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Potential and prospects for utilization of avocado by-products in integrated biorefineries

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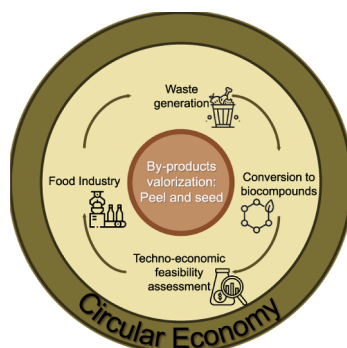
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HIGHLIGHTS

- Avocado residues' biorefineries are tackled in this review.
- Eco-friendly processing of avocado wastes as key to obtain valuable products.
- A novel biorefinery strategy for the integral valorization of avocado residues.
- Technical and economic feasibility of avocado biorefineries was discussed.
- Hurdles to overcome for multiproduct avocado biorefinery within bioeconomy concept.

GRAPHICAL ABSTRACT



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ABSTRACT

The industrial processing of avocado to extract oil, and produce guacamole or sauces generates enormous quantities of peels and seeds (around 2 million tons worldwide in 2019) without commercially valuable applications. However, various studies have suggested the presence of a wide range of interesting compounds in the composition of these by-products. This review depicts a thorough outline of the capacity of avocado residues to be converted into a portfolio of commodities that can be employed in sectors such as the food, cosmetics, pharmaceuticals, environment, and energy industries. Therefore, a novel biorefinery strategy to valorize avocado-processing residues to obtain a polyphenolic extract, pectooligosaccharides, and succinic acid was presented. Additionally, the prospects and challenges facing a biorefinery based on the valorization of avocado residues are presented, particularly its techno-economic feasibility on an industrial scale, aiming for a resource-efficient circular bio-economy.

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1. Introduction

During the last decades, there has been an increasing demand for energy, products, and chemicals, commonly come from fossil resources that are not renewable. This has provoked a current urgency in the search for long-term sustainable feedstock that can meet this demand and smooth the impact of climate change around the world. In this sense, biomass, i.e., the organic matter coming from living, or recently living organisms, is considered one of the most plentiful resources in the world, with extensive potential for the manufacture of bio-based energy, products, and chemicals (Attard et al., 2020; Lorenci Woiciechowski et al., 2020; Moncada et al., 2016; Morales et al., 2020a).

On the one hand, the use of edible biomass (barley, palm oil, corn, or potato, among others) as a feedstock is controversial. It can bring environmental, socio-economic, and ethical issues, increasing the food price and encompassing a thorough depletion of different feedstocks, while aggravating soil degradation due to the extensive use of fertilizers (Cherubini, 2010; Robak and Balcerek, 2018; Saha et al., 2019). On the other hand, vegetable and fruit consumption is growing every year, according to data from FAOSTAT (2020), and is foreseeable to keep growing despite the COVID-19 global crisis (Martins et al., 2022). This growth implies the consequently increased generation of wastes without direct aim, which negatively affects the environment and the economy via land use, transport, and waste disposal (Del Castillo-Llamas et al., 2021a; Martins et al., 2022). For that reason, the utilization of these residues as a source of marketable products may favor not only the decrease of environmental issues and the increase of wealth but the transition to a circular economy (Zabaniotou and Kamaterou, 2019).

The circular economy concept relies on transmuting the value chain from linear to closed loop, limiting the generation of residues, and improving the efficacy of the whole process, counteracting the socio-economic and environmental problems provoked by the current situation. Hence, the bio-economy is based on the conversion of organic renewable carbon-sourced (carbohydrates, proteins, and lipids) waste into a spectrum of bio-commodities such as energy, fuels, chemicals, polymers, food or feed, among others (Dahiya et al., 2018; Maina et al., 2017; Pinales-Márquez et al., 2021).

In this perspective, the biorefinery concept gains value as it tries to satisfy the search for green, renewable and sustainable systems to obtain different marketable products from biomass, pursuing economic profitability and environmental sustainability (Aristizábal et al., 2015; Hingsamer and Jungmeier, 2018). The use of this strategy combined with the differentiated composition of agro-food wastes may promote a more efficient valorization to produce high-value-added products while preserving resources and protecting the environment (Santiago et al., 2020).

Although there are generally two main biorefinery schemes based on the primary product (either strongly energetically-oriented or strongly materially-oriented biorefineries) (Hingsamer and Jungmeier, 2018), the development of a multiproduct biorefinery approach employing cascade technologies enables the integral valorization of one feedstock, obtaining various high-added value products at once (Gullón et al., 2020). For that reason, integrated biorefineries are being developed and improved in the recent years to recovery valuable wastes and evade the current risk of land, feed and, food competition (Santiago et al., 2020).

In this context, the European Commission also supports the use of biomass refineries through the 17 Sustainable Development Goals (SDGs) of the 2030 Agenda, which promote the manufacture of clean and affordable energy, while strengthening the economy, industry, and innovation, *inter alia*, taking into account climate change and the protection of oceans and forests. In addition, SDGs also promote a 'Responsible consumption and production', aiming efficient and sustainable management of natural resources, greatly reducing the waste generated through prevention, reduction, recycling and reuse (Santiago et al., 2020). To this end, various official documents have been published, namely the EU Green New Deal (European Commission, 2019),

the Circular Economy Action Plan (European Commission, 2020) and the EU Bioeconomy Strategy (European Commission, 2018).

Within this biorefinery concept, different commodities can be manufactured in one strategy. Hence, both low-value with high volume biofuels (biodiesel, bioethanol, or biogas) and high-value with low volume bioproducts (also known as added-value products such as pharmaceuticals, cosmetics, nutrients, chemicals, fertilizers, or materials) can be obtained during the process. In this sense, high-value low-volume bioproducts would upsurge the profitability of the biorefinery while the low-value high-volume bioproducts, related to the production of biofuels, would reduce the energy cost and deliver supplementary incomes (Budzianowski, 2017; Rosales-Calderon and Arantes, 2019).

