A comparison between avocado peel var. Hass and var. Lorena to obtain polyphenolic compounds

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Extended Abstract.

In 2020 the avocado world production was eight million tonnes, whereas Colombia was the second producer in the world with 876,754 tonnes [1]. During the processing of avocado (mainly into oil and guacamole products), residues such as peel and seed are generated [2]. Avocado pulp represents between 57 and 81% of the weight of the fruit. In contrast, peel and seed represent 8 - 12% and 10 - 29%, respectively [3]. The avocado variety, place of cultivation, and growing conditions are some of the reasons that lead to variations in avocado pulp, peel, and seed proportions. Davila et al, [4] reports that avocado peel is rich in cellulose, hemicellulose, and extractives. Several authors report that avocado peel present a high potential for obtaining phenolic compounds [5]–[8] Functional compounds such as phenolic acids have been identified in this residue. Chlorogenic acid and quercetin are the major polyphenols present in avocado peels [9], [10]. Quercetin has analgesic, antibacterial, antiviral, antidiabetic, anti-inflammatory, antioxidant, and anticancer properties [11].

This work proposes a comparison between the SE and UAE using avocado peel var Hass and var Lorena as raw materials to obtain polyphenolic compounds. Additionally, based on the experimental results, the simulations are proposed to perform the energetic (based on exergetic assessment) and economic assessment. The methodology used to achieve this objective is divided into five parts: (i) Avocado peels characterization, (ii) estimation of extraction conditions based on solubility analysis, (iii) process extraction (SE and UAE), (iv) quantification and extract characterization, and (v) simulation and assessment.

First stage: orange peel characterization: The physicochemical characterization of raw material is performed with three repetitions. The moisture, extractives (NREL/TP-510-42619), ash (NREL/TP-510-42622), holocellulose (ASTM D1104), cellulose (T203 os-74 ASTM 1695-77) and lignin (T222). The contents are determined according to international norms and methods [12]–[14].

Second stage: estimation of extraction conditions based on solubility analysis: The Peng–Robinson equation of state with the Stryjek Vera modification (PRSV equation of state) with the Van der Waals and Wong–Sandler (WS) mixing rules have been used to calculate solubility of quercetin in CO_2 [15]. In addition, the UNIFAC DORTMUND model is used to estimate the parameters required by the WS mixing rules [16]. The equation used to calculate the solubility of a solid in gas is:

$$y_2 = \frac{P_2^{subli}\varphi_2^{subli}}{P\varphi_2}\exp\left[\frac{V_2^s}{RT}\left(P - P_2^{subli}\right)\right]$$

P_2^{subli} corresponds to the sublimation pressure, V_2^s is the solid molar volume, φ_2^{subli} is the sublimation fugacity coefficient and φ_2 is the fugacity coefficient in the supercritical phase.

Third stage: process extraction (SE and SFE): From the solubility analysis it is possible to estimate the best combination of temperature, and solvent for the extraction process. In this work ethanol is considered as solvent in concentrations of 100%, 50%, and 0%. The process used a concentration of 0.2 g/mL of solid/solvent. In the SE 200 rpm are used, and in the UAE, an amplitude of 100%, an ultrasound power of 750 W, and a frequency of 20 kWh are considered.

Fourth stage: quantification and extract characterization: In the obtained extracts are quantified the Total Phenolic Compounds (TPC) [17], the Flavonoid content (FLA), reductor sugars (DNS), antioxidant activity using DPPH and ABTS methods [18], [19]. The equipment used is an LC-2010A HT (SHIMADZU), with a liquid chromatograph, a UV-visible detector, a quaternary pump, a vacuum-degasifier, and an automatic sampler. The chromatographic separation was performed in column C18 with a size of 150 mm x 4.6 mm and a particle size of 5 µm. The conditions for the flavonoids (epicatechin and quercetin) quantification are reported by Faraneh Zareiyanab y Habibollah Khajehsharifia [20].

Fifth stage: Simulation and assessment: The SE and UAE process design considered the experimental results and conditions used in the experimental part. The simulation is performed using Aspen plus v.9. software. The thermodynamic model used is the Non-Random Two-Liquids (NRTL), the model recommended by Bitchikh et al. and Luo et al., [21], [22]. The mass flow of avocado peel considered in the simulations in this work is 40 kg/h. The economic assessment is based in the work of Solarte et al. [23]. The cost used for the economic assessment are presented in the **Table 1**. The energetic assessment is based on previously obtained mass and energy balance using the methodology proposed by Restrepo et al [24]. As last aspect to compare the technologies, is performed an environmental assessment based on the Life Cycle Assessment (LCA). The methodology for the LCA is reported in the ISO 14040.

