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Review

Avocado-Derived Biomass as a Source of Bioenergy and Bioproducts

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Featured Application: This review gives new insights into the valorization of avocado waste. It can help researchers and the industry involved in the processing of avocado fruit to look for integrated approaches within a biorefinery context and to move towards a circular bioeconomy.

Abstract: The avocado (*Persea americana* Mill.) is a tree native to Mexico and Guatemala. Avocado consumption, fresh or in the form of processed products, is growing everywhere and it has caused a large number of countries to invest heavily in avocado production. The industrialization of avocado gives as a result a huge amount of waste, not only the peel and stone but also that waste generated by the pruning practices and oil extraction. These biomasses could be converted into raw materials to obtain different types of co-products, but this implies changes in the use of these resources, the design of efficient production systems, and integration to take full advantage of them, e.g., by developing biorefinery models. Therefore, this review firstly gives a snapshot of those residues generated in the avocado industry and provides their chemical composition. Secondly, this review presents updated information about the valorization ways of avocado-derived biomass to obtain bioenergy, biofuels, and other marketable products (starch, protein, phenolic compounds, and biosorbents, among others) using a single process or integrated processes within a biorefinery context. Green technologies to obtain these products are also covered, e.g., based on the application of microwaves, ultrasound, supercritical fluids, etc. As a conclusion, there is a variety of ways to valorize avocado waste in single processes, but it would be promising to develop biorefinery schemes. This would enable the avocado sector to move towards the zero-waste principle.

Keywords: avocado biomass; bioenergy; bioproducts; biorefinery; natural antioxidants; valorization

1. Introduction

The avocado (*Persea americana* Mill.) is a tree native to Mesoamerica, whose origin is in the central part of Mexico and some parts of northern Guatemala. The name of the avocado comes from Nahuatl (Ahuacatl), a word that means "tree testicles" [1]. Avocado belongs to the family Lauraceae [2]. The Lauraceae family is one of the oldest among the flowering plants; particularly, avocado is the most important and only edible fruit of this family and has a high commercial value [3–5]. Production areas were concentrated in Central and South America, but it is currently cultivated worldwide. Avocado consumption is growing everywhere, and it has caused a large number of countries to invest heavily in avocado production (Figure 1a). Based on the average production between 1998 and 2018, the top 10 avocado producing countries were firstly México, followed by the Dominican Republic, Indonesia, Colombia, United States, Peru, Brazil, Chile, Kenya, and China [6]. Figure 1b shows the production of avocados in these top 10 countries in 1998, 2008, and 2018. It highlights that Mexico is the major producer and the production was generally increased not only in this country but also in all these countries. In 2018, the world's avocado production was around 6.4 million tons, of which these countries produced 77.4% [6].

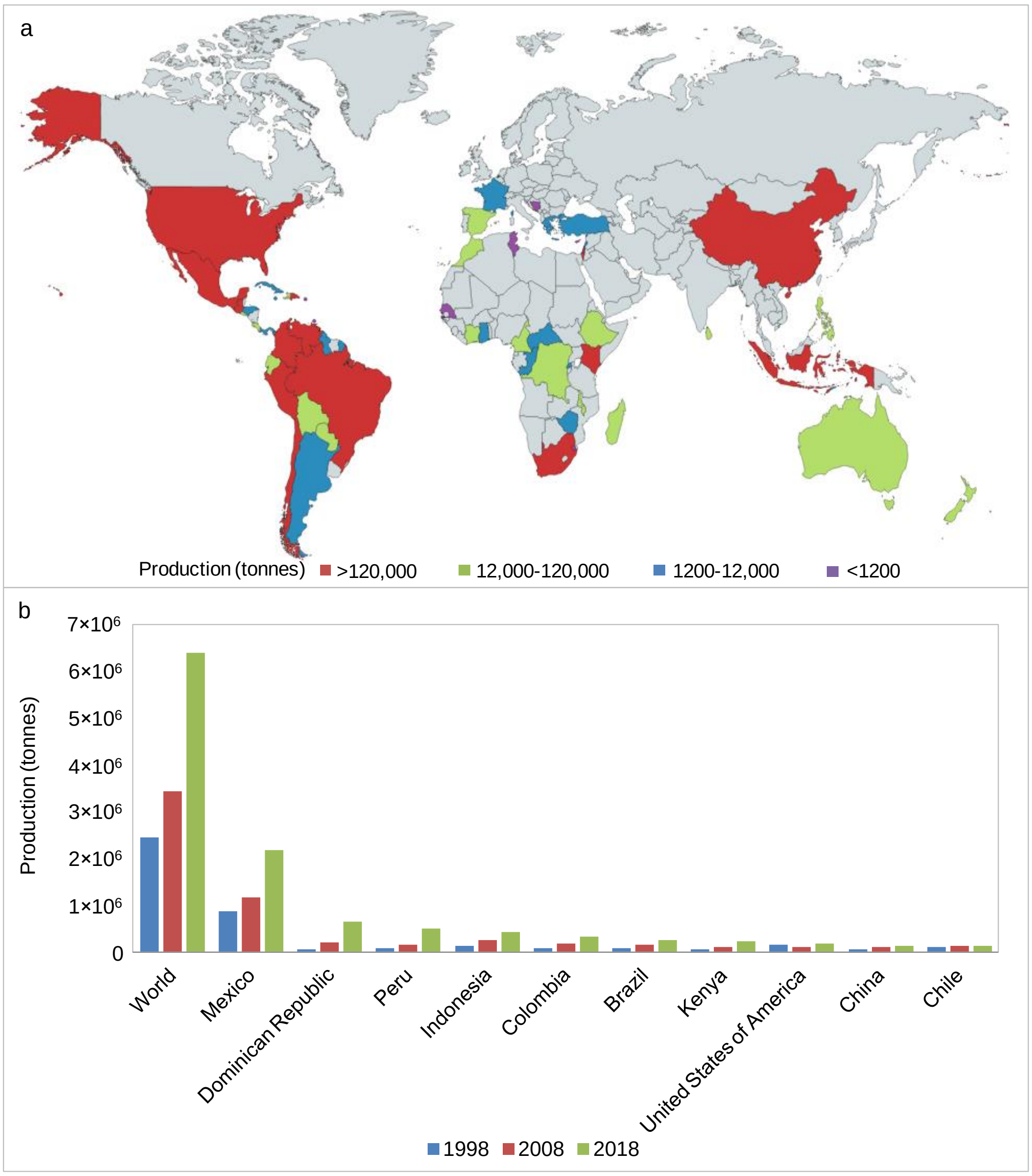

Figure 1. Production quantities of avocados by country in 2018 (created with mapchart.net) (**a**) and by the top 10 producers in 1998, 2008, and 2018 (**b**). Based on FAOSTAT data [6].

Avocado has a dark green, rough rind that covers a yellow-green pulp rich in oil [7]. Avocado has a unique texture, a smooth, buttery consistency, and an exquisite taste and aroma compared to most fruits, which present a typically sweet or acidic taste [8]. In addition to its pleasant organoleptic characteristics, avocado consumption has caught consumers' attention owing to its high nutritional value and reported health-benefits, the main driver for buying avocados [9]. An avocado fruit consists of the peel (7–15%), pulp (65–73%), and stone (including the seed) (14–24%) (Figure 2) [10–13]. The pulp of the avocado is consumed fresh or in the form of halves and frozen cubes. Other processed products are also obtained from avocado, such as guacamole, oil, jams, candy juice, ice cream, or as a sauce like dips, chutney, sandwich spreads, mayonnaise, etc. In addition, research has been done on the conservation of avocado fruit by dehydration, freezing, and canning [14,15].

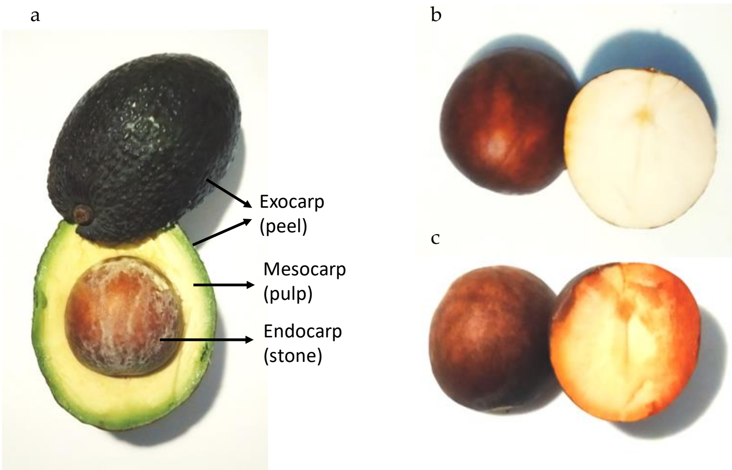

Figure 2. (**a**) Parts of the avocado fruit; stone split in half before (**b**) and after (**c**) partial oxidation, in the latter appearing the orange color.

The consumption and the industrialization of avocado gives as a result a huge amount of waste, not only the peel and stone but also the waste generated by the pruning practices and oil extraction. As Figure 1b highlights, avocado production has a tendency to grow and thus this waste is going to generate more environmental pressure. However, these biomasses could be converted into raw materials to obtain different types of co-products, but this implies several changes in the use of these resources, the design of efficient production systems, and integration to take full advantage of them. In particular, the integration of several valorization ways to produce a portfolio of products, such as energy, fuels, and/or bio-based products—in a single installation—is attractive; i.e., a biorefinery [16–18]. Therefore, this review firstly gives a snapshot of those residues generated by the avocado industry. Then, it presents updated information about the valorization ways reported to obtain marketable products from avocado waste in a single process or integrated processes within a biorefinery context. In the framework of a circular bioeconomy, it can be the basis for improving the regional economy, generating jobs in the localities where avocado is grown and processed and promoting economic growth by extending the value chain.

2. Avocado Processing and By-Products

Throughout the avocado value chain, from tree planting to industrialization, there are stages where different types of biomass are generated and they can be recycled as resources in a biorefinery. The activities prior to industrialization are planting, harvesting, selection, cooling, washing/brushing, packing, and temporary storage [1] (Figure 3). In the traditional plantation system, trees are planted with distances of 10 × 10 m between them, so that the tree grows up to 8 or 10 m high and the density is around 117 trees per hectare. In the orchards, the tree grows up to a maximum height of around 3 m to facilitate the practices of phytosanitary control, harvesting, foliar fertilization, and cutting. This enables plantation distances of 6 × 3 m or up to 3 × 3 m, increasing the density to 300 and up to 1000 trees per hectare [1,19]. Accordingly, maintenance pruning practices results in a big amount of biomass (branches and leaves) that must be removed from the fields to avoid propagation of plant diseases. One sustainable alternative is to use it for compost, although in most occasions these residues are burned.

In addition to the market of avocado fruit as a fresh food product, avocado is processed into several types of foods, as commented before, and the associated by-products are generated. Because the pulp is the only part of the fruit that is used as raw material, a significant amount of peel and stone are generated. The percentage of this waste depends on the cultivar of the fruit; for example, the proportion of avocado by-products (peel and stone) in the cultivar 'Fuerte' was higher than in 'Hass', i.e., 31% vs. 24%, respectively [13]. Even, some differences can be found in the same cultivar, e.g., 24% and 27% of avocado waste have been reported for the Hass cultivar [12,13]. If the processing of avocado is intended to recover oil from the pulp, a by-product rich in pulp is obtained, as commented on next.

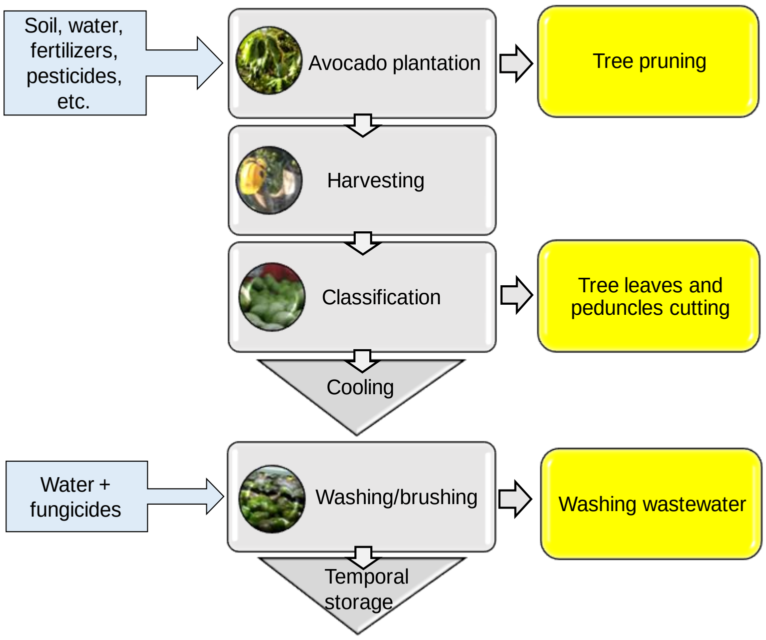

Figure 3. Activities prior to commercialization of avocado and by-products/waste generated in the field (yellow squares).

Avocado oil and guacamole are the most conventional processed products. In order to extract avocado pulp oil, several processes have been suggested, some industrially consolidated (Figure 4) and others only used on a laboratory scale: (i) chemical extraction by organic solvents, which is the most widespread, using mainly hexane; and (ii) physical methods like mechanical extraction (the traditional method) and centrifugation, also known as cold-pressing. Many other combination methods have been tested, including microwave + pressing, oven-drying + pressing, or solvent extraction, aided or not by enzymes, sonophysical processes, supercritical CO_2 extraction, etc. [11].

During chemical extraction (Figure 4a), the shell and bone are totally removed to obtain the pulp that is dried with hot air, and then the oil is extracted with an organic solvent, such as hexane; an up to 95% extracted oil content is obtained [20,21].

The mechanical extraction of avocado oil (Figure 4b) is obtained by peeling and destoning the fruit, crushing the pulp, and finally drying it. Then, the paste is heated with hot water with $CaCO_3/CaSO_4$ or NaCl, and rotated, pressed or skimmed (by natural decantation) to obtain the oil phase. In both methods the oil is refined for most applications [21]. Considering the oil content of avocado, the generated residual pulp fraction can be around 46% of the avocado weight.