Therefore, agro-food wastes can be a source of a wide variety of valuable products within a biorefinery scheme. The major constituents of plant-derived wastes are glucan (cellulose or starch), hemicelluloses, and lignin that can be employed as intermediates for manufacturing other compounds. However, there are other interesting minority products with higher value such as antioxidant compounds (e.g. polyphenols), vitamins, oils, and proteins, among others, that can be obtained from agro-food wastes (Chew et al., 2017; Jin et al., 2018).

One of the most consumed fruits worldwide, especially in the last decades, is avocado. Its processing causes huge amounts of wastes (peel and seed) that possess a high potential for the obtainment of marketable products (phenols, flavonoids, saponins, tannins, steroids...) with interesting and promising applications in the food industry. In this context, given that the seed and peel represent up to the 30 % of the total avocado weight, their valorization may open the path towards the reduction of waste production and provide economic profitability (Dávila et al., 2017b).

Therefore, this review displays diverse strategies described in the literature for the valorization of avocado industry residues and proffer a novel strategy for the integral valorization of its wastes, boosting the economic profitability of this industry and lessening the negative environmental effects. In addition to that, a comprehensive review of the state of the art was performed whilst taking into consideration the prospects and challenges for implementing a biorefinery based on the valorization of avocado wastes.

2. Avocado and its processing waste -Composition & characterization of avocado wastes

Avocado is one of the most widely produced and consumed tropical fruits in the world, whose demand has significantly grown in the last few years (Tamayo-Ramos et al., 2022). The global avocado production raised 13.9 % between 2019 and 2020, raising the avocado production from 7 million tons in 2019 to 8 million tons in 2020. The main producers are Central American and Caribbean countries, accounting for 78 % of the world output. In particular, Mexico is the leading avocado producer, with 2,330,889 tons in 2019, almost 33 % of the world's production (FAOSTAT, 2020). However, the main avocado importer is the USA followed by the Netherlands and France (Ahmad and Danish, 2022). Different varieties of avocados are grown around the world, including Bacon, Ettinger, Pinkerton, Reed, Fuerte, and Lula, among others (Araújo et al., 2018). In particular, the Hass variety stands out since it dominates the international market thanks to its long shelf life and high nutritional quality (Ahmad and Danish, 2022).

Avocado fruit is pear-shaped, oval, or nearly round, which pulp (mesocarp) vary from entirely pale to rich-yellow, buttery and soft, and nutlike in flavor (Araújo et al., 2018). The skin (exocarp) may be deep-green or a very dark-green, smooth or pebbled, glossy or dull, thin or leathery, up to 6 mm thick, pliable or granular and brittle. The avocado fruit presents a single seed (endocarp) rounded or ovoid, of ivory color, enclosed in two brown, thin, papery seed coats (Araújo et al., 2018).

Avocado is mostly consumed as fresh fruit; however, in recent years, industrial processing to extract oil or produce guacamole or sauces has attracted growing interest. The avocado processing industry only uses

pulp, so the seeds and peels are commonly discarded. These by-products represent about 21–30 % of the fresh fruit weight (Mora-Sandí et al., 2021), which accounted for an average production of 2 million tons of avocado seeds and peels in 2019. Their improper management generates a serious environmental problems due to the large quantities produced and the lack of commercially valuable applications for these biowastes (Salazar-López et al., 2020). However, various studies on avocado by-products have suggested the presence of a wide range of interesting compounds in their composition. Table 1 shows the chemical composition of avocado by-products of different varieties. The predominant constituents include carbohydrates, lipids, proteins, dietary fiber, vitamins, minerals, and phenolic compounds (Salazar-López et al., 2020). The differences in the composition of the wastes can be mainly attributed to the different cultivars analyzed, as well as other factors that influence the composition of the fruit during its growth, such as the region of avocado production, climate, altitude, and others (Araújo et al., 2018).

The composition of avocado by-products clearly indicates that these biomasses have tremendous potential as source of valuable compounds with uses in different industrial sectors. Particularly, bioactive compounds such as phenolic compounds (hydroxycinnamic acids, hydroxybenzoic acids, flavonoids and proanthocyanidins), carotenoids, alkaloids, acetogenins and phytosterols have been identified (Salazar-López et al., 2020). These compounds can be used as nutraceuticals but also with other applications in food, health, pigment and material sectors. Starch and pectin, widely used in the food industry, can be solubilized from avocado by-products. Additionally, avocado by-products represent a very important source for energy and biofuel production, due to their composition rich in polysaccharides and lipids.

3. Green processing of avocado wastes for integral valorization

Current biomass processing technologies must promote environmentally friendly practices while, at the same time, providing high extraction yields. Attending to the chemical composition of avocado wastes, an attractive strategy for its integral valorization could include the first stage to extract bioactive compounds (such as phenols and/or oligosaccharides), yielding a solid residue that could be subsequently processed under harsher conditions to improve the enzymatic access to polysaccharides (including cellulose and/or starch) for biofuels production.

Nevertheless, few works in the literature reported a process configuration using sequential biomass treatments for selective separation to obtain multi-products from avocado wastes. For instance, an integrated strategy for the co-production of oligosaccharides (14 g/100 g of avocado peel) and phenolic compounds (3.48 g GAE (gallic acid equivalent)/100 g of avocado peel) with antioxidant activity (10.80 g Trolox equivalents/100 g of avocado peel) using hydrothermal treatment at 150 °C was proposed by Del Castillo-Llamas et al. (2021b). This work

shows the potential of autohydrolysis as a suitable technology for the conversion of this residue into bioactive compounds. Alternatively, di Bitonto et al. (2021) proposed the recovery of lipids (enriched in terpenoids) from avocado seeds, followed by the valorization of structural carbohydrates for the synthesis of biofuels and fine chemicals and lignin as bioadsorbent for wastewater treatment. Ahmad and Danish, (2022) reviewed the application of avocado waste as raw material to develop an efficient adsorbent and its use against various pollutants.