Table 1. Cost for raw material, reagents, utilities, and product sale

Raw material, reagents, and supplies			**Utilities**		
Component	**Price**	**Ref.**	**Component**	**Price**	**Ref.**
Avocado peel	0.022 USD/kg*		Electricity	0.13	[25]
Ethanol	0.72 USD/kg	[26]	LP steam	7.89 USD/ton	[27]
Water	0.326 USD/cum	[28]	**Product prices**		
			Extract rich in flavonoids	17 USD/kg	[29]

* Estimated transport cost taking into account transport in a six-axle truck at a distance of 20 km

Results.

Avocado peels have a high content of extractives. For example, the Hass variety has a percentage of extractives of 35.43%, while the Lorena variety has 23.42%. The extractives of the Hass variety are mainly ethanol-soluble (21.10%). In contrast, the extractives present in the Hass variety are mainly soluble in water (19.88%). The avocado peel var Lorena has a high content of polysaccharides such as cellulose and hemicellulose (52.27%). Cellulose is the most representative polysaccharide for this peel, with 33.67%. The percentage of cellulose in the Hass avocado peel is 28.41%. The hemicellulose composition corresponds to approximately 18% in both avocado peel varieties.

Using SE allowed for obtaining yields between 1.41% and 19.52% for the Hass variety and 6.76% and 8.62% for the Lorena variety. The TPC of the extracts of the two varieties presented maximum values close to 1,800 mg GAE/100 g. With the application of ultrasound to the process, keeping the other conditions constant (t=60 min, T = 60°C), an increase in extraction yield was obtained by an average of 8% for each variety. However, a decrease in TPC of 350 mg GAE/100 g is observed. Using 50% ethanol as a solvent in each process allowed for maximizing the concentration of flavonoids, among which quercetin stands out. Therefore, using SE, the Hass avocado peel had a TPC of 4,468.17 mg GAE/100 g and an FLA value of 2,868.20 mg quercetin/100 g. When UAE is used, the TPC and FLA were 4,114.16 mg GAE/100 g and 2,225.25 mg quercetin/100 g, respectively. For the Lorena variety using SE, the TPC and FLA correspond to 4,586.83 mg GAE/100 and 3,231.24 mg quercetin/100 g. When UAE is used, the TPC of the Lorena variety decreased to 4,219.9 mg GAE/100 g. The results of this work show that the extraction processes using avocado peel should be carried out in the presence of ethanol-water solutions. Ethanol is the solvent that maximizes the extraction of flavonoids such as quercetin.

The high content of extractives in the Hass variety contributes to the fact that this variety has a profit margin 15.18% higher than that of the Lorena variety. On the other hand, Hass avocado peel extract rich in flavonoids such as quercetin and quercetin have a production cost of 13.21 USD/kg using SE. Therefore, the use of UAE leads to an economic unfeasibility of both processes by increasing utility costs by 85%. Another aspect is reflected in the results of the environmental analysis by LCA. Since the varieties are grown in the same region during the same time of year under the same conditions, there are no differences in the agronomic stage of the processes. Therefore, in this work, the LCA focuses on a gate-to-gate analysis, i.e., only the processes are considered. The results showed that the main impacts are due to the generation of the exhausted solid product of the extraction. Such solids are rich in polysaccharides, showing how the biorefinery concept can contribute to the integral valorization of these residues and reduce their environmental impact.

Conclusion.

The variety of the fruit from which a residue comes is a fundamental element for selecting its valorization processes. When comparing the results of this work, it is evident that the Hass avocado peel shows higher yields in the extraction processes compared to the Lorena variety. The above is evidenced both in the SE and the UAE. The extracts of the Hass variety showed higher polyphenol content (TPC) and higher antioxidant activity (DPPH and ABTS) than those of the Lorena variety. However, the flavonoid content of both varieties is very similar. Therefore, both varieties are good sources of flavonoids. When considering the economic part in which the process yields are involved, a difference in the indicators can be appreciated. As a result, the Hass variety shows a higher profit margin than the Hass variety. As a result, the extract of the Hass variety has a lower cost in the market and is a more promising raw material for its valorization through extraction processes.

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