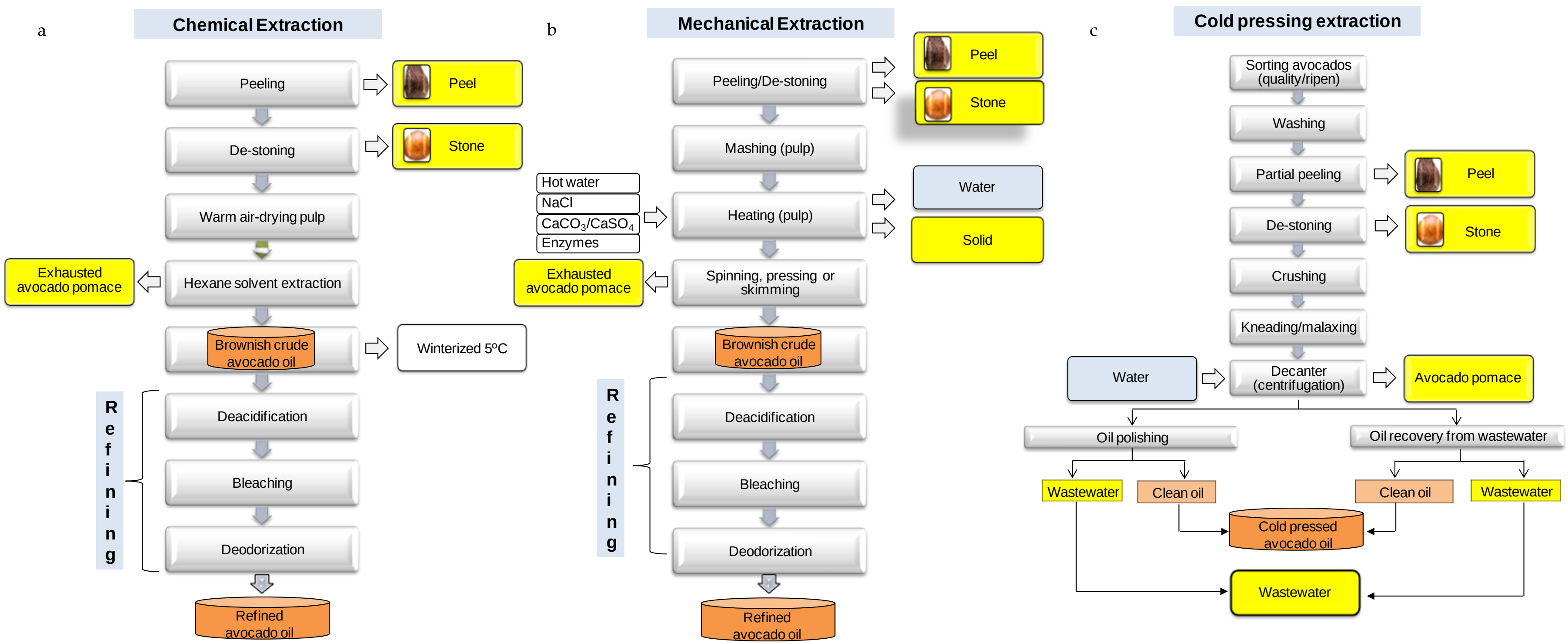

Figure 4. Chemical (**a**), mechanical (**b**), and cold-pressing extraction (**c**) of avocado oil and the by-products/waste obtained (yellow squares).

At the end of the last century, a New Zealand food producer, in collaboration with a market-leading food producer, began to extract avocado oil by cold pressing (CPAO), which does not require refining (Figure 4c). This has the advantage that oil maintains the organoleptic characteristics of the fruit pulp. For this process, the cultivar 'Hass' was chosen as the raw material, due to its characteristics; particularly, its thick skin, which protects the fruit during transport, and its superior oil yield (around 31%) with respect to the rest of the cultivars or varieties. "Hass" is also the main cultivar commercialized worldwide [22,23]. If this CPAO is extracted from high-quality fruits, the avocado oil is defined as extra virgin avocado oil [21]; this is similar to the nomenclature that the olive oil industry follows—according to its quality. Another similarity between CPAO and olive oil is that both oils are rich in the monounsaturated fatty acid oleic acid [20]. However, the yield is lower than using the aforementioned methods, up to 85% [20].

Currently, the use of this method has become more popular and it is also used in Chile, South Africa, Kenya, Israel, Samoa, and other countries [20,21]. In general, this process begins with washing, draining, and destoning of the avocado, where the stones and around 90% of skin are separated from the pulp. Skin separation can be calibrated according to the desired quality, since the proportion of skin into the processed mash may affect the pigment composition of the avocado oil. The flesh goes through a grinder where it is simultaneously sliced and crushed, i.e., broken down. Subsequently, the avocado paste is continuously stirred, and the oil separated by centrifugation using a horizontal three-phase decanter. It spins the malaxed paste, separating the pomace (exhausted pulp and residual skin; fibrous material), a liquid phase (wastewater), and the oil (CPAO). In some cases where a vertical two-phase decanter is used, the liquid phase can be further processed in a centrifuge to remove the remaining CPAO from the wastewater [21]. The estimated amounts of waste per avocado fruit processed can be around 15% pomace, 45% wastewater, 27% skin + stones, and 5% residual water, while the CPAO is around 8% (or 8.5 L), depending on the avocado type [20].

Another star product of the avocado is guacamole, whose production process (Figure 5) consists of the selection of ripe avocados, washing, and, as for the extraction of oil, removing the peel and stone to recover the pulp. Then, it is mixed with others elements (onion, tomato, and salt, basically) to finally obtain the guacamole, which is packaged [24].

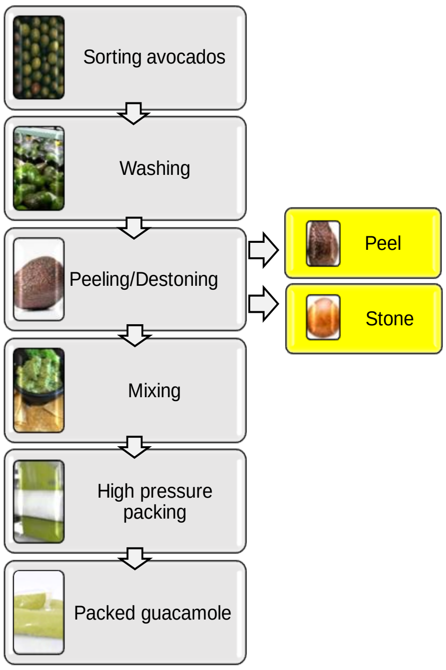

Figure 5. The guacamole process and by-products/waste generated (yellow squares).

Regardless of the type of production method, the stone, peel, and/or exhausted pulp are discarded as waste, which results in a large amount of solid residues that can represent 21–76% of the fruit weight, with some exceptions in some varieties [25,26], and also the wastewater. In the CPAO method, at most 10% of the skin can be included in the process [21], but the proportion of biomass material that is discarded remains very high, as commented on before. Therefore, the valorization of avocado waste deserves further attention on the basis of its chemical composition, including the major constituents and also the minor ones (but relevant).

3. Chemical Composition of Avocado Waste

The moisture content and the chemical characterization of the aforementioned by-products are shown in Table 1. All residues were characterized by high moisture; the stones presented the lowest value (up to 57%) and the wastewater the highest value (88%). This is one of the main limitations since dried samples are required for some technologies before processing. If it cannot be used as fresh biomass or there is a shortage in time to process, a drying step can transform this waste into storable commodities, but the energy cost will depend not only on the technology but also on the moisture content, as well as on the type of avocado by-product. Some authors have applied air-drying, convective drying, freeze-drying, and microwave drying before further application of the stone, peel, and avocado pomace [12,20,27,28], and freeze-drying and spray-drying for wastewater [20]. Alternatively, to be used as a biofuel for heating, Perea-Moreno et al. [29] recommends a cheap drying system that is used in other industries, such as making wood chips, in order to achieve around a 10% moisture content.

Table 1. Moisture (%, fresh weight) and chemical composition of some avocado residues (%, dry weight) [12,20,27,29–33].

By-Product	Moisture	Ash	Lipids	CP	Ext	Hem [3]	Cel/Glu [4]	Lignin
Exhausted pulp/pomace	81.4–82.8	4.5–7.0	9.3	14.7–12.8	18.2 [1]	8.5	29.8	26.9
Peel	70.9–75.3	1.0–8.7	6.3–10.4	6.0–9.3	43.7 [1]/20.5–34.4 [2]	11.5–25.3	12.1–27.6	4.4–35.3
Stone	35.2–57.0	0.9–2.9	2.3–6.0	3.7–5.3	21.0–35.9 [2]	3.0–47.9	6.5–40.9	1.8–15.8
Wastewater	88.3	17.9	53.8	10.3	ND	ND	ND	ND

CP, crude protein; Cel/Glu, cellulose/glucans; Ext, extractives; Hem, hemicellulose; ND, not determined; PC, phenolic content. [1] Ether extract. [2] Aqueous-ethanolic extractives, which refer to non-structural material determined using the standard method reported by the National Renewable Energy Laboratory (NREL). [3] As xylan, arabinan, galactan, and/or mannan. [4] In some studies, cellulose was determined on the basis of the glucose content as glucans, and so starch can contribute to this value. Other studies determined the available carbohydrate content (free sugars, dextrins, and starch), which was pomace (0.6%), peel (1.2%), stone (69.1%), and wastewater (0.9%).

In all cases, the higher components are the sugar fraction (glucans + hemicellulosic sugars), the extractives fraction (non-structural components), and lignin, but a high variability has been found in the literature [12,27,30–33] (Table 1). The variety/cultivar, ripeness, pedoclimatic conditions, and fertilizer used may affect the chemical composition of these residues, as well the methodology applied. Moreover, among the avocado waste, a large part of the carbohydrates from the stone are available (69%), making it an unconventional, yet viable starch source [20].

Moreover, the elemental analysis (%, dry weight) of some of these by-products is shown in Table 2. These values are similar to that of olive stones, an agro-industrial by-product used as a biofuel, but the carbon content is lower than vegetable coal. Both products were added in Table 2 for comparison and as references for Section 4.1.

Table 2. Elemental analysis of some avocado residues and other biomasses [12,29,34].

Element (%)	Avocado Peel	Avocado Stone	Olive Stone	Vegetal Coal
C	49.8	42.1–48.0	46.6	79.3
H	5.7	5.6–5.8	6.33	2.7
N	1.0	0.5–0.7	1.81	0.7
O	42.2	43.0–50.8	45.20	17.0
S	ND	ND–0.1	0.11	0.3

ND, not detected.

4. Valorization Technologies of Avocado-Derived Biomass through Obtaining Bioenergy and Biofuels

In the orchards, after the avocado harvest, the trees are pruned, and it is necessary to correctly manage this waste. The biomass volume is very large and so the removal of all this material represents a lot of work and a high cost. One sustainable alternative is to use it for compost, although in most occasions these residues are burned. In the processing to obtain avocado oil, depleted pulp, peels, and stones are produced; the guacamole industry also generates peels and stones, and in all phases, a part of the fruit is discarded because it suffers some damage. These residues can be used as raw material in a biorefinery, taking advantage of their heat capacity and chemical composition, integrating the production of two or more bioproducts, which can be used in different industries, such as the energy, food, cosmetic, and pharmaceutical sectors.

In general, the conversion of biomass into biofuel is accomplished by means of mechanical transformations, chemical transesterification, thermochemical transformations, and biological transformations (fermentation, anaerobic digestion, etc.). In general, for energy purposes, the initial humidity of the biomass must be considered, as commented on before. In this sense, in the energy production process from the dry biomass, the methods of direct combustion, pyrolysis, gasification, and transesterification to biodiesel can be used. Alternatively, when the generation of energy is from wet biomass, hydrothermal treatments, enzymatic hydrolysis, fermentation to bioethanol/biohydrogen/biobutanol, and anaerobic digestion can be used [35]. In this section, the potential that avocado biomass has to obtain bioenergy and biofuels is highlighted, giving an overview of the available processes, including those mentioned here (Figure 6). These technologies applied to avocado waste make it an alternative energy source to fossil fuels; also, greenhouse gas emissions can be reduced while, compared to other renewable resources, they do not compete with food production.

4.1. Bioenergy

Considering the increasing energy needs, the imminent depletion of fossil resources and the consequent global warming, alternative energy sources have been sought. Because biomass is the only renewable source of carbon, bioenergy would reduce environmental pollution, meet climate targets, and replace fossil energy; it is the best alternative with the potential to reduce greenhouse gas emissions. It has been the fourth largest energy source in the world after coal, oil, and natural gas, accounting for 9.5% of the world primary energy supply and 69.5% of the world renewable energy supply in 2016 [36].

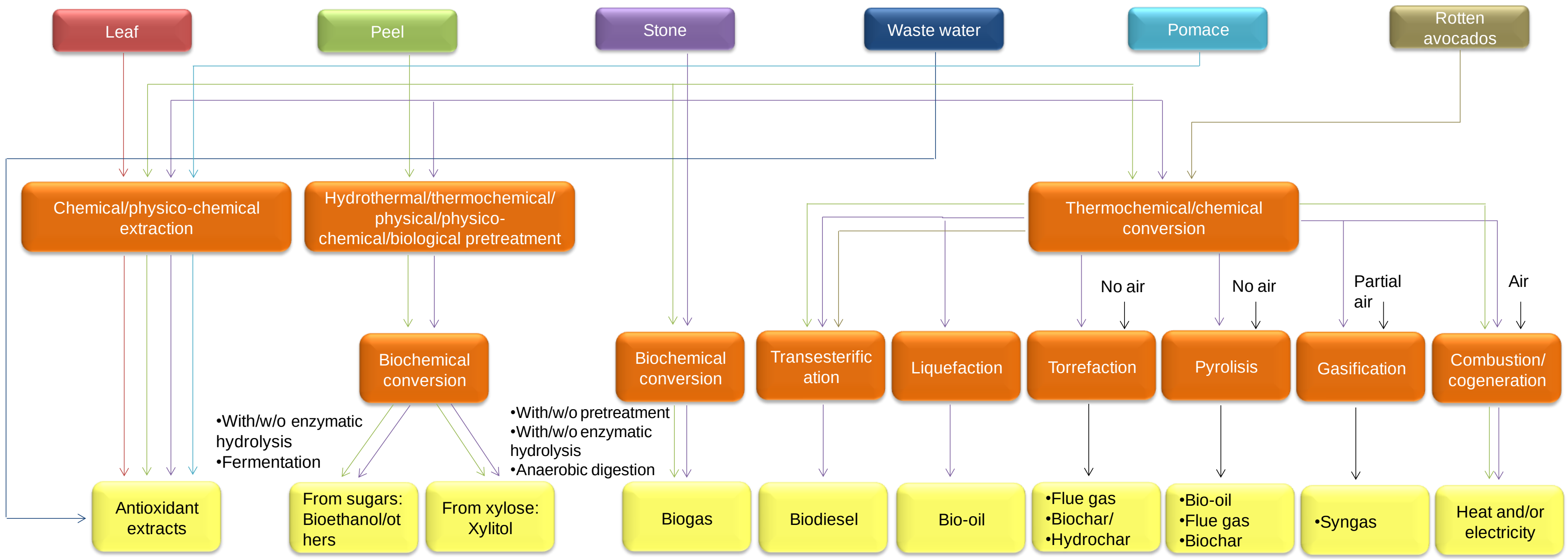

Figure 6. Overview of the valorization ways applied to the avocado-based waste/by-products.