For instance, leaves, peels, seeds, and pomace can be treated by chemical and/or physicochemical extraction to obtain antioxidant compounds. On the other hand, avocado peels and seeds may be submitted to hydrothermal, thermochemical, physical, physicochemical, or biological pretreatment in order to enhance the biochemical conversion of cellulose and hemicellulose into ethanol and xylitol by saccharification and fermentation processes. Moreover, thermochemical processes (such as transesterification, liquefaction, torrefaction, pyrolysis, or gasification) could be also proposed to produce biodiesel, bio-oil, biochar, and/or syngas from avocado peels, seeds, and rotten fruit.

Therefore, the technologies employed for avocado waste processing play a key role in the development and feasibility of multi-product biorefineries since they allow the selected separation of main compounds enabling their further valorization. In this sense, recent advances in cutting-edge technologies for the extraction of value-added compounds within a biorefinery approach were recently reviewed by Del Castillo-Llamas et al. (2021a). Among these extraction methods, the most common division includes: i) traditional or conventional techniques (such as maceration, hydro-distillation, and liquid-liquid extraction), and ii) emerging or unconventional technologies (namely, ultrasound, microwave-assisted extraction-MAE, supercritical fluid extraction, pressurized liquid extraction-PLE). Generally, the optimization for phenols extraction evaluates parameters such as time, temperature, and percentage of solvent mixture (Colombo and Papetti, 2019). Maceration can include the use of dried avocado raw material and boiling water or a mixture of solvents (such as acetone/water or ethanol/water) to yield an extract enriched in antioxidant phenolics. For instance, hexane and ethanol were employed for the extraction of minerals, phenolic compounds, flavonoids, and lipids from avocado peels and seeds, evaluating their nutritional and functional value (namely, antioxidant potential, neuroprotective efficacy and acetylcholinesterase inhibition) (da Silva et al., 2022).

Certain procedures, such as oil extraction from exhausted avocado pulp, still use conventional extraction methods. As for instance, Soxhlet extraction allowed oil extraction yields of 61.51 % (Arimalala et al., 2022) and 78.95 % (Li et al., 2019) (Table 2). Comparatively, unconventional methods of extraction show several advantages such as shorter extraction times, higher efficiency and selectivity, lower solvent and energy consumption than traditional methods, and the capability to recover bioactive compounds that are particularly sensitive to thermal treatments (Del Castillo-Llamas et al., 2021a). Among these emerging

Table 1
Chemical composition of avocado by-products of different varieties (wet basis, % w/w).

| Variety | Moisture | Protein | Lipid | Ash | Carbohydrates | Reference | |
|---------|--------------------|--------------------|-----------------------|--------------------|-------------------|-------------------|------------------------------------|
| Seed | Thompson red | 60.511 | 0.20 | 2.09 | 1.93 | 35.27* | Tan et al. (2022) |
| Peel | | 68.44 | 0.52 | 8.62 | 2.89 | 19.53* | |
| Pulp | | 73.67 | 0.73 | 20.79 | 1.47 | 3.34* | |
| Seed | n.d. | 67.20 | 2.30 ¹ | 3.90 ¹ | 2.30 ¹ | – | Morais et al. (2017) |
| Peel | | 65.70 | 6.30 ¹ | 3.50 ¹ | 1.50 ¹ | – | |
| Pulp | | 86.70 | 12.50 ¹ | 28.60 ¹ | 2.10 ¹ | – | |
| Seed | Negra de la Cruz | 58.701 | 0.60 | 1.32 | 1.10 | 33.51 | Flores et al. (2019) |
| Seed | Hass | 57.61 | 1.91 | 2.02 | 1.52 | 32.04 | |
| Pulp | Fortuna | 72.10 | 1.20 | 15.60 | 0.68 | n.d. | Abaide et al. (2017) |
| | Lignin | Cellulose | Hemicelluloses | Extractives | Ash | Moisture | Reference |
| Peel | 41.91 ¹ | 19.43 ¹ | 26.51 ¹ | 8.01 ¹ | 2.81 ¹ | – | Del Castillo-Llamas et al. (2021b) |
| Peel | 4.37 ¹ | 27.58 ¹ | 25.30 ¹ | 34.38 ¹ | 1.04 ¹ | 7.33 ¹ | Dávila et al. (2017b) |
| Seed | 1.79 ¹ | 6.48 ¹ | 47.88 ¹ | 35.95 ¹ | 0.87 ¹ | 7.02 ¹ | |

* carbohydrates calculated by difference; ¹ dry basis (%).

Table 2

Multi-products obtained from Avocado Waste Biorefinery: technologies for processing, yields and waste sources.

