressed-form biofuels (pellets and briquettes). In particular, the higher oil content and pulp residues are well suited to act as a binder in drier materials [49,50].

3.2. Chemical Composition of Raw Materials

The waste materials have not undergone any chemical treatment as part of the manufacturing process and, thus, are natural products in this respect. In addition, since they are materials that are used for direct consumption, their processing is subject to higher demands in terms of quality, low residue content, limit of heavy metal concentration and compliance with limits on the content of other harmful substances. Thus, their use for energy generation is unlikely to pose a problem in terms of meeting the limits or restrictions for environmental and public health reasons [13]. However, it should be also kept in mind that the restrictions and thus controls are for the edible parts of the fruit, and waste can still have above-limit contaminants.

A number of authors point out that the accumulation of substances can vary significantly according to the plant part and the tissue that is burned [12,51]. For example, elevated concentrations of foreign or harmful substances are reported in leaves or seeds and are often related to contaminations present in the environment and the use of chemicals during cultivation. These waste products have been evaluated in other regions as well, and the results are similar in terms of energy and content [40,41,43,52–54]. Even comparisons with materials exotic to Europe or with vegetable residues give similar results [42,55–57].

Madadian et al. [35] report very similar C, O, H and S compositions for grape pomace and grape seeds to ours. Osman et al. [40] report similar results for berry pomace for C and H to ours, while reporting 43% for O, compared to our value of 33%. Conversely, for S they report a significantly lower content of only 0.1%. Atimtay and Kaynak [41] report very similar results for C, O, and H for peach stones, but again, a slightly lower S content. Elevated concentrations of chlorine, sulphur or copper, which probably originate from agrochemicals, as well as iron, calcium and nitrogen, which probably originate from fertilizers, can be observed. Monitoring the chemical composition is all the more important, as the burned waste materials may not reach normal combustion temperatures or the combustion process may be non-standard, resulting in increased emissions to the environment, or condensates in the boilers, or increased concentrations in the ash. The resulting energy generation may, therefore, not only be limited by lower calorific value of the fuel used, but also by the need to respond to the limits of contaminants, with utilization of different filters or modifications to the combustion equipment, or increased requirements for ash disposal [5,38].

In the samples tested, no elevated concentrations of the elements (As, Cr, Cu, Pb, Hg, Ni and Zn) exceeding the ISO 17225-6 standard were detected, and all materials meet the standard in this respect (Tables 3 and 4).

Fruit Species and Characteristics	C (%, Dry Matter)	O (%, Dry Matter)	H (%, Dry Matter)	O:C
Raspberry pomace	$51.9\pm2.0~^{\mathrm{bc}}$	$33.46\pm0.15~^{\rm d}$	6.5 ± 0.4 ^b	0.65
Sea-buckthorn pomace	54.9 ± 0.9 b	$29\pm1~^{e}$	6.82 ± 0.15 ^b	0.64
Grape vine pomace	53.28 ± 0.12 ^b	$35\pm1~^{ad}$	5.3 ± 0.8 a	0.53
Grape vine seed cake	53.0 ± 0.3 ^b	$40.1\pm0.4~^{ m c}$	$8.61\pm0.21~^{ m c}$	0.80
Almond shell	46.4 ± 0.9 a	$37.1\pm0.9~^{ m ab}$	5.78 ± 0.11 $^{ m ab}$	0.69
Pistachio shell	$47.43\pm0.24~^{\rm a}$	$40.28\pm0.21~^{\rm c}$	5.0 ± 0.3 a	0.81
Almond seed coat	45.8 ± 0.3 a	$38.2\pm0.4~^{ m bc}$	5.6 ± 0.4 $^{ m ab}$	0.85
Peach stone	$52.5\pm0.5~{ m bc}$	$36\pm2~^{ab}$	5.2 ± 0.4 a	0.83
Plum stone	$49\pm2~^{ m ac}$	$37.1\pm0.9~^{ m ab}$	6.1 ± 0.4 $^{ m ab}$	0.75
Date stone	$49\pm2~^{ m ac}$	$39.8\pm0.3~^{\rm c}$	$5.8\pm0.6~^{\mathrm{ab}}$	0.76

Table 3. Results of the elemental analysis (C, O, H).

Note: Data are expressed as an average \pm standard deviation. Averages with different letters within the column are significantly different, according to Tukey's test ($p \le 0.05$).

In the samples tested, no elevated concentrations of the elements (As, Cr, Cu, Pb, Hg, Ni and Zn) exceeding the ISO 17225-6 standard were detected and all materials meet the standard in this respect (Tables 3 and 4).