Bioenergy refers to the use of biological products (or biomass) used specifically for purposes such as the generation of electricity and heat and the conversion of biomass into secondary products, such as biofuels for use in the transport sector. Concerning agri-food residues, there is much work to do. However, research is ongoing to incorporate this biomass into sustainable processes to produce solid, liquid, and/or gas fuels. To determine which type of transformation process is the most suitable for each type of biomass, it must be previously characterized by determining the humidity, size, and shape of the particles, as well as the chemical composition (carbohydrates, lignin, ash, etc.) and calorific value [37]. This can help to exclude agri-food residues with a low energy potential [38,39]. Several studies have been performed to characterize the residual biomass of avocado and whether there are chemical compounds with industrial value and/or the ability to generate biofuels (Tables 1 and 2). From these studies, it can be concluded that the avocado peel and stone are in the range of desired values for ultimate analysis, but the nitrogen content in the peel is slightly high. García and coworkers recommend nitrogen values up to 0.5%, since it can lead to NOx in combustion gases [40].

Concerning calorimetry studies, Table 3 shows the high heating value (HHV) and low heating value (LHV) of some avocado biomasses, along with the volatile matter (VM) and fixed carbon (FC). One of the main drawbacks of avocado-derived biomass is the humidity (Table 1), as commented on before. Despite the percentage of humidity, the avocado stone has advantages in energy terms (a high calorific value, HHV, up to 19.1 MJ/kg) (Table 3) compared to other common biomass sources for combustion in small boilers; e.g., its low sulfur content (0.010–0.032%) minimizes the generation of SO_x (acid rain compound), and in addition the amount of chlorine (0.024 and 0.025%) is less than in other biomasses, which helps prevent corrosion in the boilers. Another parameter determined was an LHV of 17.9 MJ/kg [29]. Therefore, as a fuel for domestic or industrial heating, these authors recommend drying and grinding before burning. Concerning other avocado biomasses, the HHV is closer to that of an avocado stone. The VM is in the range volatile matter of 65% to 85%, as recommended for general biomass, and this parameter and the FC values are similar to those of olive stones, a reference biomass.

Alternatively, the ash content in these avocado resources is higher than in other biomasses, such as olive stone and almond shell. This implies that more frequent boiler maintenance tasks are required [29]. After combustion, even the ash can be subjected to further valorization following the example of other biomasses [41].

Table 3. Energetic characteristics of some avocado residues and other biomasses [29,34].

By-Product	Volatile Matter (%)	Fixed Carbon (%)	HHV (MJ/kg)	LHV (MJ/kg)
Avocado branches	ND	ND	16.4	ND
Avocado leaves	70.0	22.7	18.0	ND
Avocado peel	82.0	14.9	18.7	ND
Avocado stone	72.0	26.0	15.2–19.2	17.9
Olive stone	78.3	20.4	17.9–20.5	19.2
Vegetal coal	26.0	68.1	29.7	ND

ND, not determined; HHV, high heating value; LHV, low heating value.

Domínguez and coworkers also agree that avocado stones can be a viable energy resource due to its high content of polysaccharides, high calorific value, and a relatively low amount of ash [42]. By mechanical densification technology, these authors compacted avocado stones (milled and dried) to produce pellets at 919 bar and 80 °C with a residence time of 3 min. It increased their density to 1378 kg/m^3, but with lower mechanical resistance, which can be increased using pinewood [42]. Moreover, co-firing of avocado stones (oven-dried at 110 °C) with coal is also another solution, with the advantages of using the existing infrastructure for coal combustion to reduce the economic costs and lowering the net CO_2 and SO_x emissions. Nonetheless, the heating value is lower than using coal alone and a higher reactivity could lead to fuel segregation, resulting in burn-out at lower temperatures, loss of steam generation efficiency, and fouling [43]. To overcome this disadvantage or the moisture problem, some researchers have applied other thermochemical and biochemical methods to improve the conversion of biomass into biofuels, as shown in the next sections. Moreover, Dávila and coworkers provided a theoretical biorefinery scheme in which the residual lignin fraction from the valorization of avocado peel and stone could be applied to obtain steam and electricity via cogeneration [31].

4.2. Biogas through Biochemical Conversion

As commented on before, there are biofuels in the three states of matter: in the solid state are wood and chips, coal, pellets, and biochar; in liquid form, bioethanol, butanol, biodiesel, etc.; and in the gaseous state, biogas and synthesis gases [44]. In particular, biogas is a mixture of 55–70% (*v*/*v*) methane (17–25 MJ/m^3), 30–45% (*v*/*v*) carbon dioxide, and some other gases in traces. It is produced by anaerobic fermentation of the organic matter and thus in an oxygen-free environment [45,46]. In addition to being a renewable energy source, biogas does not have any geographical limitations nor does it require advanced technology for producing energy [47]. Overall, the share of biogas supply in the bioenergy sector accounts for only about 2%, but it has the potential to contribute much more since it can be supplied to a variety of markets, including electricity, heat, and transportation [48]. Biogas production can therefore provide a sustainable alternative fuel via utilization of agricultural organic wastes with a high percentage of humidity content [49], which is the case of avocado by-products.

Biogas production depends on factors such as the nature of the substrate, temperature, pH, loading rate, C:N ratio, retention time, and alkalinity. Besides that, the organic material added as inoculums into the organic substrate and the size of the inoculums affected the rate of gas generation [50]. Research was conducted on the production of biomethane from organic waste based on its sugar, starch, lipid, protein, and fiber content. According to their composition, avocado residues were chosen for its high lipid content. The results indicated that the biomass with a high lipid content decreases the methane content, probably owing to low C/N ratio below 20:1. Moreover, the accumulation of lipids could inhibit the production of methane thanks to the formation of long-chain fatty acids [51]. Considering this result, it would not be advisable to use residual avocados (overripe and rotten avocados that are generally discarded) as raw material in biogas production. Alternatively, Vintila and coworkers [52] evaluated the potential of avocado stones (10% dry matter) after milling (micronized) and steam-alkaline pretreatment (with or without the addition of cellulolytic enzymes) at the laboratory scale. The best results were achieved using the latter conditions: from 105.7 NmL/g (vs. 87.7 NmL/g biomass d.m.) (micronized biomass) to 214.2 NmL/g (vs. 177.8 NmL/g biomass d.m.). These values are in the range of other agro-industrial by-products, which varied from 78 (cottonseed cake) to 421 mL/g (soybean oil cake) [45].

Other studies investigated the production of biogas from mixtures of organic matter of animal and vegetable origin, incorporating avocado residues. For example, Deressa and colleagues studied the efficiency in the production of biogas from a mixture of vegetable waste, including avocado residual peels, which were mixed with cow manure; this resulted in 37 mL/g, without the need of nutrients or chemical addition to the system [53]. In a similar study, Kenasa and coworkers investigated the ideal conditions for the generation of biogas from the avocado peel. These authors reported that the maximum production occurred at 25 °C, neutral pH, and 0.5% salt, and that it can be optimized by the co-digestion of the avocado waste with ruminal fluid and animal manure (up to a cumulative production of 453 mL within four days of incubation for 75% avocado peel + 25% poultry manure) [47].

In addition to these laboratory studies, an avocado oil production plant for export is located in Kenya that uses scraps from the process as raw material in two digesters, where up to 5000 m^3 of biogas (66% methane) is generated per day. Purified biogas (94% methane) is achieved with a potential around 300 KW, which is enough to power the factory, and the excess energy is used to power the tractors of the local farmers [54].

4.3. Biofuels through Thermochemical Methods: Gasification, Pyrolysis, Torrefaction, and Liquefaction

In addition to the latter transformation ways, the conversion of biomass into biofuels is also accomplished by means of thermochemical transformations, such as gasification, pyrolysis, torrefaction, and liquefaction. Gasification implies a partial combustion of the biomass to produce bio-char and gas while pyrolysis is a thermal degradation (400–800 °C) of the biomass in the absence of oxygen to generate bio-char, condensed liquids (bio-oil), and flue gas. Torrefaction is like a pyrolysis but using lower temperatures (200–300 °C) [42,55].

For the valorization of avocado stones, Domínguez et al. [42] applied combustion/gasification in a porous media reactor, while for torrefaction and pyrolysis a rotary furnace was applied at temperatures between 150 °C and 900 °C. The former was used to improve the concentration of synthesis gases (H_2, CO) and CO_2 by incorporating avocado seeds in the reactor that works with methane/air when operating at high gas fuel equivalence ratios. Applying the second strategy, their findings indicated that the large-scale production of biochar, liquid fuel, and gas from avocado stone, which were pre-dried at 40 °C and milled, is possible. The partial drying and dehydration of the biomass was executed between 150 °C and 250 °C. The thermal degradation of the sugar polymers and lignin occurred between 250 °C and 500 °C, forming a gaseous and condensable fraction and the solid fraction was reduced from 90% to 25% by weight. Using also torrefaction at 300 °C on avocado stone (pre-dried at 110 °C and milled), a bio-char (fuel ratio, 0.66 fixed carbon/volatile matter, HHV, 23.3 MJ/kg; BET surface area, 2.263 m^2/g char) with similar characteristics to the coal was produced, eliminating fuel segregation and the energy input required to carbonize the biomass [43]. This value is higher than those reported in Table 3. Similarly, in a rotary reactor, Sanchez et al. [56] found the optimum torrefaction conditions for avocado stone (pre-dried at 40 °C) at 304 °C, which yielded a biochar product (50%) with 36.7% FC, HHV of 24.3 MJ/kg, and LHV of 23.2 MJ/kg for an energy yield of 76.7%. Alternatively, the bio-oil produced had a low carbon content (11.0%) and low HHV (2.5 MJ/kg) due to the high water content of the samples.

New trends include the use of microwave heating instead of conventional heating. Hot spots, which form under microwave irradiation, affect the yield and the characteristics of the pyrolysis products. For example, solids can reach high heating values and specific surface areas with higher gas and solid yields than conventional pyrolysis, but a lower liquid yield is obtained. Furthermore, almost half of the biomass can be converted into a higher energy gas product, due to the high H_2 yields [57]. Another greener possibility is to use solar pyrolysis by using concentrated solar energy as the heating source. However, none of them have been explored using avocado waste and some challenges have to be overcome, such as those about the design and scaling-up [58].

Another option is liquefaction. In this technology, temperatures between 250 °C and 500 °C at high pressure (5–40 MPa) are applied to obtain the bio-oils. In comparison to some of the aforementioned methods, relatively lower temperatures are required but solvents are used. Ayu and Durak [55] investigated the effects of the solvent type, temperature, and catalyst type during liquefaction of avocado stone (pre-dried and milled <0.425 mm) for bio-oil production. They reported that acetone as a solvent and zinc chloride (10%) as a catalyst at 290 °C offer the optimal conditions for liquefaction, achieving a 76.9% conversion (52.4% liquid + 24.5% gaseous products) [55].

4.4. Biodiesel

Biodiesel is primarily produced from oilseeds, which are limited and relatively expensive. It also competes with food for human consumption. As a consequence, it is necessary to investigate inedible options for the production of second-generation biofuels, so as not to compete with food uses [59]. In this context, several documents highlight the potential of different type of avocado oils for biodiesel production through, mainly, catalyst-assisted alcoholysis of its oil fraction [60–64]. It is also known as the transesterification reaction of triglycerides and the esterification of free fatty acid [65].

Table 4 shows methods applied to produce biodiesel and the characteristics of the biodiesel produced using oils from avocado waste. Rachimoellah et al. [60] reported that avocado seed contains triglycerides and it has a low content of free fatty acids (around 0.37%); hence, this oil can be processed to obtain biodiesel through transesterification. They found that the highest content of methyl ester for biodiesel from avocado seed oil is obtained at 60 °C, with a 1:6 molar ratios of oil to methanol, and that the best washing method is dry washing [60]. Other studies have applied catalyzed methanolysis and ethanolysis to produce biodiesel from avocado oils at temperatures of 65–75 °C, in a time of 1–2 h, and with an alcohol-to-oil ratio of 6:1 or 9:1, and 1–7% catalysts [62,63]. Their results show the technical viability (Table 4) and environmental friendliness potential of avocado oil for diesel engines, and thus underused avocados can be collected for this use. In this way, using rotten avocados, Jung et al. [66] applied catalyzed (with KOH) and non-catalyzed (with silica) methanolysis and dichloromethane for transesterification to obtain biodiesel. The latter experiment with dichloromethane provided a yield of 93%, avoiding the use methanol as an acyl acceptor, but it requires the use of high temperatures (up to 380 °C). Furthermore, the peel also contains lipids (up to 10.4%, Table 1) and thus it could be a potential source of biodiesel. Even the wastewater from the CPAO process has around 54% of lipids, but a feasible recovery is firstly required.

4.5. Fermentable Sugars and Bioethanol

For obtaining fermentable sugars, a pretreatment is necessary to break down the lignocellulosic matrix and to facilitate the access to the hydrolyzing enzymes. Several strategies have been developed to fractionate agri-food biomasses, which can be classified according to the function of the main driver forces: chemical treatment with diluted acids, alkalis, metal salt solutions, and organosolv treatments with organic solvents; physical/physico-chemical treatments, such as liquid hot water, steam-explosion, and microwave; and biological treatments and combined treatments [41,67].