| Target product | Avocado Waste | Processing technology and conditions | Main results (yield) | References |
|--|----------------------|--|--|-------------------------------------|
| Bioactive Compounds (phenolic compounds) | Seed | MAE (70 % acetone–water; 72.18 °C and 19.01 min) | 307.09 mg GAE/g extract of polyphenolic content | Araújo et al. (2020a) |
| | Seed and Peel | Vacuum microwave-assisted aqueous extraction (VMAAE) 79.64 °C/11.89 min (Peel) 43.90 °C/10.18 min (Seed) | 0.352 g GAE/g fresh AP/min 0.124 g GAE/g fresh AS/min | Skenderidis et al. (2021) |
| | Peel | Hydrothermal treatment (150 °C, LSR = 8 kg/kg) | 3.48 g GAE/100 g AP | Del Castillo-Llamas et al., (2021b) |
| | Peel | Sonication (15 min at 60 °C) followed by MAE (95.1 s) with 80 % ethanol–water | 166.3 mg GAE/g dry matter | Trujillo-Mayol et al. (2019) |
| | Seed | Ultrasound-assisted batch extraction (60 °C and 80 % of power) | 42.5 mg GAE/g fresh matter | Segovia et al. (2016) |
| | Peel | Hexane maceration | 26.33 mg GAE/g extract; 1243.78 mg QE/g extract | da Silva et al. (2022) |
| | Peel | UAE (38.46 % of ethanol–water, 44.06 min and 50 °C) | 45.34 mg GAE/g dried avocado peel | Rodríguez-Martínez et al. (2021) |
| | Seed | Hexane maceration | 32.48 mg GAE/g extract; 1199.04 mg QE/g extract | da Silva et al. (2022) |
| | Ethanol | Seed | Starch extraction (water solvent, alkali and enzymes) | 15.1 % of ethanol |
| Biogas | Seed | Steam pretreatment and cellulases enzymes | 152.5 NmL methane/g biomass | Vintila et al. (2019) |
| Lipids | Seed | Hexane (solid liquid ratio 1:4) | terpenoids | di Bitonto et al. (2021) |
| Oligosaccharides | Peel | Hydrothermal treatment (150 °C, LSR = 8 kg/kg) | 14.3 g/100 g of peels | Del Castillo-Llamas et al., (2021b) |
| Starch | Seed | Treated at 39.9 °C for 2.7 h | 64 % of starch yield | Tesfaye et al. (2018) |
| | Seed | Microwave-assisted extraction (161.09 °C for 56.23 min) | 49.52 % extraction yield | Araújo et al. (2020b) |
| Pectin | Peel | 70 % ethanol–water extraction (80 °C for 5 min) | 70–85 % of pectin recovery | Sivamani et al. (2021) |
| Biochar nanocomposite (adsorbent) | Peel | mixed with FeCl ₃ ·6H ₂ O, treated at 180 °C for 12 h and dried | 25.98 m ² /g surface area and 8.25 nm pore diameter | Prabakaran et al. (2022) |
| Biochar (enzyme immobilization) | Seed | Pyrolysis from 25 to 500 °C at a rate of 10 °C /min; treated with citric acid and glutaraldehyde | 26.7 % yield; efficient for acetaminophen sorption and biotransformation | Hoinacki Da Silva et al. (2022) |
| Pigments | Peel, seeds and pulp | Chloroform/methanol (2:1) extraction, drying, and dissolved in acetone (80 %) | Chlorophyll and carotenoids were concentrated in the peels | Wang et al. (2010) |
| Oil | Pulp | Soxhlet extraction with hexane (70 °C for 12 h) | 61.51 % of oil yield | Arimalala et al. (2022) |
| Oil | Pulp | Soxhlet aqueous extraction (75 °C for 150 min) | 78.95 % of oil extraction yield | Li et al. (2019) |
| Food preservative powder (preventing lipid peroxidation) | Wastewater | Three-phase decanter at 20 °C and spray drying (flow rate of 5.8 g/min at 160 °C) | 49 % of wastewaters spray dried yield | Permal et al. (2020) |

MAE: microwave-assisted extraction; UAE: ultrasound assisted extraction; GAE: gallic acid equivalent for the measurement of total phenolic content; QE: quercetin equivalent for the measurement of total flavonoid content AP: avocado peel, AS: avocado seed.

techniques, MAE has been widely employed for antioxidant compounds extraction from several agro-industrial residues, such as avocado by-products (see Table 2). The evaluation of acetone and ethanol as solvents for bioactive compounds extraction from avocado peels using microwave technology was carried out by two experimental designs, yielding similar optimized values for total phenolic compounds of 379 and 354 mg GAE/g dry extract, respectively (Araújo et al., 2021). Comparatively, MAE was also evaluated for bioactive compounds extraction from avocado seeds obtaining 307 and 254.4 mg of GAE/g of extract using acetone and ethanol as solvents, respectively (Araújo et al., 2020a). In order to avoid the use of organic solvents, vacuum microwave-assisted aqueous extraction emerges as interesting alternative enabling the efficient extraction of polyphenolic compounds from peels and seeds (Skenderidis et al., 2021). Moreover, other unconventional methods such as ultrasounds, pressurized liquid extraction and accelerated solvent extraction were also used to extract antioxidant compounds from fruit residues such as avocado wastes (see Table 2). Segovia et al. (2016) employed mathematical modelling for the optimization of ultrasound-assisted batch and continuous extraction of polyphenols from avocado seeds, showing a significant effect of the power and temperature used. Shear forces produced by this method provoke the cavitation of food waste, improving the extraction of bioactive molecules. Interesting results were reported by Rodríguez-Martínez et al. (2021) from avocado peels using ultrasound-assisted extraction with 38.46 % of ethanol–water, for 44.06 min and at 50 °C, achieving 45.34 mg of GAE/g of dried avocado peel, which was composed mainly by 4-hydroxybenzoic acid, chlorogenic acid, benzoic

acid and *p*-coumaric acid. In addition, these extracts negatively affected cancer cells while exhibiting no toxic effects on normal cells.

PLE, considered a clean and eco-friendly alternative, was also employed to improve phenolic compounds yield compared to the conventional extraction method from avocado peels (Figueroa et al., 2018).

Besides antioxidant phenolic compounds, starch, oligosaccharides even pectin and/or pectin oligosaccharides can be also solubilized from avocado by-products using green technologies such as aqueous processing (also known hydrothermal treatment or autohydrolysis) or with other green solvents (Araújo et al., 2020b; Del Castillo-Llamas et al., 2021b; Silva et al., 2017).

Recently, different Mexican waste biomasses were evaluated for the production of bioenergy and fine chemicals, and avocado seeds stood out for their lipid and starch content (di Bitonto et al., 2021). Replacement of fossil fuels with biomass as raw material for biofuel and chemical production is the main driving force for the development of biorefineries. In this sense, avocado wastes were also investigated as renewable sources to produce biofuels (solid fuel, ethanol, and biogas). Direct use of solid fuel was evaluated, achieving a high heating value of 19.145 MJ/kg from avocado seed (Perea-Moreno et al., 2016). On the other hand, bioethanol was produced from starch derived from avocado seed pretreated by water, alkali and enzymatic saccharification (Ginting et al., 2020). On the other hand, Araújo et al. (2020b) optimized the operational conditions for starch extraction by hydrothermal-microwave processing using Mexican avocado seeds, attaining a yield of 49.52 % at 161.09 °C for 56.23 min, which was higher than that obtained via conventional extraction methods. Besides the potential use

of starch as source of fermentable sugars for bioethanol production, 19.54 % of this polysaccharide was extracted from avocado seed (using distilled water containing 0.2 % of sodium metabisulfite) and physico-chemically characterized for further application as edible and/or biodegradable films (Martins et al., 2022). Moreover, batch extraction of oil from avocado seeds was proposed for biodiesel production with comparable fuel features (Sathish et al., 2021).