A significant result of the analyses is the mineral composition of the samples, with some differences in the specific elements such as K, S, Fe, Ca, Cl, Al, P and Si. Differences in the content of individual metals are another reason for the higher ash content [58]. The mineral matter of biomass in combination with organic composition, moisture content, etc. plays a major role in determining the properties of the resulting fuel [51].

According to the results of the analyses, it is clear that similar materials, such as pomaces or stones, do not have similar mineral composition. This also confirms the results of a number of authors who report that different parts of the fruit can have diametrically different compositions [18,59]; in our case, for example, grape vine pomace and grape vine seed cake, or almond seed coat and shell.

A typical feature of waste materials is the elevated concentrations of the elements Cl and S. The content of these elements and also heavy metals (as Cd) is higher in fruits and seeds and is related to the natural accumulation by the plant. All the test samples had high natural content of S and Cl, which is in agreement with the literature results. The aforementioned may lead to problems related to increased emissions and boiler corrosion. Biofuel producers must, therefore, respond adequately to the composition of materials in the feedstock blending process [20,60,61].

Element Content (mg·kg ⁻¹)	Raspberry Pomace	Sea- Buckthorn Pomace	Grape Vine Pomace	Grape Vine Seed Cake	Almond Shell	Pistachio Shell	Almond Seed Coat	Peach Stone	Plum Stone	Date Stone	Limit Value ISO 17225-6
Мо	12.7 ± 1.2	9.2 ± 1.3	9.4 ± 1.1	10.6 ± 1.2	10.3 ± 1.1	12.5 ± 1.1	11.7 ± 1.1	12.5 ± 1.1	11 ± 1	10.6 ± 1.1	
Zr	11.6 ± 1.0	11.3 ± 1.1	6.7 ± 0.9	9.4 ± 1.0	9.8 ± 0.9	8.9 ± 0.8	9.5 ± 0.9	11.3 ± 0.8	10.1 ± 0.7	10.1 ± 0.8	
Sr	30.3 ± 1.0	11.3 ± 1.3	20.7 ± 0.8	23.9 ± 0.9	16.9 ± 0.8	6 ± 0.5	17.3 ± 0.8	8.0 ± 0.5	4.4 ± 0.5	10.1 ± 0.6	
U	5.6 ± 1.7	ND	ND	ND	ND	ND	ND	6.5 ± 1.3	ND	3 ± 1.2	
Rb	12.4 ± 0.9	9.3 ± 1	5.6 ± 0.6	6.3 ± 0.8	4.0 ± 0.7	3.3 ± 0.6	4 ± 0.6	1.9 ± 0.5	1.3 ± 0.5	5.1 ± 0.6	
Zn	43.5 ± 4.1	58 ± 9	12 ± 3	14.9 ± 3.0	ND	ND	7 ± 3	7.2 ± 2.5	$11 \pm 2.$	19 ± 3	100
W	216 ± 26	427 ± 36	ND	ND	140 ± 20	197 ± 20	195 ± 23	81 ± 18	180 ± 18	76 ± 17	
Cu	81 ± 7	35 ± 13	28.2 ± 4.3	30 ± 5	22 ± 5	19 ± 5	28 ± 6	17 ± 5	29 ± 5	14 ± 4	20
Fe	1720 ± 33	3500 ± 70	908 ± 17	560 ± 20	570 ± 19	140 ± 12	319 ± 17	980 ± 21	110 ± 11	513 ± 16	
Ti	400 ± 26	500 ± 31	437 ± 13	250 ± 19	260 ± 16	122 ± 13	151 ± 17	220 ± 19	76 ± 15	253 ± 17	
Ca	$53,700 \pm 500$	$52,\!500\pm 500$	$34,\!600\pm 300$	$27,900 \pm 300$	$30,400 \pm 400$	5960 ± 70	$13{,}100\pm300$	$23,\!400\pm 300$	6530 ± 80	$20,\!800\pm 300$	
K	$46,\!300\pm 300$	$41,\!900 \pm 300$	$\textbf{21,}\textbf{350} \pm \textbf{120}$	$11,\!400\pm130$	$74,500 \pm 400$	7000 ± 100	$70,\!600 \pm 400$	6500 ± 120	$11,\!100\pm130$	$14,\!000\pm150$	
S	5300 ± 110	1000 ± 160	4280 ± 50	3450 ± 60	1600 ± 80	1750 ± 90	1330 ± 80	2370 ± 70	2440 ± 70	3010 ± 70	3000
Sb	ND	11 ± 7	ND	ND	ND	ND	ND	6 ± 4	ND	ND	
Sn	15 ± 5	9 ± 6	ND	ND	ND	ND	8 ± 4	7 ± 4	6 ± 3	5 ± 4	
Cd	25 ± 3	23 ± 4	ND	ND	ND	ND	17 ± 3	25 ± 3	17 ± 2	19 ± 2	0.5
Ag	8.4 ± 1.7	10.4 ± 2.1	ND	ND	ND	ND	3.6 ± 1.3	9.1 ± 1.3	3.7 ± 1.1	6.2 ± 1.2	
Pd	17.1 ± 2.1	14.2 ± 2.4	ND	ND	ND	ND	7.1 ± 1.5	15.3 ± 1.6	8.1 ± 1.2	10.2 ± 1.3	
Nb	16.5 ± 1.3	16.1 ± 1.6	11.4 ± 1.7	12.1 ± 1.2	12.7 ± 1.1	13.6 ± 1.1	14.1 ± 1.2	15.3 ± 1.1	14.4 ± 1.1	12.8 ± 1.1	
Al	7000 ± 500	9300 ± 700	3300 ± 210	3500 ± 230	5900 ± 400	1800 ± 300	1800 ± 400	5340 ± 300	1690 ± 230	4000 ± 300	
Р	$10,\!500\pm 200$	$14{,}700\pm300$	6000 ± 100	6150 ± 110	6180 ± 150	5300 ± 160	8520 ± 170	6380 ± 140	5630 ± 120	5620 ± 130	
Si	$41,\!100\pm500$	$57{,}400\pm700$	$\textbf{29,800} \pm \textbf{300}$	$\textbf{22,}200\pm300$	$\textbf{33,800} \pm 500$	$10{,}400\pm300$	$11,\!200\pm300$	$33,\!500 \pm 400$	7660 ± 220	$\textbf{26,700} \pm \textbf{300}$	
Cl	1000 ± 38	2160 ± 50	90 ± 13	95 ± 16	600 ± 30	$40,\!900\pm170$	1000 ± 35	1400 ± 30	3120 ± 40	3610 ± 40	3000
Mg	ND	ND	ND	ND	ND	ND	ND	3900 ± 1100	2300 ± 900	ND	