Thanks to the high content of hydrolysable sugars of the avocado biomasses, in particular, the peels, stones, and pomace (Table 1), they are a valuable and a profitable alternative for the production of sugars. Our previous work has shown that the peel contain mainly glucose and xylose, while the stone is highly rich in glucose (93.2% of the polymeric sugar fraction) [12].

In this line, to promote the enzymatic hydrolysis of the polymeric sugars, an appropriate combination of different enzyme activities is required to complete the hydrolysis [67]. Once these sugars are released, they can serve to obtain biofuels like bioethanol and other valuable commodity chemicals, such as xylitol and furfural (from xylose), hydroxymethylfurfural (from glucose), organic acids, etc. [41,68]. For example, Dávila et al. (2017) proposed the use of dilute acid hydrolysis, using sulfuric acid (2% *v*/*v*) at 121 °C for 90 min, to recover a liquid fraction rich in xylose from avocado waste and then to produce xylitol using *Candida guilliermondii* at 30 °C. Alternatively, the residual solid fraction, rich in cellulose and lignin, could be enzymatically hydrolyzed to recover glucose [31].

New trends include the use of microwaves as the heating source, as commented on before, and hydrothermal treatments to avoid the use of chemicals [69,70]. An example of the application of microwaves to avocado waste is the study by Vintila et al. [52]. Alternatively, in another study, microwave heating was applied to dry avocado seed (without the outer layers) and then an hydrothermal treatment was performed at 60 °C for 60 min to recover the starch sugars (14.9%), as a first step to produce bioethanol [28].

Table 4. Methods applied to obtain biodiesel from avocado stone and peel oils and avocado oil, as well as the characteristics of the biodiesel.

Sample Type	Conditioning	Oil Extraction	Procedure [a]	Heating Value (MJ/kg)	Density at 15 °C (kg/m^3)	Viscosity at 40 °C) (mm^2/s)	Flash Point (°C)	Ester Content (%)	Ref.
Biodiesel (stone oil)	Size reduction (120 mesh) and drying (110 °C)	Hexane	Methanolysis with NaOH (60 °C; 60 min; r, 6:1 1% catalyst)	41.3	877.7	5.0	184.0	84.6	[60]
Biodiesel (peel oil)	Size reduction (2.6 mm) and air drying	Hexane (Soxhlet)	Methanolysis with NaOH (60 °C; 67.5 min; r: 6:1; 1.21% catalyst)	40.0	910.0	4.2	161.0	95.2	[61]
Biodiesel (avocado oil)	-	-	Ethanolysis glycerol-enriched CaO (75 °C; 1 h; r: 9:1; 7% catalyst)	ND	ND	4.9	ND	91.2	[62]
Biodiesel (avocado oil)	-	-	Methanolysis with NaOH (65 °C; 2 h; r: 6:1; 1% catalyst)	40.1	ND	3.8	148.0	ND	[63,64]
Biodiesel (avocado oil)	Size reduction and drying (85 °C)	Hexane (Soxhlet)	Methanolysis with KOH (60 °C; 2 h; r: 6:1; 5% catalyst)	ND	ND	ND	ND	61.2	[66]
Biodiesel (avocado oil)	Size reduction and drying (85 °C)	Hexane (Soxhlet)	Dimethyl carbonate with KOH (85 °C; 2 h; r: 9:1; 8.5% catalyst)	ND	ND	ND	ND	7.3	[66]
Biodiesel (avocado oil)	Size reduction and drying (85 °C)	Hexane (Soxhlet)	Methanolysis non-catalyzed (380 °C) with silica					90.1	[66]
Biodiesel (avocado oil)	Size reduction and drying (85 °C)	Hexane (Soxhlet)	Dimethyl carbonate non-catalyzed with silica (380 °C) with silica (r, 8:1)					93.0	[66]
Avocado oil				39.5		34.0	186.0		[63]
Diesel				45.3		3.0	58.0		[63]

[a] r, the solvent:oil ratio.

In this regard, to obtain bioethanol, different process configurations, including the aforementioned pretreatments, enzymatic hydrolysis, and fermentation conditions, are applied (Figure 7). Concerning fermentation, *Saccharomyces cerevisiae* is mainly utilized to convert glucose into ethanol, while microorganism such as *Pachysolen tannophilus* can ferment pentoses to ethanol and xylitol [71]. In co-fermentation approaches, some ethanologenic *Escherichia coli* strains and *Pichia stipitis* can ferment xylose and glucose to ethanol, while the combination of microorganisms is also plausible [41,67,70].

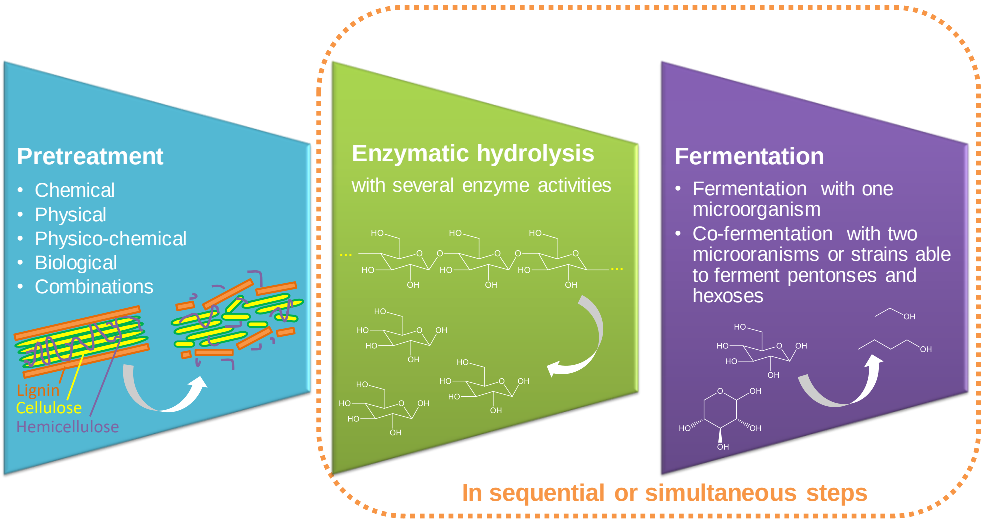

Figure 7. Summary of the steps followed to produce liquid biofuels.

However, the production of sugars and bioethanol (butanol, etc.) from avocado waste is still in its initial stage and few examples have been found in the reviewed literature. Milling, milling + steam-NaOH (1%) at 140 °C for 10 min, and milling + microwave-assisted fractionation (1% NaOH; 300 W for 25 min) of avocado stones (pre-dried at 105 °C) were recently compared by Vintila et al. [52]. Using sequential hydrolysis and fermentation, the yield of sugars was high using the second pretreatment with a hydrolysis rate of 75% using the enzymatic cocktail Cellic CTec2. However, the yield of bioethanol was the lowest (102 mL/kg or around 8%). This was explained by the presence of a higher level of inhibitors.

5. Other Valorization Ways through Obtaining Starch and Protein

In addition to the aforementioned applications, avocado by-products contain other macrocomponents that can be used in the food sector or for bioenergy purposes. In this sense, the avocado stone presents starch, as commented on before. Although some authors reported values up to 30% [10], specific enzymatic methods should be applied to determine its content in future studies (e.g., https://permanent.fdlp.gov/LPS94088/42624.pdf).

In a recent work, starch was isolated from the avocado stone by sodium tripolyphosphate (STPP) at different concentrations, with the best results obtained after 1 h of reaction and at a concentration of 6% STPP. This led to a modified starch that improves the stability of the stickiness in the cream soup and prevents viscosity breakdown [72]. Microwaves were also applied to assist the extraction of starch at 161.1 °C for 56.2 min, with an extraction yield of 49.5%. The yield using this technology was higher than using conventional methods and the properties of the starch were adequate. Some differences were found since the former starch showed high solubility, a low water absorption capacity, and a non-granular structure with small particle size (lower than 2 μm), with potential to be applied in biotechnological and food applications [73]. Alternatively, other authors have applied a wet extraction method to obtain starch with a yield of 64% [74].

Moreover, the application of avocado stone starch for second generation bioethanol is interesting after its conversion into free glucose [26], but limited works are available, as commented on before.

Our preliminary results show that avocado stone (dried and milled), can release glucose in relatively high amounts (>40% of the initial glucose in the raw biomass) by enzymatic hydrolysis with Cellic® CTec2 and β-glucosidase for 72 h (Figure 8; see also Supplementary Files). This value is higher than that for the peel and other agri-food residues [75,76], probably due to its starchy or highly available characteristics.

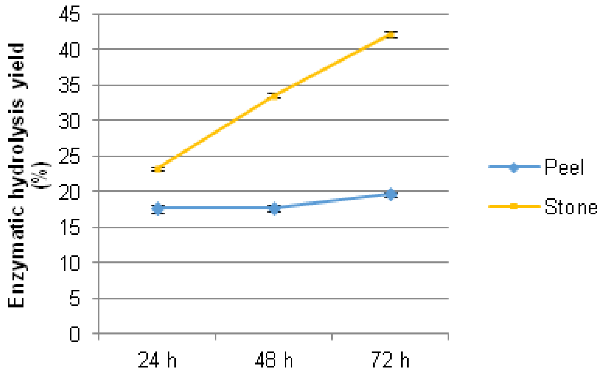

Figure 8. Enzymatic hydrolysis yield in terms of the glucose of the avocado waste.

Avocado waste also contains protein, whose content depends on the type of biomass. The highest values are found in defatted avocado waste (up to 15%) (Table 1). Therefore, in a recent work, this residue was chosen to obtain protein, which was separated by water adjusted to a pH of 8.5 with 1.0 M NaOH and acid-precipitated to an isoelectric point of 4.5 with 1.0 M HCl. This was a high-quality protein since it contained all the essential amino acids and provided higher water and oil absorption capacities as well as a higher radical scavenging capacity than soy protein, the latter used as the reference. Nonetheless, avocado protein showed a lower in vitro digestibility. Moreover, as an emulsifier, it enhanced the stability of the oil-in-water emulsion system and it also showed a greater emulsifying stability than soy protein, even with a lower interfacial tension and emulsifying activity [77]. Due to these promising results, future studies could be addressed to recover edible protein from avocado pomace for human nutrition or as a feed and new technology can be applied for this purpose. In this regard, besides alkaline extraction, a plethora of possibilities have been applied to recover protein from agri-food by-products, including novel trends like electro-based techniques and those using ultrasounds, microwaves, and subcritical water conditions [16]. As far as we know, none of them has been applied to avocado waste or used in an avocado-based biorefinery.

6. Valorization Technologies for Avocado-Derived Biomass through Obtaining Bioactive Compounds

6.1. Phenolic Compounds

Besides the latter applications based on the use of the major chemical components, this tropical fruit can be better exploited if the residual parts are also used as alternative sources of bioactive substances with different industrial purposes. In particular, research on sources of natural antioxidants, such as phenolic compounds, for the food industry has increased because consumers prefer products that contain few or no synthetic compounds. So, the avocado by-products could be used to obtain extracts with high antioxidant power to replace synthetic antioxidants [78–80].

As a preliminary study, we showed that the peel is richer in phenolic compounds than the stone using Soxhlet extraction, with the water and the peel extract also showing a higher purity. Water can be used for extraction as a green solvent since the major part of the total phenolic content (TPC) (87%) and antioxidant activity (>90%) remained in the water extract [12] (Table 5). In another work, Tremocoldi et al. [81] extracted the bioactive compounds from the peel and stone with the ultrasound technique and the solution consisted of ethanol/water (80/20, *v*/*v*). It enabled the authors to reduce the processing time, cost, and thermal damage and to improve the total bioactive compounds recovered. Their results also indicated that the peel extracts have a higher phenolic content than those from the stone. Nonetheless, other studies have obtained extracts from avocado stone with high antioxidant capacity. For comparison, Table 5 shows some examples of the technologies applied to assist the extraction process or to recover phenolic compounds; it also depicts the TPC and the antioxidant activity determined by two common in vitro assays. In general, there is a high variation between the results in terms of the solubility (avocado waste weight) and purity of the extracts (extract weight), even when in most studies the cultivar 'Hass' was used. The different biomass types, preconditioning and extraction methods, and solvents used, in addition to the place of origin, among others, can explain these differences.

Concerning the technology, some authors have investigated the feasibility of microwave-assisted extraction [82,83] and accelerated solvent extraction [84] as thermal-type extractions, and ultra-sound assisted extraction [79,83] and supercritical CO_2 extraction (with ethanol as co-solvent) [85] as non-thermal procedures (Table 5). These techniques require shorter processing times, less energy, and considerably lower amounts of chemicals or solvents. They also tend to generally provide higher extraction efficiencies. Among them, supercritical CO_2 extraction and microwave-assisted extraction seem to have a higher efficiency to solubilize the phenolic compounds from the peel and stone, while the highest purity of the extracts were reached using Soxhlet extraction with water for the peel and microwave-assisted extraction with 70% acetone for the stone. The latter is characterized to be a fast and efficient extraction method due to the rapid heat generation by the microwaves energy, which causes destruction of the cellular matrix to release phenolic compounds, with extraction times lower than 20 min [82,83]. Furthermore, in a recent work, another strategy was followed to recover phenolic compounds from the pomace part, i.e., using aqueous two-phase systems, based on two immiscible liquid phases. It can avoid thermal treatments and has a high potential to be scaled-up due to its simplicity [86]. These authors used polyethylene glycol and magnesium sulfate or sodium citrate as the polymeric material and salt, respectively, for extraction that is based on a salting-out phenomenon.

Having the biorefinery concept on one's mind, greener extraction trends should be considered for further deployment. Although the integration of these technologies in a biorefinery could address more sustainable processes, food and pharma grade solvents should replace highly toxic ones, such as methanol. Thus, water, aqueous-ethanolic solutions, and CO_2 as solvents could be some options. For example, Weremfo et al. [83] have shown that microwave-assisted extraction (400 W) with 58% ethanol can be applied to obtain phenolic compounds from avocado stone in a short time (4.8 min). This enables the recovery of an even higher TPC than using ultrasound-assisted extraction.

Alternatively, Permal et al. [20] opted for the use of direct drying methods when wastewater was studied as a source of antioxidants. The best option was spray-drying at 160 °C when compared with lower temperatures and lyophilization (Table 5).