4. A new biorefinery strategy for avocado waste valorization

The use of food processing waste as substrates in an integrated biorefinery system to produce high-value marketable biochemicals enables the sustainable management of these by-products while promoting economic opportunities, environmental benefits, and energy security (Kahar et al., 2022; Qin et al., 2021). In addition, biowaste-based biorefinery can promote the development of a circular bio-economy and contribute to the implementation of 'zero waste policies' proposed by the 2030 Agenda (Dahiya et al., 2018).

Taking into account the chemical composition of the avocado by-products reported in the literature (feedstock rich in cellulose, starch, lignin, protein, phenolic compounds, etc.), in this review it is proposed another possible integrated biorefinery design focused on the avocado by-products to obtain three major compounds with attractive market demand, namely phenolic extracts (PE), succinic acid (SA) and pectooligosaccharides (POS). To the best of the authors' knowledge, there is no study evaluating the conversion of avocado residues for the manufacture of these three products in the same biorefinery scheme. The selection of these three target compounds was based on the following criteria:

- The global demand for antioxidants compounds is estimated to be valued USD 1.3 billion in 2020 and is expected to achieve a value of USD 1.8 billion by 2025. This high market potential is mainly due to the many beneficial effects associated with these compounds, as well as their important role in food preservation. In addition, antioxidants obtained from natural sources are expected to have a greater commercial interest due to the harmful effects on human health related to synthetic antioxidants.
- POS are attracting much attention as novel prebiotic ingredients due to their many health benefits including the modulation of gut

microbiota, prevention of colon cancer, reduction of cholesterol levels and obesity risk, and cardiovascular protection, *inter alia* (Gullón et al., 2021). In this framework, the avocado peel shows great potential for the recovery of these compounds in an integrated biorefinery model. In fact, Del Castillo-Llamas et al. (2021b) reported the production of POS at a laboratory scale using hydrothermal processing.

- The global SA market is valued at USD 175.7 million in 2017 and is projected to achieve USD 900 million by 2026, growing at a compound annual growth rate (CAGR) of 20 % (Oreoluwa Jokodola et al., 2022). SA (1,4-butanedioic acid) is a dicarboxylic acid that has been identified by the US Department of Energy's list as one of the top value-added chemicals that can be obtained from biorefinery carbohydrates. The high market potential of SA is due to its wide range of applications in chemical, food, pharmaceutical and biodegradable polymer fields (González-García et al., 2018). Moreover, this organic acid is also used as a precursor for the synthesis of many petrochemical products such as 1,4-butanediol, tetrahydrofuran, γ -butyrolactone and polybutylene succinates, among others (Xu et al., 2021).

Fig. 1 displays the block diagram process for integrating avocado residues in a possible biorefinery model. In summary, the integrated process involves three main sections: extraction of phenolic compounds, autohydrolysis treatment and fermentation.

To recover antioxidant compounds from the combined seed and peel by-products, conventional extraction can be applied. This method was selected due to its ease of implementation on an industrial scale, and the lower economic cost compared to other technologies (Santiago et al., 2020). Ethanol was considered as a solvent for the extraction of polyphenols. Both matrices are authorized by the European Food Safety Authority (EFSA) for food, pharmaceutical and cosmetic applications (Gullón et al., 2018). In this sense, around 4.37–4.50 kg of phenolic compounds would be obtained from ethanol extraction of avocado peel (Rodríguez-Martínez et al., 2021) and avocado seed (Segovia-Gómez et al., 2014) (see Fig. 1).

After this initial processing, the antioxidant-free solid can be subjected to hot water treatment (also called autohydrolysis) for the solubilization of pectooligosaccharides (in the case of peels) and starch (in

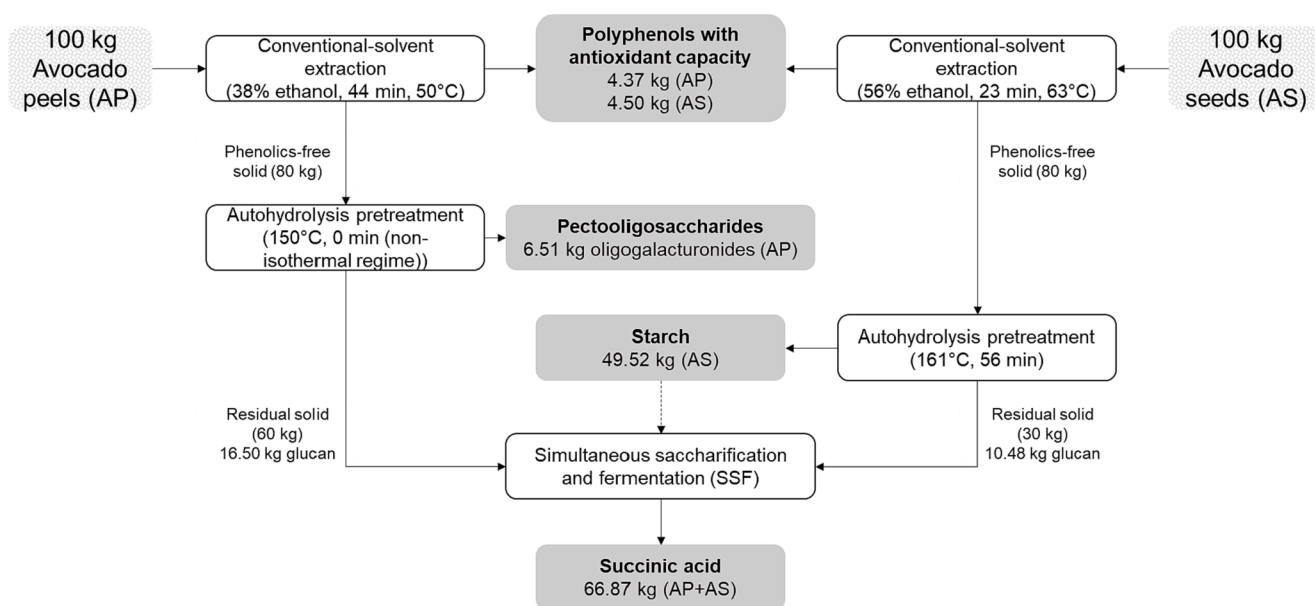


Fig. 1. Designed biorefinery for the integral valorization of avocado by-products proposed in this review. Mass balance diagram expressed in kg of component per 200 kg of avocado by-products (100 kg of avocado peel (AP) and 100 kg of avocado seed (AS)). Data and information extracted from Araújo et al., 2020b; Del Castillo-Llamas et al., 2021b; Rodríguez-Martínez et al., 2021; Segovia-Gómez et al., 2014; Song and Lee, 2006.