Table 4. Elemental composition acquired by X-ray fluorescence (XRF) (major and trace elements).

Note: Th, Pb, Au, Se, As, Hg, Ni, Co, Mn, Cr, V, Sc, Ba, Cs, Te, Bi, Re, Ta and Hf are not listed as they were not detected. ND—not detected (low concentration) or not measured.

Samples originating from pomace (grape vine pomace and seed cake and raspberry pomace) have high sulphur concentrations. In addition, higher Cl concentrations can be seen in samples of materials originally from seeds (peach, plum and sea-buckthorn pomace, which also contains seeds). However, the excess is not significant, and these samples meet the limit for class B (biofuel pellets). Only the pistachio shell and date stone sample exceeds the Cl limit.

3.3. Assessment of Energy Generation Potential

Within the Czech and even the European market, there exist a number of agriculturalindustrial and processing plants that can provide a somewhat substantial amount of waste materials. These producers have a relatively difficult time disposing of this material considering its quick spoilage, increased treatment costs, composting or transport.

Our findings are consistent with other work [43,53] suggesting that there is a potential for energy generation from a range of materials, although the use of some will entail significant costs for the construction or modification of combustion and preparation facilities. For example, as reported by Lipiński et al. [53], the total heat energetic potential from fruit waste in Poland can be considered negligible (0.15% of total Poland energy consumption in 2016). However, there are many others reasons why its use should be interesting. The advantage of the waste combustion is its relatively stable production, both over the years and seasonally. Many plants are oriented towards processing commodities with similar characteristics and are designed to process them throughout the year. The use of waste can provide diversification and locally independent sources of energy and, with the use of modern technologies, will also be environmentally friendly [6].

The bulk density of the different studied materials (Table 2) is quite variable. However, it may not play a significant role for the on-site energy generation utilization. On the other hand, when these materials need to be transported to another place for utilization, the lower calorific value of those materials (pomace, almond seed coat, or pistachio shells) may already reduce their economic efficiency. Another factor to be considered is the required drying of wetter materials (pomaces and almond seed coat), which could be done with the waste heat produced at the processing plant, but is technology- and space-intensive [62]. The most advantageous for energy generation from the samples in our study would appear to be grape vine seed cake. While there is fairly similar calorific value for all the dry materials assessed, the cake stands out by two features; first, it is already very dry and, thus, additional energy used for drying is minimized, and second, it has significantly higher mass density, which reduces the volume of the material to be transported and handled.