Among the phenolic compounds identified in avocado waste, Tremocoldi et al. [81] found procyanidin B2 and epicatechin in the peel and trans-5-*O*-caffeoyl-D-quinic acid, procyanidin B1, catechin, and epicatechin in the stone. Melgar and coworkers [80] characterized 29 phenolic compounds, fourteen flavan-3-ols ((epi)catechin derivatives), nine flavonols (quercetin, kaempferol and isorhamnetin glycoside derivatives), and six phenolic acids (chlorogenic and coumaric acid derivatives). Peel and stone presented very different phenolic profiles, with only two common compounds.

Table 5. Extraction methods applied to recover the phenolic compounds from avocado waste, total phenolic content (TPC) (g gallic acid equivalents/100 g), and antioxidant activity, determined by the trolox equivalent antioxidant capacity (TEAC) and ferric reducing antioxidant power (FRAP) (mmol TE/100 g).

Biomass	Cultivar	Conditioning	Extraction Method	Solvent	TPC	TEAC	FRAP	Reference
In terms of biomass weight								
Peel	Hass	Air-drying and milling	Soxhlet extraction	Water	4.13 [1]	17.5 [1]	15.2 [1]	[12]
Stone	Hass	Air-drying and milling	Soxhlet extraction	Water	0.31 [1]	1.7 [1]	1.3 [1]	[12]
Stone	Hass	Cutting, sun-dried and milling	Microwave-assisted extraction	58.3% Ethanol	8.4 [1]	ND	ND	[83]
Stone	Hass A	Drying, grinding and sieving	Soxhlet extraction	Ethanol	2.0 [1]	ND	ND	[85]
Stone	Hass B	Drying, grinding and sieving	Soxhlet extraction	Ethanol	3.0 [1]	46.3 [1]	ND	[85]
Peel	Hass B	Drying, grinding and sieving	Soxhlet extraction	Ethanol	10.7 [1]	111.2 [1]	ND	[85]
Stone	Hass B	Drying, grinding and sieving	Supercritical fluid extraction	CO_2 with ethanol	5.1 [1]	ND	ND	[85]
Peel	Hass B	Drying, grinding and sieving	Supercritical fluid extraction	CO_2 with ethanol	4.7 [1]	ND	ND	[85]
In terms of extract weight								
Peel	Hass	Air-drying and milling	Soxhlet extraction	Water	26.6 [2]	112.2 [2]	97.8 [2]	[12]
Stone	Hass	Air-drying and milling	Soxhlet extraction	Water	1.8 [2]	9.9 [2]	7.7 [2]	[12]
Stone	-	-	Homogenization	70% Acetone	6.1 [2]	ND	ND	[13]
Peel	-	-	Homogenization	70% Acetone	9.0 [2]	ND	ND	[13]
Stone	Hass	Freeze-drying	Homogenization	50% Methanol → 70% acetone	8.1 [2]	ND	30.8 [2]	[20]
Peel	Hass	Freeze-drying	Homogenization	50% Methanol → 70% acetone	13.7 [2]	ND	54.7 [2]	[20]
Pomace	Hass	Freeze-drying	Homogenization	50% Methanol → 70% acetone	3.6 [2]	ND	16.0 [2]	[20]
Wastewater	Hass	Freeze-drying/spray-drying			1.6–5.1 [2,3]	ND	8.0–21.6 [2,3]	[20]
Stone	Hass	Chopping and drying	Homogenization	70% Acetone	4.1 [2]	ND	ND	[27]
Peel	Hass	Cutting and drying	Homogenization	70% Acetone	5.1 [2]	ND	ND	[27]
Stone	Hass	Milling, lyophilization	Stirring in bath	Methanol	2.5 [2]	12.4 [2]	31.7 [2]	[78]
Stone	Hass	Milling, lyophilization	Stirring in bath	50% Ethanol	3.1 [2]	26.4 [2]	43.9 [2]	[78]
Stone	Hass	Lyophilization, milling	Ultrasound-assisted extraction	80% Ethanol	5.7 [2]	64.6 [2]	ND	[79]
Peel	Hass	Lyophilization, milling	Ultrasound-assisted extraction	80% Ethanol	6.4 [2]	79.2 [2]	ND	[79]
Stone	Hass	Cutting and freeze-drying	Microwave-assisted extraction	70% Acetone	30.7 [2]	242.5 [2]	ND	[82]
Stone	Hass	Cutting and freeze-drying	Microwave-assisted extraction	58.5% Ethanol	25.4 [2]	206.2 [2]	ND	[82]
Stone	Hass	Oven-drying and milling	Accelerated solvent extraction	50% Ethanol	ND	30.0 [2]	ND	[84]
Pomace	Hass	Freeze-drying and milling	Aqueous two-phase systems	Sodium citrate–PEG4000 or magnesium sulfate–PEG4000	3.3 [2]	ND	ND	[86]
Stone	Hass	Grinding and drying	Boiled, stirred and filtered	Water	0.6 [2]	ND	3.8 [2]	[87]
Peel	Hass	Grinding and drying	Boiled, stirred and filtered	Water	2.0 [2]	ND	9.2 [2]	[87]
Stone	Shepard	Lyophilization and milling	Thermostatic shaking water bath	80% Methanol	1.3 [4,5]	9.1 [4]	ND	[88]
Peel	Shepard	Lyophilization and milling	Thermostatic shaking water bath	80% Methanol	1.6 [4,5]	11.2 [4]	ND	[88]
Stone	Hass	Lyophilization and milling	Thermostatic shaking water bath	80% Methanol	1.0 [4,5]	9.4 [4]	ND	[88]
Peel	Hass	Lyophilization and milling	Thermostatic shaking water bath	80% Methanol	2.5 [4,5]	16.1 [4]	ND	[88]

A, from Brazil; B, from Mexico; ND, not determined; values expressed as %, mg/mL, or showed in graphs. [1] Dried biomass. [2] Dried extract. [3] The samples were directly dried. [4] Not reporting the basis. [5] Expressed in terms of catechin.

In addition to the peel and stone, a recent study evaluated the chemical composition of the seed coat, considering it also has important content of phenolic compounds. To perform the characterization of the avocado stone and the stone peel, Figueroa et al. [84] used the accelerated solvent extraction and liquid chromatography coupled to quadrupole-time-of-flight mass spectrometry for characterization. They reported the presence of phenolic acids, derivatives of phenolic alcohols, and flavonoids, including catechins, procyanidins, and other polar compounds, such as organic acids. Their results also revealed that the seed coat showed a significantly higher antioxidant activity than the whole stone, in addition to a higher content of organic acids and flavonoids, with the exception of the quinic acid [84]. Furthermore, using ultrasound-assisted extraction, antioxidant extracts from avocado leaf were obtained. In these samples, phenolic acids, flavan-3-ols, flavones, and flavonols, among others, were characterized [89]. As a summary, Table 6 depicts the phenolic components characterized in avocado waste, including the phenolic compounds.

Table 6. Phenolic compounds and other compounds characterized in avocado waste according to [80,81,84,89–92].

Compound	By-Product	Compound	By-Product
Phenolic alcohol derivatives		Flavan-3-ols	
Hydroxytyrosol glucoside	S	(+)-Catechin	P/S/SC
Tyrosol-glucoside	S	(-)-Epicatechin	P/S/SC
Tyrosol-glucosyl-pentoside	S/SC	(Epi)gallocatechin	S/SC
3-hydroxytyrosol	P/S	Isomers 1 and 2 of (epi)catechin glucopyranoside	S/SC
Oleuropein	P/S	(Epi)catechin gallate	SC
Flavonols		B-Type (epi)catechin dimer, including B1 or B2	P/S/SC
Quercetin	P/S/SC/L	B-Type (epi)catechin trimer	P/S/SC
Quercetin-pentoside-hexoside	P	B-Type (epi)catechin tetramer	P/S/SC
Quercetin-glucoronide	P	B-Type (epi)catechin pentamer	P/SC
Quercetin-3-*O*-glucoside or other hexoside	P/S/SC	B-Type (epi)catechin hexamer	P
Quercetin-hexoside	P	A-Type (epi)catechin dimer	S/SC
Quercetin-dihexoside	P	A-Type (epi)catechin trimer	S/SC
Quercetin-rhamnoside-pentoside	P	A-Type (epi)catechin tetramer	S/SC
Quercetin-3-β-glucoside		Other phenolic compounds	
Isomers 1 and 2 of quercetin-diglucoside	SC	Catechol	P/S/SC
Isorhametin-glucuronide	P	Ellagic acid	P/S
Rutin	P/S	Dimethyl ellagic acid hexoside	L
Kaempferol	P/S	Pyrogallol or 1,2,3-trihydroxybenzene	P/S/SC
Kaempferol-glucuronide	P	Vanillin	P/S/SC
Flavanones		Flavalignan isomers	S/SC
Naringin	P/S	Non-phenolic compounds	
Hesperidin	P/S	Quinic acid	S/SC
Hesperetin	P/S	Citric acid	S/SC
Naringenin	P/S/SC	Citric acid isomer	S/SC
Sakuranetin	S/SC	Malic acid	S/SC
Flavone		Succinic acid	S/SC
Acacetin neorutinoside	P/S	Penstemide acid	SC
Apigenin	P/S/L	Hydroxyabscisic acid glucoside	SC
Apigenin-*C*-hexoside-pentoside	L	Perseitol	SC/L

L: Leaf; P: Peel; S: Stone; SC: Stone Coat.

Despite the fact that there are discrepancies between some of these studies as to whether the peel or stone have a higher concentration of phenolic compounds and capacity antioxidant, all agree that the extracts of these by-products have a greater antioxidant capacity and a higher concentration of phenolic compounds than the avocado pulp. The recovery of these phenolic compounds from avocado waste represents a new alternative to obtain raw materials of biological origin for the food industry thanks to their natural antioxidant properties [90]. Considering that flavonoids are not only powerful antioxidants but also they present other positive effects against various diseases, such as cancer, neurodegenerative, or cardiovascular diseases, the extracts from avocado waste are of great interest for medicinal purposes [86,93]. Moreover, Soldera et al. [91] showed that the avocado stone exhibited in vitro antihelmintic activity against third-stage larvae of *Haemonchus contortus*, with epicatechin and quercetin being some of the active constituents.

Efforts have also been made to generate synergy in new supplements by mixing the antioxidant properties of the stone and peel extracts with other substances to reduce costs, in addition to avoiding the environmental problems that this waste generates. One example is the optimization of the composition of natural additives with antioxidant and antimicrobial effects by adding avocado peel extracts to reduce the amount of nisin used at an industrial level [87]. Another study reported that a lyophilized stone extract can be mixed with egg albumin to minimize the oxidation of oil-in-water emulsions, achieving a 60% decrease in oxidation compared to the 30% obtained when only stone extracts were used. In hamburger meat, the formation of tio-barbituric acid substances (TBARS) was also avoided in 90% [78].

In addition, new forms of presentation are being investigated, such as the possibility that avocado stones can be, as a finished product, in powder form by using spray drying [94]. Wastewater power, also obtained by spray drying, was used as a preservative in pork sausages, being effective in preventing lipid oxidation [20].

6.2. Other Bioactive Compounds

Wang et al. [92] found a higher content of carotenoids and chlorophylls in avocado peels than in the pulp and stone. The concentration was up to 17.3 mg/kg and 66.9 mg/kg, respectively, and depended on the cultivar. Nonetheless, as far as we know, there are not studies about the optimization of the extraction of these minor components, maybe because there are other underutilized sources with higher concentration of carotenoids [95].

Furthermore, wastewater contains tocopherols, which are other important natural antioxidants. Permal et al. [96] optimized an antioxidant avocado wastewater powder adding 5% whey protein concentrate and spray drying parameters were set at a feed flow rate of 5.8 g/min and an inlet drying temperature of 160 °C. The yield was 49% and the α-tocopherol content was 181.6 mg/kg powder.

7. Extraction of an Orange Colorant

Besides being a source of pigments like chlorophylls and carotenoids, recent studies suggest that avocado stones can be applied as a natural orange dye with applications in different areas as food, cosmetics, and others. In this regard, Dabas et al. [97] indicated that avocado seed when crushed with water gives an orange color (see, Figure 2c) in a time-dependent manner; the maximum wavelength was 480 nm. The color formation is an inverse of the concentration of polyphenols, and that color development is polyphenol oxidase dependent. It was also reported that the intensity of the orange color varies with pH and oxygen interaction and thus it should be considered for further applications. Concerning extraction, ultrasound-assisted extraction has been also employed, observing different results; i.e., the highest color intensity and the phenolic content were obtained in parallel at 40 °C using methanol as the solvent [98]. This technology was also applied to recover a colored extract from avocado stone with in vitro antioxidant and cancer inhibitory activity, and so it can be regarded as a functional food ingredient or as a source of novel natural antioxidants and anticancer compounds [99].

Whether furfural or phenolic compounds are the responsible compound of the orange color, it requires more study. Nonetheless, recent studies suggest that a glycosylated benzotropolone could be the new orange pigment [100,101]. This novel compound has been called perseorangin (Figure 9).

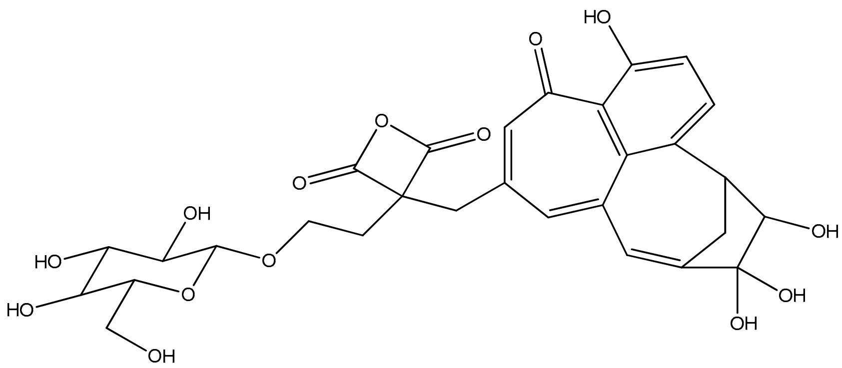

Figure 9. The chemical structure of perseorangin.