the case of seeds). This technology has been widely used for the solubilization of different polysaccharides present in agri-food wastes, including avocado seeds (Araújo et al., 2020b), avocado peels (Del Castillo-Llamas et al., 2021b), walnut shells (Morales et al., 2020b), and almond shells (Morales et al., 2020a), among others. This stage may also be carried out by applying an innovative technology such as microwave extraction (del Río et al., 2021). In fact, Araújo et al. (2020b) demonstrated the suitability of this technology to extract starch from avocado seeds and del Amo-Mateos et al. (2022) to recover POS from sugar beet pulp. This processing would enable the recovery of 6.51 kg of pectooligosaccharides (measured as oligogalacturonides) from AP (Del Castillo-Llamas et al., 2021b), and around 49.52 kg of starch from AS (Araújo et al., 2020b) (see Fig. 1).

The remaining solid fraction obtained from the hydrothermal processing is essentially composed by cellulose and presents good enzymatic digestibility to produce glucose, which can be converted into SA via biotechnological processes. Moreover, the liquid phase from the autohydrolysis treatment (rich in starch) would also be used to produce SA. Among the different microorganisms identified as natural SA producers, *Actinobacillus succinogenes* has been described as one of the most promising bacterial species for industrial use (Nieder-Heitmann et al., 2019). In this sense, considering a maximum potential production of 1.5 mol of SA per mol of glucose, with a yield of 80 %, up to 66.87 kg of SA could be obtained from the residual glucan of AP and AS, and the starch extracted from AS (see Fig. 1).

Some biorefinery models to produce SA, and other value-added compounds from different agro-industrial by-products, have been considered in the literature. For instance, Ioannidou et al. (2022) developed a novel biorefinery scheme using various waste streams generated by wineries for the production of SA, crude phenolic-rich extract, grape-seed oil, calcium tartrate and crude tannin-rich extract. Filippi et al. (2022) also used winery wastes to design a holistic biorefinery for the manufacture of bacterial cellulose, SA, and other value-added co-products. In another study, Dogbe et al. (2021) reported a novel biorefinery based on the valorization of molasses into SA and fructooligosaccharides. Patsalou et al. (2017) proposed a citrus peel waste-based biorefinery platform to obtain essential oils, pectins, and SA.

Although the production of SA is already carried out at an industrial scale, the development of biorefineries based on agro-industrial wastes for the production of this top platform chemical is still in the research and development stage.

5. Prospects and challenges of the avocado waste bio-based refinery in bio-economy

The new bio-economy vision is based on unlocking the full potential of all types of sustainably sourced biomass including residual biomasses such as avocado waste from the avocado processing industry. As detailed in this review, this residual stream can be converted into a wide range of marketable bioproducts and materials with application in several sectors, including food, cosmetics, pharmaceutical, energy, and the environmental. However, for their full utilization moving towards the zero-discharge system, extensive research and development work should be performed to develop appropriate technologies. Hence, integrating the production of two or more bioproducts with energy and/or biofuel is a desired goal in the avocado waste biorefinery schemes. In this sense, some of the valorization strategies reviewed here could be compatible and hence integrated with a new avocado waste biorefinery. Dávila et al. (2017b) reported that the model biorefinery of avocado towards microencapsulated phenolic compounds extract, ethanol, oil, and xylitol can be an attractive opportunity. On the other hand, the model scheme reported by Del Castillo-Llamas et al. (2021a) proposed the manufacturing of several high value-added products with significant applications in the food, pharmaceutical, chemistry and cosmetic industries: i) oil or essential oils, ii) polyphenols, iii) starch, pectin and/or

oligosaccharides, iv) aromatic compounds from lignin, v) nanocrystalline cellulose and vi) ethanol, xylitol and/or SA. In the developed biorefinery scheme, the authors selected cutting-edge extraction techniques such as MAE, UAE as well as alternative solvents (for instance, deep eutectic solvents).

Most of the studies presented in this review are developed at a low technology readiness level and therefore, lack information on their viability and performance at industrial scale. Critical aspects for the development of future sustainable industrial processes include: i) the technical feasibility at industrial scale, ii) the analysis of their techno-economic potential, and iii) a life cycle-based environmental assessment (Caldeira et al., 2020). In this sense, most of the reported works evaluated valorization strategies at laboratory scale, treating a few grams of avocado waste. Only a few of them were tested in pilot plants, as reported in the work by Skenderidis et al. (2021) who used an industrial microwave extractor for the extraction of 2 kg of peel and seed residues. It should be considered that many valorization options of food waste can be difficult to implement at a larger scale. As for instance, enzyme assisted extraction, supercritical fluid extraction with CO₂ or steam diffusion are still difficult to implement at industrial scale with good yields (Caldeira et al., 2020). Other techniques involving the use of solvents, such as conventional extraction, would require explosive atmosphere-certified facilities (ATEX) with the subsequent capital expenditure. Therefore, the scale-up of these preliminary investigations is still a pending issue for both the scientific and the industrial communities (Caldeira et al., 2020).