The presented results are in line with the new requirements of the market, business and the governmental policies in the Czech Republic and the EU. The results of our analyses and the findings of similar studies allow us to recommend most of the studied materials be utilized for energy generation. Based on our knowledge of the market, legislative constraints, subsidies, preferences of residents and businesses and the properties of the materials, we expect to use them directly in the processing plants at the local level. We even lean towards the recommendation of the studies that suggest to co-fire these materials with conventional biofuels [63–66].

Of course, the energy obtained from burning such biomass will be lower than from conventional biofuels. The waste biomass that we have tested normally reaches a calorific value (HHV) of 17 to 21 MJ·kg⁻¹, compared to biofuels such as, e.g., wood pellets reaching 15 to 18 MJ·kg⁻¹, coniferous dried wood 16 MJ·kg⁻¹, or possibly black coal of 27 to 31 MJ·kg⁻¹. However, the efficiency comes through cost savings after taking into account the reduced costs of waste treatment and disposal, the potential to use cheaper energy (in the case of CHP, combined heat and power) to provide energy at times of high tariffs and the certain self-sufficiency of the processing plant. Local thermal energy generation needs to be addressed in a feasible solution directly in the processing plant. To this end, lower energy efficiency can also be offset by subsidies or, conversely, higher fees for biowaste disposal.

The energy self-sufficiency of companies obtained through the incineration of their own waste also seems to us more beneficial and logical compared to the construction of other alternative energy sources such as PV plants. This presented paper does not aim to elaborate and model in detail all energy/heat recovery technologies for all investigated materials, as their efficiency will vary considerably according to the conditions of each individual operation. However, our results give the professionals and interested companies some idea of how waste can be utilized and how the amount of waste needed to be disposed of can be reduced.

From a pan-European perspective, waste by-products from the manufacturing industry represent about 15 million tonnes per year [17]. If at least 20% of this amount were to be used as energy recoverable waste, and with an average LHV of 14 MJ·kg⁻¹, this would represent 4.2×10^7 GJ of energy, which is 11.6 TWh. This energy corresponds to about 2.36 million tonnes of wood pellets, while in 2022 Europe consumed 24.8 million tonnes of pellets [67]. Targeting only the Czech market, where about 50,000 tonnes of fruit and 92,000 tonnes of grapes are processed annually, and again with an average production of 20% of the waste available for combustion, this represents 4×10^5 GJ, which is 0.11 TWh of energy. To put this into perspective, all PV plants in the Czech Republic produced 2.15 TWh of electricity in 2022 [68].

4. Conclusions

The processing industry generates a large amount of organic waste that should be utilized. There are opportunities for extraction of valuable substances, production of secondary raw materials and a range of other technologies, but these are demanding in terms of available quantity and continuity of material inputs and costly in technology development. However, a relatively easy way is to convert this waste directly into heat energy by combustion.

The relatively good composition and properties of the waste, such as low moisture content, higher calorific value, etc., make many materials potentially suitable as biofuels. The results of this study support for this purpose the applicability of fruit and nut stones and shells in particular, with calorific values (LHV) between 14.83 to 17.99 $MJ \cdot kg^{-1}$. In terms of other material properties and the complexity of storage or transportation and drying, we also recommend local on-farm or in-plant use. Use of these waste materials further supports the concept of circular economy, greening and diversification of resources and can help companies to rationalize their production by converting waste into energy. Further research activities in this area should be directed towards emissivity and waste material agglomeration processes.

Author Contributions: Conceptualization, V.M. and P.V.; methodology, P.B. (Petr Bača) and P.B. (Patrik Burg); software, V.M.; validation, T.B., P.V. and P.S.; formal analysis, P.S., L.V. and V.M.; investigation, V.M. and P.V.; resources, P.B. (Petr Bača) and P.B. (Patrik Burg); data curation, P.B. (Petr Bača), V.M. and P.B. (Patrik Burg); writing—original draft preparation, V.M. and P.V.; writing—review and editing, P.B. (Petr Bača), P.V. and V.M.; visualization, P.B. (Patrik Burg); supervision, P.B. (Petr Bača) and P.V.; project administration, P.B. (Petr Bača); funding acquisition, P.B. (Petr Bača). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the specific research project at BUT No. FEKT-S-23-8286 and was supported by the project CZ.02.1.01/0.0/0.0/16_017/0002334 Research Infrastructure for Young Scientists, co-financed from Operational Programme Research, Development and Education.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

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

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