8. Production of Biosorbents

Avocado waste has revealed good properties as sorbent material. In a recent study, the stone was firstly dried and milled (particle sizes between 0.15 and 0.50 mm) and then used to remove toxic heavy metals like Cr(VI) and total chromium, which depend on the pH shift [102]. Moreover, several treatments have been applied to improve these properties. For example, avocado stone was treated with sulfuric, citric, and tartaric acids to improve the sorption of heavy metal ions from aqueous solutions, up to 600%: Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. The best removal performance was 3.3 to 21.8 mg/g [103]. Another application is the use of avocado treated stone to remove organic pollutants. In this way, Leite et al. [104] applied conventional pyrolysis to produce activated carbons. As a result, the activated carbon prepared at a higher temperature of pyrolysis (700 °C) has the best sorption capacity to uptake this type of contaminant. This was correlated with less total functional groups and a high hydrophobicity–hydrophilicity ratio.

Avocado peel has also demonstrated biosorption properties after acid and heat treatments. As an example, Palma and coworkers carbonized avocado peel at 900 °C and 65 min, generating an adsorbent with 87.52 m^2/g of surface area and, according to Brunauer, Emmett and Teller, a mesopore volume of 74% and a zero-point charge at 8.6. It was applied to remove dyes; around 0.5 mg/g was removed [105]. Using physical and acid treatments, the peel served as a biosorbent to remove the lead (II) or cadmium (II) in water, with a capacity of 16.37 and 13.91 mg/g, respectively [106].

9. Biorefinery Approaches, Techno-Economic, and Environmental Impact Analyses

Avocado consumption and the avocado-processing industry generate a huge amount of residues. Given its large scale globally, serious challenges from the sustainability perspective should be faced in producing countries. Moreover, these residues have no practical application and end up as wastes. However, this review has revealed a wide portfolio of valuable bioproducts that can be obtained from avocado waste with numerous applications in the food, cosmetic, pharmaceutical, energy, and environmental sectors, among others (Figure 10).

In this context, it is of crucial importance to implement innovative platforms based on the circular bioeconomy concept to enhance the sustainability around this tropical fruit and to move towards the zero-discharge system. Thus, the design of biorefinery schemes based on avocado waste to integrate the production of two or more bioproducts together with energy and/or biofuel is a desired goal since some of these valorization ways could be compatible. Moreover, avocado waste is a low-cost residue and it is generated in concrete localization points, i.e., guacamole and avocado oil industries. Thus, the cost of supply (including logistics and freight) can be reduced if the biorefinery is placed closer to those industries. In any case, the biorefinery design should be supported by techno-economic and environmental impact analyses before scaling up.

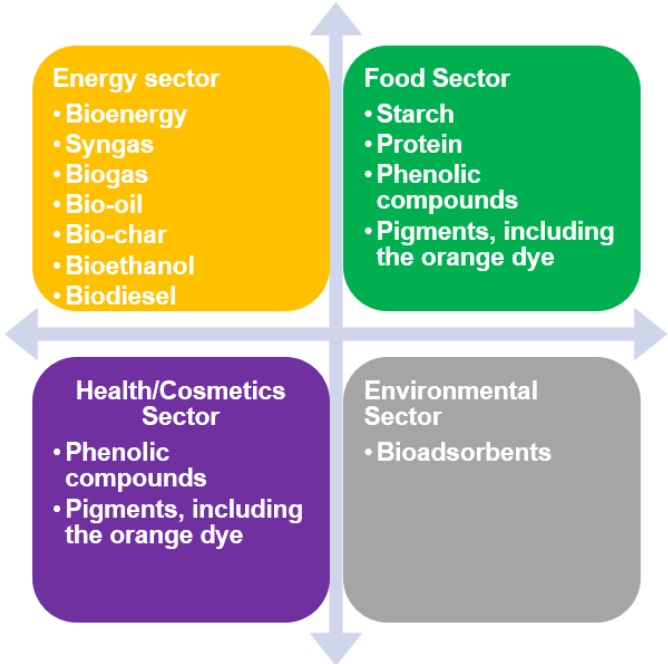

Figure 10. Summary of products that can be obtained from avocado waste and the sectors of application.

The techno-economic evaluation is needed to assess the biomass-to-product yield, energy efficiency, and production cost of the entire process to identify biorefineries with high economic performance to be cost-competitive with their fossil fuel counterparts [107]. The environmental analysis, considering total inputs, outputs, and potential integrated environmental impacts throughout the product life cycle, i.e., a life cycle assessment, is especially relevant to guarantee that the production is completely sustainable [108].

In this regard, Dávila and coworkers [31] have recently evaluated the feasibility of a biorefinery for processing 'Hass' avocados into oil from the pulp, and extracting the microencapsulated phenolic compounds, ethanol, and xylitol from the peel and stone (Figure 11). The study considered four scenarios with a different extent of mass and energy integration as well as the incorporation of a cogeneration plant using the residual lignin. The process simulation to obtain the mass and energy balances of the avocado-based biorefinery was performed using Aspen Plus and mass integration was considered for CO_2 and ethanol recovery that allows calculating the savings of these inputs. These authors suggested that full mass and energy integration, including cogeneration, have to be performed in order to obtain the most profitable scenario and to be environmentally better; i.e., it enables to reduce the total production cost of the biorefinery proposal, inputs consumption, and also the environmental impact. However, this scheme considered Colombian avocado production and thus a part (26.4%) was used for the simulation to avoid competition with its use as food. In this context, other results can be obtained if, for example, the biorefinery process is simulated in Mexico or New Zealand, and particularly if the biorefinery plant is associated with Guacamole and CPAO production plants, respectively; the tax and interest rates are probably some other important factors.

Another remarkable result from Dávila et al.'s work [31] is that, within a biorefinery scheme, the production of some products can compensate the high production costs of other products. In this case, the production of the microencapsulated antioxidant extract has a lower production costs but higher economic benefits than the rest of the co-products, and so it is beneficial for the entire biorefinery. An interesting feature of the study is that the authors applied supercritical CO_2 extraction to recover the phenolic compounds from the avocado waste, which is a green technology. Alternatively, it would also be interesting to consider other techniques, such as microwave- and ultrasound-assisted extraction using water or aqueous-ethanol solutions, since ethanol is a co-product of this biorefinery and these methods were able to extract considerable amounts of antioxidants.

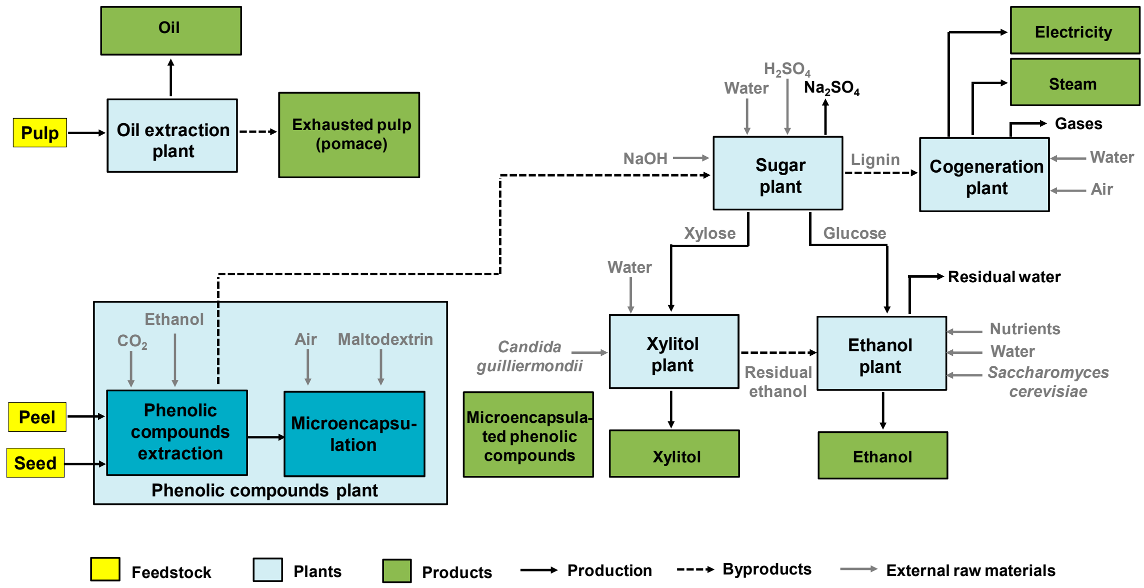

Figure 11. Scheme of a biorefinery proposal based on avocado [31].

Avocado pomace has a relatively high amount of residual avocado oil that can be further obtained following the valorization of, for example, olive oil. In Spain, the residual oil in the olive pomace is generally recovered with hexane to obtain pomace olive oil and the by-product obtained is used as a biofuel for heating [41]. Protein can also be obtained from the residual avocado pulp and considered in the techno-economic evaluation, as well other interesting bioproducts can be obtained, for example, the natural orange dye.

As a final remark, it seems that to provide second generation biofuels from agri-food residues, designing sustainable and cost-efficient biorefinery schemes is crucial. It presents a great potential for reducing both biofuel production costs and climate change impacts. For these reasons, future policies can decide if these processes/bioproducts can obtain a distinction label that offers merit to the practices, such as the EU Ecolabel. The latter is a label of environmental excellence awarded to products/services meeting high environmental standards throughout their life cycle. It intends to promote the circular bioeconomy by encouraging producers to generate less CO_2 and waste during the manufacturing process [109].

10. Conclusions

The agricultural practices and industry around avocado, i.e., guacamole and CPAO industries, generate a huge amount of waste whose valorization is of merit. Although this waste has a considerable moisture content, the chemical composition and the minor components make it a renewable source of valuable products. In particular, several studies have demonstrated that avocado waste can be used to obtain bioenergy and biofuels and a variety of methods have been applied to valorize the entire waste, mainly, the stones and peels. These include thermochemical methods, such as gasification, pyrolysis, torrefaction, and liquefaction, and biochemical methods to produce fuels in the gas, liquid, and/or solid state. Biodiesel and bioethanol have been produced from the fat and sugar fractions, respectively, but further work is required to use other avocado parts or to evaluate other methodologies. Moreover, other bioproducts can be obtained, particularly, antioxidant extracts from the peel, stone, and CPAO by-products, such as an orange natural dye from the stone, biosorbents from the peel and stone to remove heavy metals, organic pollutants and dyes, starch from the stone, protein from the defatted pulp/pomace, etc., with application in the food, cosmetic, pharmaceutical, and environmental sectors.

Regarding green technologies, most advances have been made in the extraction of antioxidants from avocado stones and peels, obtaining the best results using microwave-assisted extraction and supercritical CO_2 extraction. Microwave- and ultrasound-based technologies have also been applied to fractionate avocado stones or to recover a natural orange pigment. Further studies can reveal more applications of these technologies or improve the results reported here.

In addition to this variety of options, which have mostly been evaluated as single processes and at the laboratory scale, their integration would be promising, as Dávila and coworkers suggested [31]. In fact, the composition of avocado waste has several major macrocomponents and reinforces the development of biorefinery approaches to take full advantage of them, as well as to recover minor but valuable compounds, such as phenolic compounds, the orange pigment, etc. New greener technologies can be applied in some of the steps to produce the latter bioproducts, and thus it would be interesting to evaluate other biorefinery proposals using techno-economic and environmental analyses to support the laboratory studies. Moreover, the cost of supply can be reduced if the biorefinery is placed closer to avocado processing industries.

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References

1. Subsecretaría de Fomento a los Agronegocios. *Monografía de Cultivos*; SAGARPA Mexico DF: Mexico City, Mexico, 2011.
2. Zhang, Z.; Huber, D.J.; Rao, J. Antioxidant systems of ripening avocado (*Persea americana* Mill.) fruit following treatment at the preclimacteric stage with aqueous 1-methylcyclopropene. *Postharvest Biol. Technol.* **2013**, *76*, 58–64. [CrossRef]
3. CONABIO. Qué Nos Aportan Los Aguacates. Available online: https://www.biodiversidad.gob.mx/diversidad/alimentos/que-nos-aportan/N_aguacate (accessed on 10 September 2020).
4. Ding, H.; Chin, Y.W.; Kinghorn, A.D.; D'Ambrosio, S.M. Chemopreventive characteristics of avocado fruit. *Semin. Cancer Biol.* **2007**, *17*, 386–394. [CrossRef] [PubMed]
5. Ranade, S.S.; Thiagarajan, P. A review on *Persea americana* Mill. (Avocado)—Its fruit and oil. *Int. J. PharmTech Res.* **2015**, *8*, 72–77.
6. Food and Agriculture Organization of the United Nations (FAO) FAOSTAT. Available online: http://www.fao.org/faostat/en/#data/QC/visualize (accessed on 10 September 2020).
7. Leite, J.J.G.; Brito, É.H.S.; Cordeiro, R.A.; Brilhante, R.S.N.; Sidrim, J.J.C.; Bertini, L.M.; De Morais, S.M.; Rocha, M.F.G. Chemical composition, toxicity and larvicidal and antifungal activities of *Persea americana* (avocado) seed extracts. *Rev. Soc. Bras. Med. Trop.* **2009**, *42*, 110–113. [CrossRef] [PubMed]
8. Yahia, E.M.; Woolf, A.B. Avocado (*Persea americana* Mill.). In *Postharvest Biology and Technology of Tropical and Subtropical Fruits*; Yahia, E.M., Ed.; Woodhead Publishing Limited: Sawston, CA, USA, 2011; Volume 2, pp. 125–185.
9. Shahbandeh, M.U.S. Consumers' Main Drivers for Buying Avocados. 2019. Available online: https://www.statista.com/statistics/317753/us-consumers-main-drivers-for-buying-avocados/ (accessed on 10 September 2020).
10. Camila, D.B.; Waiga, L.H.; Soltovski De Oliveira, C.; Lacerda, L.G.; Schnitzler, E. Morphological and thermoanalytical study of modified avocado seeds starch with lactic acid. *Chem. J. Mold.* **2017**, *12*, 13–18. [CrossRef]