Furthermore, data from pilot studies are essential to perform techno-economic and environmental analyses. The environmental analysis, considering total inputs, outputs, and potential environmental impacts throughout the product life cycle, i.e., a life cycle assessment, is especially relevant to ensure the sustainability of the integrated biorefinery. Situations in which the additional impact caused by the valorization processes exceeds the environmental benefit derived from re-using a stream of avocado residues should be avoided. However, relatively few environmental analyses were found. To the best of the authors' knowledge, there are no studies on the environmental assessment of avocado waste biorefineries. Only two works estimated the environmental impacts of avocado biorefineries, but using the whole fruit as feedstock (Dávila et al., 2017b; Solarte-Toro et al., 2022). Energy and mass integration are considered critical factors in the environmental analysis, as reported by Dávila et al. (2017a). In this work, recovery of the CO₂ and ethanol used for the extraction of phenolics was shown to substantially decrease the potential environmental impact (PEI) of the process.

In parallel, the techno-economic evaluation is needed to identify high performance biorefineries, which can manufacture a wide spectrum of bio-based products competitive with their conventional equivalents. In the work by Dávila et al. (2017b), the feasibility of a biorefinery processing avocado fruit into oil, microencapsulated phenolic compounds, ethanol and xylitol was evaluated. Energy and mass integration were found as critical factors to reduce the total production costs. Regarding the extraction and production of microencapsulated phenolic compounds, the high sale prices of this product would compensate the high production costs associated to all products in the biorefinery. Also, starch extraction from waste avocado seeds has been shown to be an economically viable and environmentally sustainable process (Tesfaye et al., 2021). On the other hand, the study carried out by Trujillo-Mayol et al. (2019), showed that microwave technology is the most economically viable extraction technique compared to ultrasound or conventional method since it reduces energy costs.

Table 3 shows some works focused on the technoeconomic and life cycle assessment of different biorefinery models using several agri-food by-products.

It is important to highlight that these biorefinery systems do not consider the production capacity of the raw material by region or the needs of the country, being key aspects to define the biorefinery scale

Table 3

Techno-economic and/or environmental analysis of biorefineries based on the valorization of agro-industrial by-products for the production of succinic acid, oligosaccharides, oils and antioxidant compounds.

| Agro-industrial by-product | Capacity | Target compounds and proposed scenarios | LCA | TEA | Methodology and software | Outcomes | Reference |
|--|---|---|-----|-----|---|--|-------------------------------|
| Apple pomace | 8444 kg (batch) | Succinic acid production with enzyme production (<i>Plant A2</i>) Succinic acid production without enzyme production (<i>Plant C</i>) | + | | CML 2001 method v2.05 SimaPro v8.2 | 4669 kg Succinic acid GWP: 504 kg CO ₂ eq with enzyme production; GWP: 5.38 kg CO ₂ eq without enzyme production | González-García et al. (2018) |
| Onion solid waste | 60766 kg (batch) | Flavonol quercetin and fructooligosaccharides (FOS) | + | | Apex Plus® software University-CML 2001 method v2.05 SimaPro v9.0.0. | 5 kg Flavonol quercetin and 1 kg FOS GWP: 473 kg CO ₂ eq/kg Quercetin GWO: 214 kg CO ₂ eq/kg FOS | Santiago et al. (2020) |
| Winery waste: Grape pomace, grape stalks and wine lees | 805,536 wet t/year | Succinic acid (SA), crude phenolic-rich extract (CPE), grape-seed oil (GO), calcium tartrate (CaT) and crude tannin-rich extract (CTE) | + | + | CML 2011 methodology LC software GaBi | 30,250 t/year AS; 8,819 t/year CPE; 1,982 t/year CaT; 3,763 t/year GO; 60,332 t/year CTE MSP: \$1.23–2.76/kg SA GWP: 1.47 kg CO ₂ -eq/kg waste ADP: 25.2 MJ/kg waste | Ioannidou et al. (2022) |
| Waste apple slurry | 99,244.17 kg/h | Succinic acid and bioelectricity (<i>scenario1</i>) Succinic acid and biogas (<i>scenario2</i>) | | + | Aspen Plus® V11 | Mass flow of succinic acid: 14,858.7 ton/year Electricity generated: 385.4 kW MSP: 0.73 \$/kg <i>Scenario1</i> ; 0.33 \$/kg <i>Scenario2</i> | Okoro and Shavandi, (2022) |
| Sugarcane Sucrose-rich Molasses | 21.2 t/h | Succinic acid-SA (<i>scenario1</i>); fructooligosaccharides-FOS (<i>scenario2</i>); FOS syrup (<i>scenario3</i>); 30 % FOS syrup + 70 % succinic acid (<i>scenario4</i>); FOS syrup + invert sugar + succinic acid (<i>scenario5</i>) | | + | Aspen Plus® V.8.8. Aggregated system exergoeconomics | Scenario1: total cost rate of 1690 \$/h, investment cost 713 \$/h and SA production of 11,576 kg/h Scenario3: total cost rate of 547 \$/h | Dogbe et al. (2021) |
| Citrus peel waste (CPW) | 1 t/day for 300 days per year | Essential oils, pectin and succinic acid: acid treatment for hydrolysis (<i>scenario1</i>), combination of acid and enzymatic hydrolysis (<i>scenario2</i>) | | + | not provided | 4.3 kg essential oils and 23.25 kg of pectin per t of CPW 12.26 kg/t CPW of succinic acid (<i>scenario1</i>) and 16.6 kg/t (<i>scenario2</i>) Annual revenue: \$12,900 (<i>scenario1</i>); \$141,420 | Patsalou et al. (2017) |
| Sugarcane bagasse and trash lignocellulose | 421,200 t/year | PHB and electricity (<i>scenarioA</i>) Succinic acid, PHB and electricity (<i>scenarioB</i>) Succinic acid and electricity (<i>scenarioC</i>) | | + | Aspen Plus® v8.8 | For selling price of 1500 \$/t of succinic acid; 11,424 \$/t PHB and 0.08 \$ kW-h of electricity, all scenarios except <i>scenario A</i> are profitable. | Nieder-Heitmann et al. (2019) |
| Sugar beet pulp | | antioxidant-rich extract, pectin and succinic acid | | + | Preliminary techno-economic evaluation | 40,000 t/year succinic acid Indicative profitability potential of 2.7 \$/kg 7.2 t CO ₂ per t of succinic acid | Alexandri et al. (2019) |
| Spent pulp of Colombian Andes Berry | 16,000 t/year | Phenolic compounds, ethanol, xylitol and cogeneration plant | + | + | Aspen Plus V8.0; Waste Reduction algorithm (WAR) | 150.8 t/year of xylitol, 217.76 t/year of ethanol and 8.06 t/year of phenolic compounds Sale to total production cost ratio: 19.36 GWP: 5.03·10 ⁻³ PEI/kg of product for leaving PEI | Dávila et al. (2017a) |
| Creole avocado | 420 t/year (<i>scenario1</i>) 5600 t/year (<i>scenario2</i>) | Small-scale biorefineries: a) Avocado oil, animal feed and electricity production-Small-B ₁ ; b) Guacamole and electricity-SmallB ₂ (<i>scenario1</i>) Large-scale biorefineries: a) Levulinic acid, furfural and lignin production from seeds and peels processing-LargeB ₁ ; b) lactic acid, xylitol and lignin production-LargeB ₂ (<i>scenario2</i>) | | + | Aspen Plus v9.0 | 78.2 kg of avocado oil, 150 kg of animal feed and 28.52 m ³ biogas per t of avocado 28.52 kg/t of avocado 1.25 kg avocado oil/day; 23.83 kg of levulinic, 1.1 kg formic, 19.45 kg furfural and 21.98 kg lignin per h 1.25 kg avocado oil/day; 19.75 kg lactic, 16.70 kg xylitol and 21.98 kg lignin per h MPSEF: 0.85 t/year for SmallB ₁ ; 1.1 t/year for SmallB ₂ ; 15.50 t/day for | Solarte-Toro et al. (2021) |

(continued on next page)

Table 3 (continued)

| Agro-industrial by-product | Capacity | Target compounds and proposed scenarios | LCA | TEA | Methodology and software | Outcomes | Reference |
|----------------------------|-------------|---|-----|-----|--|---|----------------------------|
| Creole avocado | 420 t/y | Avocado oil and animal feed at small scale (<i>scenario1</i>) Guacamole production at small scale (<i>scenario2</i>) | + | | E-LCA methodology (ISO 14040); SimaPro 8.3 software Aspen Plus v.9.0. | LargeB ₁ ; 41.95 t/day for LargeB ₂ Carbon and water footprints of 8.99 kg CO ₂ -eq/kg and 6.63 m ³ /kg for scenario1 Carbon and water footprints of 0.72 kg CO ₂ -eq/kg and 1.38 m ³ /kg for scenario2 | Solarte-Toro et al. (2022) |
| Waste avocado seeds | 2000 t/year | Starch biopolymer | + | + | | 837.5 US\$/t selling price Pay-back period of 2 years Return on investment of 75.12 % | Tesfaye et al. (2021) |

*LCA: Life cycle Analysis; *TEA: Techno-economic Analysis; GWP: Global Warming Potential; ADP: Abiotic Depletion Potential; MSP: Minimum selling Price; SA: succinic acid; PEI: Potential environment impact; MPSEF: Minimum Processing Scale for Economic Feasibility.

(small or large scale) or the most appropriate portfolio of products (Solarte-Toro et al., 2021). In this sense, small-scale facilities have the advantage of reducing the costs associated with the transport of raw materials, so implementing these systems could be a suitable strategy in rural areas, improving the socioeconomic and environmental problems of these areas. In contrast, large-scale biorefineries require large amounts of feedstock, so they are more prone to face supply chain problems issues and the increase in costs associated with raw materials. However, these large-scale systems could meet the demands of a country and have a positive effect on its economic growth. In this context, Solarte-Toro et al. (2021) evaluated the impact of the processing scale, the contextualization of the process and the different target products obtained in an avocado biorefinery. In this case, the research showed that a small-scale biorefinery to produce avocado oil, animal feed, biogas, and electricity was the most suitable option to be implemented in rural areas. In the case of large-scale facilities, the production of levulinic acid, furfural, and lignin was the most promising option for the valorization of these wastes. In this sense, the authors highlighted the importance of selecting products with high added value to achieve good economic performance.

The comprehensive economic analysis of avocado waste valorization strategies is crucial to assess whether this waste is generated in sufficient amounts in a certain geographical area, close enough to the potential biorefinery facility. Because of the characteristics of avocado waste, it can deteriorate quickly which can bring limitations in its use to produce value-added products. In fact, logistics issues of food waste valorization can be a limiting factor on the profitability of the conversion of some substrates (Banerjee et al., 2018), and these aspects have been overlooked in the literature. Except in Mexico, where avocado production takes place over the whole year, the seasonal operation of avocado industries can be a major problem that should be tackled in order to develop highly efficient and sustainable biorefineries. Seasonal flow could be buffered to some extent using air-tight storage and preservation techniques such as ensiling or bio-drying. However, supply interruptions could be addressed through the development of a multi-feedstock biorefinery approach, in which the same value-added products are obtained from different types of food waste available during the whole year. Such diversity would make biorefineries more resilient to potential feedstock availability problems. In this scenario, biorefineries must be designed to switch between seasonal feedstocks or use mixed supplies rather than a single source. As for instance, the region of Malaga in Spain, which is the largest European avocado producer, also leads the production of other subtropical fruits such as mango, custard apple or dragon fruit, which are well-known for their high amounts of health promoting bioactives as compared to traditional fruits (Villacis-Chiriboga et al., 2020). Co-production of bioactive compounds (phenolics, oils and/or pigments), biofuels and bioenergy from these seasonal feedstocks in a location, minimizing transportation costs and logistical challenges, could be a feasible alternative for a sustainable industrial process (Manhongo et al.,

2022).

6. Conclusions

Efficient utilization of avocado processing by-products through novel sustainable approaches would allow converting these residues into high-value products, reducing their accumulation, disposal and negative environmental problems. Although the biorefinery strategies are challenging due to the diverse yields, market value and demand for different range of bioproducts, integrating the manufacture of more than one bioproduct is key. Hence, the proposed biorefinery scheme would enable the production of phenolic extracts, SA and pectooligosaccharides. In addition, the lack of industrial-scale data and the scarcity of economic and environmental feasibility studies are critical aspects for the potential development of future sustainable industrial processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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