11. Krumreich, F.D.; Borges, C.D.; Mendonça, C.R.B.; Jansen-Alves, C.; Zambiazi, R.C. Bioactive compounds and quality parameters of avocado oil obtained by different processes. *Food Chem.* **2018**, *257*, 376–381. [CrossRef]
12. García-Vargas, M.C.; del Contreras, M.; Gómez-Cruz, I.; Romero-García, J.M.; Castro, E. Avocado-derived biomass: Chemical composition and antioxidant potential. *Proceedings*. 2020. Available online: https://sciforum.net/paper/view/7750 (accessed on 18 November 2020).
13. Rodríguez-Carpena, J.G.; Morcuende, D.; Estévez, M. Avocado by-products as inhibitors of color deterioration and lipid and protein oxidation in raw porcine patties subjected to chilled storage. *Meat Sci.* **2011**, *89*, 166–173. [CrossRef]
14. Chel-Guerrero, L.; Barbosa-Martín, E.; Martínez-Antonio, A.; González-Mondragón, E.; Betancur-Ancona, D. Some physicochemical and rheological properties of starch isolated from avocado seeds. *Int. J. Biol. Macromol.* **2016**, *86*, 302–308. [CrossRef]
15. Gutierrez-Contreras, M.; Lara-Chavez, M.B.N.; Guillen-Andrade, H.C.-B. Agroecoloy of the avocado-producing belt area in Michoacan, Mexico/Agroecologia de la Franja Aguacatera en Michoacan, Mexico/Agroecologia da Faixa de Abacateiros em Michoacan, Mexico. *Interciencia* **2010**, *35*, 647–653.
16. del Mar Contreras, M.; Lama-Muñoz, A.; Manuel Gutiérrez-Pérez, J.; Espínola, F.; Moya, M.; Castro, E. Protein extraction from agri-food residues for integration in biorefinery: Potential techniques and current status. *Bioresour. Technol.* **2019**, *280*, 459–477. [CrossRef]
17. Medfai, W.; Contreras, M.D.M.; Lama-Muñoz, A.; Mhamdi, R.; Oueslati, I.; Castro, E. How Cultivar and Extraction Conditions Affect Antioxidants Type and Extractability for Olive Leaves Valorization. *ACS Sustain. Chem. Eng.* **2020**, *8*, 5107–5118. [CrossRef]
18. del Mar Contreras, M.; Lama-Muñoz, A.; Espínola, F.; Moya, M.; Romero, I.; Castro, E. Valorization of olive mill leaves through ultrasound-assisted extraction. *Food Chem.* **2020**, *314*, 126218. [CrossRef] [PubMed]
19. Macías, A.M. México en el mercado internacional de aguacate. *Rev. Cienc. Soc.* **2011**, *17*, 517–532. [CrossRef]
20. Permal, R.; Chang, W.L.; Seale, B.; Hamid, N.; Kam, R. Converting industrial organic waste from the cold-pressed avocado oil production line into a potential food preservative. *Food Chem.* **2020**, *306*, 125635. [CrossRef] [PubMed]
21. Costagli, G.; Betti, M.; Laval, A.; Market, S.; Food, U.; Oil, O.; Val, T. Avocado oil extraction processes: Method for cold-pressed high-quality edible oil production versus traditional production. *J. Agric. Eng.* **2015**, *46*, 115–122. [CrossRef]
22. Wong, M.; Ashton, O.; Mcghie, T.; Requejo-Jackman, C.; Eyres, L.; Sherpa, N.; Woolf, A. Avocado Oil—The Colour of Quality. *ACS Symp. Ser.* **2008**, *983*, 328–349.
23. Tan, C.X. Virgin avocado oil: An emerging source of functional fruit oil. *J. Funct. Foods* **2019**, *54*, 381–392. [CrossRef]
24. Ramtahal, G.; Akingbala, J.O.; Baccus-Taylor, G.S. Laboratory preparation and evaluation of Pollock variety avocado (*Persea americana* Mill) guacamole. *J. Sci. Food Agric.* **2007**, *1243*, 1237–1243. [CrossRef]
25. López-Cobo, A.; Gómez-Caravaca, A.M.; Pasini, F.; Caboni, M.F.; Segura-Carretero, A.; Fernández-Gutiérrez, A. HPLC-DAD-ESI-QTOF-MS and HPLC-FLD-MS as valuable tools for the determination of phenolic and other polar compounds in the edible part and by-products of avocado. *LWT-Food Sci. Technol.* **2016**, *73*, 505–513. [CrossRef]
26. Araújo, R.G.; Rodriguez-Jasso, R.M.; Ruiz, H.A.; Pintado, M.M.E.; Aguilar, C.N. Avocado by-products: Nutritional and functional properties. *Trends Food Sci. Technol.* **2018**, *80*, 51–60. [CrossRef]
27. Saavedra, J.; Córdova, A.; Navarro, R.; Díaz-Calderón, P.; Fuentealba, C.; Astudillo-Castro, C.; Toledo, L.; Enrione, J.; Galvez, L. Industrial avocado waste: Functional compounds preservation by convective drying process. *J. Food Eng.* **2017**, *198*, 81–90. [CrossRef]
28. Pratywi, C.D.; Marantika, S.; Dwijananti, P. Masturi Characterization of starch degradation during simple heating for bioethanol production from the avocado seed. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *432*, 10–15. [CrossRef]
29. Perea-Moreno, A.J.; Aguilera-Ureña, M.J.; Manzano-Agugliaro, F. Fuel properties of avocado stone. *Fuel* **2016**, *186*, 358–364. [CrossRef]
30. Eliyahu, D.; Yosef, E.; Weinberg, Z.G.; Hen, Y.; Nikbachat, M.; Solomon, R.; Mabjeesh, S.J.; Miron, J. Composition, preservation and digestibility by sheep of wet by-products from the food industry. *Anim. Feed Sci. Technol.* **2015**, *207*, 1–9. [CrossRef]
31. Dávila, J.A.; Rosenberg, M.; Castro, E.; Cardona, C.A. A model biorefinery for avocado (*Persea americana* mill.) processing. *Bioresour. Technol.* **2017**, *243*, 17–29. [CrossRef]

32. Barbosa-Martín, E.; Chel-Guerrero, L.; González-Mondragón, E.; Betancur-Ancona, D. Chemical and technological properties of avocado (*Persea americana* Mill.) seed fibrous residues. *Food Bioprod. Process.* **2016**, *100*, 457–463. [CrossRef]
33. Morais, D.R.; Rotta, E.M.; Sargi, S.C.; Schmidt, E.M.; Bonafe, E.G.; Eberlin, M.N.; Sawaya, A.C.; Visentainer, J.V. Antioxidant activity, phenolics and UPLC-ESI(-)-MS of extracts from different tropical fruits parts and processed peels. *Food Res. Int.* **2015**, *77*, 392–399. [CrossRef]
34. García, R.; Pizarro, C.; Lavín, A.G.; Bueno, J.L. Characterization of Spanish biomass wastes for energy use. *Bioresour. Technol.* **2012**, *103*, 249–258. [CrossRef]
35. Gaurav, N.; Sivasankari, S.; Kiran, G.S.; Ninawe, A.; Selvin, J. Utilization of bioresources for sustainable biofuels: A Review. *Renew. Sustain. Energy Rev.* **2017**, *73*, 205–214. [CrossRef]
36. Kang, Y.; Yang, Q.; Bartocci, P.; Wei, H.; Liu, S.S.; Wu, Z.; Zhou, H.; Yang, H.; Fantozzi, F.; Chen, H. Bioenergy in China: Evaluation of domestic biomass resources and the associated greenhouse gas mitigation potentials. *Renew. Sustain. Energy Rev.* **2020**, *127*, 109842. [CrossRef]
37. Senthil Kumar, P.; Yaashikaa, P.R. Sources and Operations of Waste Biorefineries. In *Refining Biomass Residues for Sustainable Energy and Bioproducts*; Kumar, R.P., Gnansounou, E., Raman, J.K., Baskar, G., Eds.; Academic Press: Cambridge, MA, USA, 2020; pp. 111–133.
38. Rincon, L.; Puri, M.; Kojakovic, A.; Maltsoglou, I. The contribution of sustainable bioenergy to renewable electricity generation in Turkey: Evidence based policy from an integrated energy and agriculture approach. *Energy Policy* **2019**, *130*, 69–88. [CrossRef]
39. Di Bitonto, L.; Reynel-Ávila, H.E.; Mendoza-Castillo, D.I.; Bonilla-Petriciolet, A.; Pastore, C. Residual Mexican biomasses for bioenergy and fine chemical production: Correlation between composition and specific applications. *Biomass Convers. Biorefin.* **2020**. [CrossRef]
40. Telmo, C.; Lousada, J.; Moreira, N. Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood. *Bioresour. Technol.* **2010**, *101*, 3808–3815. [CrossRef] [PubMed]
41. del Mar Contreras, M.; Romero, I.; Moya, M.; Castro, E. Olive-derived biomass as a renewable source of value-added products. *Process Biochem.* **2020**, *97*, 43–56. [CrossRef]
42. Domínguez, M.P.; Araus, K.; Bonert, P.; Sánchez, F.; San Miguel, G.; Toledo, M. The Avocado and Its Waste: An Approach of Fuel Potential/Application. In *Environment, Energy and Climate Change II*, 1st ed.; Lefebvre, G., Jiménez, E., Cabañas, B., Eds.; Springer: New York, NY, USA, 2016; Volume 34, pp. 199–223.
43. Xue, J.; Chellappa, T.; Ceylan, S.; Goldfarb, J.L. Enhancing biomass + coal Co-firing scenarios via biomass torrefaction and carbonization: Case study of avocado pit biomass and Illinois No. 6 coal. *Renew. Energy* **2018**, *122*, 152–162. [CrossRef]
44. Perea-Moreno, M.A.; Samerón-Manzano, E.; Perea-Moreno, A.J. Biomass as renewable energy: Worldwide research trends. *Sustainability* **2019**, *11*, 863. [CrossRef]
45. Rashama, C.; Ijoma, G.; Matambo, T. Biogas generation from by-products of edible oil processing: A review of opportunities, challenges and strategies. *Biomass Convers. Biorefin.* **2019**, *9*, 803–826. [CrossRef]
46. Dhanya, B.S.; Mishra, A.; Chandel, A.K.; Verma, M.L. Development of sustainable approaches for converting the organic waste to bioenergy. *Sci. Total Environ.* **2020**, *723*, 138109. [CrossRef]
47. Kenasa, G.; Kena, E. Optimization of Biogas production from avocado fruit peel wastes codigestion with animal manure collected from juice vending house in Gimbi Town, Ethiopia. *Ferment. Technol.* **2019**, *8*, 1000153. [CrossRef]
48. Global Bioenergy Statistics. World Bioenergy Association. 2019. Available online: https://worldbioenergy.org/global-bioenergy-statistics (accessed on 9 October 2020).
49. Wang, S.; Jena, U.; Das, K.C. Biomethane production potential of slaughterhouse waste in the United States. *Energy Convers. Manag.* **2018**, *173*, 143–157. [CrossRef]
50. Colombo, R.; Papetti, A. Avocado (*Persea americana* Mill.) by-products and their impact: From bioactive compounds to biomass energy and sorbent material for removing contaminants. A review. *Int. J. Food Sci. Technol.* **2019**, *54*, 943–951. [CrossRef]
51. Streitwieser, D.A.; Cadena, I.A. Preliminary study of biomethane production of organic waste based on their content of sugar, starch, lipid, protein and fibre. *Chem. Eng. Trans.* **2018**, *65*, 661–666. [CrossRef]
52. Vintila, T.; Ionel, I.; Rufis Fregue, T.T.; Wächter, A.R.; Julean, C.; Gabche, A.S. Residual biomass from food processing industry in Cameroon as feedstock for second-generation biofuels. *BioResources* **2019**, *14*, 3731–3745. [CrossRef]

53. Deressa, L.; Libsu, S.; Chavan, R.B.; Manaye, D.; Dabassa, A. Production of Biogas from Fruit and Vegetable Wastes Mixed with Different Wastes. *Environ. Ecol. Res.* **2015**, *3*, 65–71. [CrossRef]
54. Olivado. How Our Factory in Kenya Thrives on Sustainable Practices. Available online: https://www.olivado.com/factory-kenya-sustainable-practices (accessed on 10 September 2020).
55. Aysu, T.; Durak, H. Assessment of avocado seeds (*Persea americana*) to produce bio-oil through supercritical liquefaction. *Biofuel. Bioprod. Biorefin.* **2012**, *6*, 246–256. [CrossRef]
56. Sánchez, F.; Araus, K.; Domínguez, M.P.; Miguel, G.S. Thermochemical transformation of residual avocado seeds: Torrefaction and carbonization. *Waste Biomass Valorization* **2017**, *8*, 2495–2510. [CrossRef]
57. Huang, Y.F.; Chiueh, P.T.; Lo, S.L. A review on microwave pyrolysis of lignocellulosic biomass. *Sustain. Environ. Res.* **2016**, *26*, 103–109. [CrossRef]
58. Foong, S.Y.; Liew, R.K.; Yang, Y.; Cheng, Y.W.; Yek, P.N.Y.; Wan Mahari, W.A.; Lee, X.Y.; Han, C.S.; Vo, D.V.N.; Van Le, Q.; et al. Valorization of biomass waste to engineered activated biochar by microwave pyrolysis: Progress, challenges, and future directions. *Chem. Eng. J.* **2020**, *389*, 124401. [CrossRef]
59. Elsayed, M.; Ran, Y.; Ai, P.; Azab, M.; Mansour, A.; Jin, K.; Zhang, Y.; Abomohra, A.E.-F. Innovative integrated approach of biofuel production from agricultural wastes by anaerobic digestion and black soldier fly larvae. *J. Clean. Prod.* **2020**, *263*, 121495. [CrossRef]
60. Rachimoellah, H.M.; Resti, D.A.; Zibbeni, A.; Susila, I.W. Production of biodiesel through transesterification of avocado (*Persea gratissima*) seed oil using base catalyst. *J. Tek. Mesin* **2009**, *11*, 85–90. [CrossRef]
61. Aga, T. Production and Characterization of Biodiesel from Avocado Peel Oil (Apo). Master's Thesis, Addis Ababa University, Addis Ababa, Ethiopia, 2018.
62. Avhad, M.R.; Sánchez, M.; Bouaid, A.; Martínez, M.; Aracil, J.; Marchetti, J.M. Modeling chemical kinetics of avocado oil ethanolysis catalyzed by solid glycerol-enriched calcium oxide. *Energy Convers. Manag.* **2016**, *126*, 1168–1177. [CrossRef]
63. Paul, A.A.L.; Adewale, F.J. Data on physico-chemical, performance, combustion and emission characteristics of *Persea americana* Biodiesel and its blends on direct-injection, compression-ignition engines. *Data Brief* **2018**, *21*, 1533–1540. [CrossRef]
64. Paul, A.A.L.; Adewale, F.J. Data on optimization of production parameters on *Persea americana* (Avocado) plant oil biodiesel yield and quality. *Data Brief* **2018**, *20*, 855–863. [CrossRef] [PubMed]
65. Adeniyi, A.G.; Ighalo, J.O.; Adeoye, A.S.; Onifade, D.V. Modelling and optimisation of biodiesel production from Euphorbia lathyris using ASPEN Hysys. *SN Appl. Sci.* **2019**, *1*, 1–9. [CrossRef]
66. Jung, J.M.; Oh, J.I.; Kwon, D.; Park, Y.K.; Zhang, M.; Lee, J.; Kwon, E.E. Synthesis of fatty acid methyl esters via non-catalytic transesterification of avocado oil with dimethyl carbonate. *Energy Convers. Manag.* **2019**, *195*, 1–6. [CrossRef]
67. Romero-García, J.M.; Niño, L.; Martínez-Patiño, C.; Álvarez, C.; Castro, E.; Negro, M.J. Biorefinery based on olive biomass. State of the art and future trends. *Bioresour. Technol.* **2014**, *159*, 421–432. [CrossRef]
68. Bozell, J.J.; Petersen, G.R. Technology development for the production of biobased products from biorefinery carbohydrates—The US Department of Energy's "top 10" revisited. *Green Chem.* **2010**, *12*, 539–555. [CrossRef]
69. Redwood, M.D.; Orozco, R.L.; Majewski, A.J.; Macaskie, L.E. An integrated biohydrogen refinery: Synergy of photofermentation, extractive fermentation and hydrothermal hydrolysis of food wastes. *Bioresour. Technol.* **2012**, *119*, 384–392. [CrossRef]
70. del Mar Contreras, M.; Lama-Muñoz, A.; Romero-García, J.M.; García-Vargas, M.; Romero, I.; Castro, E. Production of renewable products from brewery spent grains. In *Waste Biorefinery*; Pandey, A., Ed.; Elsevier Inc.: Amsterdam, The Netherlands, 2021; pp. 305–347.
71. Cuevas, M.; Saleh, M.; García-Martín, J.F.; Sánchez, S. Acid and enzymatic fractionation of olive stones for ethanol production using Pachysolen tannophilus. *Processes* **2020**, *8*, 195. [CrossRef]
72. Cornelia, M.; Christianti, A. Utilization of modified starch from avocado (*Persea americana* Mill.) seed in cream soup production. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, *102*. [CrossRef]
73. Araújo, R.G.; Rodríguez-Jasso, R.M.; Ruiz, H.A.; Govea-Salas, M.; Rosas-Flores, W.; Aguilar-González, M.A.; Pintado, M.E.; Lopez-Badillo, C.; Luevanos, C.; Aguilar, C.N. Hydrothermal-microwave processing for starch extraction from Mexican avocado seeds: Operational conditions and characterization. *Processes* **2020**, *8*, 759. [CrossRef]

74. Tesfaye, T.; Gibril, M.; Sithole, B.; Ramjugernath, D.; Chavan, R.; Chunilall, V.; Gounden, N. Valorisation of avocado seeds: Extraction and characterisation of starch for textile applications. *Clean Technol. Environ. Policy* **2018**, *20*, 2135–2154. [CrossRef]
75. Manzanares, P.; Ballesteros, I.; Negro, M.J.; González, A.; Oliva, J.M.; Ballesteros, M. Processing of extracted olive oil pomace residue by hydrothermal or dilute acid pretreatment and enzymatic hydrolysis in a biorefinery context. *Renew. Energy* **2020**, *145*, 1235–1245. [CrossRef]
76. López-Linares, J.C.; Romero, I.; Moya, M.; Cara, C.; Ruiz, E.; Castro, E. Pretreatment of olive tree biomass with $FeCl_3$ prior enzymatic hydrolysis. *Bioresour. Technol.* **2013**, *128*, 180–187. [CrossRef] [PubMed]
77. Wang, J.S.; Wang, A.B.; Zang, X.P.; Tan, L.; Xu, B.Y.; Chen, H.H.; Jin, Z.Q.; Ma, W.H. Physicochemical, functional and emulsion properties of edible protein from avocado (*Persea americana* Mill.) oil processing by-products. *Food Chem.* **2019**, *288*, 146–153. [CrossRef] [PubMed]
78. Segovia, F.J.; Hidalgo, G.I.; Villasante, J.; Ramis, X.; Almajano, M.P. Avocado seed: A comparative study of antioxidant content and capacity in protecting oil models from oxidation. *Molecules* **2018**, *23*, 2421. [CrossRef]
79. Daiuto, É.R.; Tremocoldi, M.A.; De Alencar, S.M.; Vieites, R.L.; Minarelli, P.H. Chemical composition and antioxidant activity of the pulp, peel and by products of avocado 'hass. *Rev. Bras. Frutic.* **2014**, *36*, 417–424. [CrossRef]
80. Melgar, B.; Dias, M.I.; Ciric, A.; Sokovic, M.; Garcia-Castello, E.M.; Rodriguez-Lopez, A.D.; Barros, L.; Ferreira, I.C.R.F. Bioactive characterization of *Persea americana* Mill. by-products: A rich source of inherent antioxidants. *Ind. Crop Prod.* **2018**, *111*, 212–218. [CrossRef]
81. Tremocoldi, M.A.; Rosalen, P.L.; Franchin, M.; Massarioli, A.P.; Denny, C.; Daiuto, É.R.; Paschoal, J.A.R.; Melo, P.S.; De Alencar, S.M. Exploration of avocado by-products as natural sources of bioactive compounds. *PLoS ONE* **2018**, *13*, e192577. [CrossRef]
82. Araújo, R.G.; Rodriguez-Jasso, R.M.; Ruiz, H.A.; Govea-Salas, M.; Pintado, M.E.; Aguilar, C.N. Process optimization of microwave-assisted extraction of bioactive molecules from avocado seeds. *Ind. Crop Prod.* **2020**, *154*, 112623. [CrossRef]
83. Weremfo, A.; Adulley, F.; Adarkwah-Yiadom, M. Simultaneous Optimization of Microwave-Assisted Extraction of Phenolic Compounds and Antioxidant Activity of Avocado (*Persea americana* Mill.) Seeds Using Response Surface Methodology. *J. Anal. Methods Chem.* **2020**, *2020*. [CrossRef]
84. Figueroa, J.G.; Borrás-Linares, I.; Lozano-Sánchez, J.; Segura-Carretero, A. Comprehensive characterization of phenolic and other polar compounds in the seed and seed coat of avocado by HPLC-DAD-ESI-QTOF-MS. *Food Res. Int.* **2018**, *105*, 752–763. [CrossRef]
85. Páramos, P.R.; Granjo, J.F.; Corazza, M.L.; Matos, H.A. Extraction of high value products from avocado waste biomass. *J. Supercrit. Fluids* **2020**, *165*. [CrossRef]
86. Jiménez-Velázquez, P.; Valle-Guadarrama, S.; Alia-Tejacal, I.; Salinas-Moreno, Y.; García-Cruz, L.; Pérez-López, A.; Guerra-Ramírez, D. Separation of bioactive compounds from epicarp of 'Hass' avocado fruit through aqueous two-phase systems. *Food Bioprod. Process.* **2020**, *123*, 238–250. [CrossRef]
87. Calderón-Oliver, M.; Escalona-Buendía, H.B.; Medina-Campos, O.N.; Pedraza-Chaverri, J.; Pedroza-Islas, R.; Ponce-Alquicira, E. Optimization of the antioxidant and antimicrobial response of the combined effect of nisin and avocado byproducts. *LWT-Food Sci. Technol.* **2016**, *65*, 46–52. [CrossRef]
88. Kosińska, A.; Karamać, M.; Estrella, I.; Hernández, T.; Bartolomé, B.; Dykes, G.A. Phenolic compound profiles and antioxidant capacity of *Persea americana* mill. peels and seeds of two varieties. *J. Agric. Food Chem.* **2012**, *60*, 4613–4619. [CrossRef]
89. Castro-López, C.; Bautista-Hernández, I.; González-Hernández, M.D.; Martínez-Ávila, G.C.G.; Rojas, R.; Gutiérrez-Díez, A.; Medina-Herrera, N.; Aguirre-Arzola, V.E. Polyphenolic profile and antioxidant activity of leaf purified hydroalcoholic extracts from seven Mexican *Persea americana* cultivars. *Molecules* **2019**, *24*, 173. [CrossRef]
90. Zaki, S.A.E.-H.; Ismail, F.A.E.-A.; Abdelatif, S.H.; El-Mohsen, N.R.A.; Helmy, S.A. Bioactive compounds and antioxidant activities of avocado peels and seeds. *Pak. J. Biol. Sci.* **2020**, *23*, 345–350. [CrossRef]
91. Soldera-Silva, A.; Seyfried, M.; Campestrini, L.H.; Zawadzki-Baggio, S.F.; Minho, A.P.; Molento, M.B.; Maurer, J.B.B. Assessment of anthelmintic activity and bio-guided chemical analysis of *Persea americana* seed extracts. *Vet. Parasitol.* **2018**, *251*, 34–43. [CrossRef]
92. Wang, W.; Bostic, T.R.; Gu, L. Antioxidant capacities, procyanidins and pigments in avocados of different strains and cultivars. *Food Chem.* **2010**, *122*, 1193–1198. [CrossRef]

93. Villacís-Chiriboga, J.; Elst, K.; Van Camp, J.; Vera, E.; Ruales, J. Valorization of byproducts from tropical fruits: Extraction methodologies, applications, environmental, and economic assessment: A review (Part 1: General overview of the byproducts, traditional biorefinery practices, and possible applications). *Compr. Rev. Food Sci. Food Saf.* **2020**, *19*, 405–447. [CrossRef]
94. Alissa, K.; Hung, Y.C.; Hou, C.Y.; Lim, G.C.W.; Ciou, J.Y. Developing new health material: The utilization of spray drying technology on avocado (*Persea americana* mill.) seed powder. *Foods* **2020**, *9*, 139. [CrossRef]
95. Contreras-Gámez, M.d.M.; Gómez-Caravaca, A.M. Underutilized Sources of Carotenoids. In *Carotenoids: Properties, Processing and Applications*; Galanakis, C.M., Ed.; Academic Press: Burlington, MA, USA, 2020; pp. 107–147.
96. Permal, R.; Chang, W.L.; Chen, T.; Seale, B.; Hamid, N.; Kam, R. Optimising the spray drying of avocado wastewater and use of the powder as a food preservative for preventing lipid peroxidation. *Foods* **2020**, *9*, 1187. [CrossRef]
97. Dabas, D.; Elias, R.J.; Lambert, J.D.; Ziegler, G.R. A Colored avocado seed extract as a potential natural colorant. *J. Food Sci.* **2011**, *76*, 1335–1341. [CrossRef]
98. Arlene, A.A.; Prima, K.A.; Utama, L.; Anggraini, S.A. The preliminary study of the dye extraction from the avocado seed using ultrasonic assisted extraction. *Procedia Chem.* **2015**, *16*, 334–340. [CrossRef]
99. Dabas, D.; Ziegler, G.R.; Lambert, J.D. Anti-Inflammatory Properties of a Colored Avocado Seed Extract. *Abbr. Adv. Food Technol. Nutr. Sci. Open J.* **2019**, *5*, 8–12. [CrossRef]
100. Shegog, R.M. Characterization of Perseoranjin a natural orange pigment found in Hass avocado (*Persea americana*) seed and its uses as a natural food colorant. Master's Thesis, The Pennsylvania State University, University Park, PA, USA, 2015.
101. Hatzakis, E.; Mazzola, E.P.; Shegog, R.M.; Ziegler, G.R.; Lambert, J.D. Perseorangin: A natural pigment from avocado (*Persea americana*) seed. *Food Chem.* **2019**, *293*, 15–22. [CrossRef]
102. Aranda-García, E.; Cristiani-Urbina, E. Effect of pH on hexavalent and total chromium removal from aqueous solutions by avocado shell using batch and continuous systems. *Environ. Sci. Pollut. Res.* **2019**, *26*, 3157–3173. [CrossRef]
103. Díaz-Muñoz, L.L.; Bonilla-Petriciolet, A.; Reynel-Ávila, H.E.; Mendoza-Castillo, D.I. Sorption of heavy metal ions from aqueous solution using acid-treated avocado kernel seeds and its FTIR spectroscopy characterization. *J. Mol. Liq.* **2016**, *215*, 555–564. [CrossRef]
104. Leite, A.B.; Saucier, C.; Lima, E.C.; dos Reis, G.S.; Umpierres, C.S.; Mello, B.L.; Shirmardi, M.; Dias, S.L.P.; Sampaio, C.H. Activated carbons from avocado seed: Optimisation and application for removal of several emerging organic compounds. *Environ. Sci. Pollut. Res.* **2018**, *25*, 7647–7661. [CrossRef]
105. Palma, C.; Lloret, L.; Puen, A.; Tobar, M.; Contreras, E. Production of carbonaceous material from avocado peel for its application as alternative adsorbent for dyes removal. *Chin. J. Chem. Eng.* **2016**, *24*, 521–528. [CrossRef]
106. Aiyesanmi, A.F.; Adebayo, M.A.; Arowojobe, Y. Biosorption of lead and cadmium from aqueous solution in single and binary systems using avocado pear exocarp: Effects of competing ions. *Anal. Lett.* **2020**, *53*, 2868–2885. [CrossRef]
107. Zetterholm, J.; Bryngemark, E.; Ahlström, J.; Söderholm, P.; Harvey, S.; Wetterlund, E. Economic evaluation of large-scale biorefinery deployment: A framework integrating dynamic biomass market and techno-economic models. *Sustainability* **2020**, *12*, 7126. [CrossRef]
108. Han, D.; Yang, X.; Li, R.; Wu, Y. Environmental impact comparison of typical and resource-efficient biomass fast pyrolysis systems based on LCA and Aspen Plus simulation. *J. Clean. Prod.* **2019**, *231*, 254–267. [CrossRef]
109. European Commission, Environment. Available online: https://ec.europa.eu/environment/ecolabel/ (accessed on 7 October 2020).

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