A biorefinery for integral valorisation of avocado peel and seeds through supercritical fluids.

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Abstract
Avocado is an important fruit of high production scale from tropical and subtropical regions. The pulp is the edible fraction of the fruit, generating great amounts of residues such as peel and seeds. These two parts present high processing possibilities, considering that they present important bioactive compounds for humans. Additionally, the residue generated from the extraction process is a promising material for gasification processes due to its composition. This work focuses on studying avocado peel and seed as raw materials for obtaining bioactive compounds and using the extraction residue in cogeneration processes, giving rise to possible integral biorefineries. Likewise, the economic feasibility of the integral use of avocado waste is analyzed.

Keywords: *Avocado Waste, Integral Biorefinery, Supercritical Fluid Extraction, Process Simulation*

1. INTRODUCTION

Avocado is a tropical and subtropical fruit native to Mexico and Central America. The pulp is the mainly consumed fraction which is rich in vitamins, minerals, and especially monounsaturated fatty acids. Two main residues are generated during processing and consumption: the peel and the seed. According to characterization studies performed by some authors (Figueroa et al., 2018; Gross et al., 1973; Tremocoldi et al., 2018; Wang et al., 2010), these residues present high contents of extractives. Functional compounds such as polyphenols, organic acids, and flavonoids have been identified in these residues. Chlorogenic acid and quercetin are the major polyphenols present in avocado peel (Kosińska et al., 2012; López-Cobo et al., 2016). While in the seed, the major components are catechin and epicatechin (Jimenez et al., 2020; Kosińska et al., 2012). Quercetin has analgesic, antibacterial, antiviral, antidiabetic, anti-inflammatory, antioxidant, and anticancer properties (Nathiya et al., 2014). Catechin has wide pharmaceutical applications due to its antimutagenic, against obesity, antibacterial, lipid-lowering, and intestinal modulating properties (Li et al., 2012). After the extraction of bioactive compounds from these residues, an exhausted solid is generated. Some studies have reported the potential of these wastes for cogeneration processes (Dávila et al., 2017). In Colombia, the avocados are cultivated in Norte de Santander, located in the eastern part of the Andes Mountains. Agriculture is one of the main pillars of the economy. In 2018 Norte de Santander had a production of 1,104,868 tons of avocado. As a result, the department presented a 1.41% national participation in avocado production (MinAgricultura, 2019). This contributes to the generation of waste that is taken to landfills. However, avocado waste has bioactive components that can be obtained through the use of different extraction technologies. Extraction with supercritical fluids is a promising alternative for the valorization of these wastes. Therefore, it offers better utilization of these wastes and decreases the load of wastes disposed of in landfills. This work analyzes the extraction process with supercritical fluids from avocado peel and seed and cogeneration of the exhausted fraction.

2. METHODOLOGY

Two main wastes are obtained from avocado (peel and seed), where their composition is presented in Table 1. In the results of the physicochemical characterization for both wastes, it is observed that both present extractive contents higher than 34%, besides presenting significant compositions of their lignocellulosic component, which leads both materials to be promising for different transformation processes. However, there is a great variety of transformation opportunities presented by avocado waste. The lignocellulosic component is the second fraction of interest in these wastes after the extractives. It is of interest to know the potential of these wastes as raw materials for cogeneration processes. By implementing this type of process, it is possible to supply the energy demand presented by the extraction processes, especially when the technology used is supercritical fluids. This is the basis for an integrated process of extraction and cogeneration. In the first process, the obtaining of bioactive compounds from each of the avocado residues is considered. Then, the solid waste is used in cogeneration processes, which will allow obtaining energy that will be fed to the extraction process. The combination of both processes would result in an integrated biorefinery, as shown in Figure 1.

Table 1. Lignocellulosic and ultimate analysis for avocado wastes

Lignocellulosic composition			**Ultimate analysis**		
Component	**Peel** [a]	**Seed** [a]	**Element**	**Peel** [b]	**Seed** [c]
Moisture	7.33	7.02	C	48.01	41.98
Extractives	34.38	35.95	H	5.755	6.77
Cellulose	27.58	6.48	N	0.447	0.66
Hemicellulose	25.30	47.88	S	0.104	NR
Lignin	4.37	1.79	O	42.8	50.58
Ash	1.04	0.87			

[a] (Dávila et al., 2017); [b] (Perea-Moreno et al., 2016); [c] (Durak and Aysu, 2015)

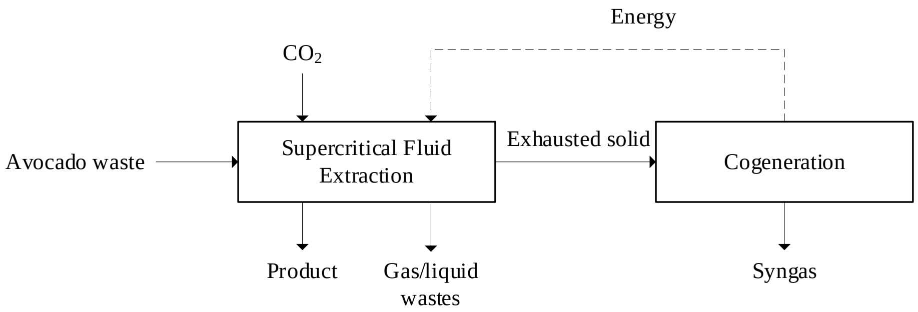

Figure 1. Processing scheme for the biorefinery based on the avocado wastes

2.1. Process design

Based on the previous information, four scenarios are proposed in this work. The cogeneration process combined with the supercritical fluid extraction (SFE) process was analyzed to propose a biorefinery system for both feedstocks. Therefore, two stand-alone scenarios (corresponding to the SFE process) and two biorefineries scenarios are proposed, as shown in Table 2

Table 2. Scenarios proposed for the use of the avocado wastes (peel and seed)

Raw material	Scenario	SFE	Cogeneration	Process type
Peel avocado	1	x		Stand-alone
	2	x	x	Biorefinery
Seed avocado	3	x		Stand-alone
	4	x	x	Biorefinery

The simulation of the processes is based on the information reported by (Cerón et al., 2012) and (Dávila et al., 2017). The design of the supercritical extraction processes and the design of the cogeneration processes are based on the work of (Puig-Gamero et al., 2018) and (García et al., 2016). According to the information presented by the authors, the design of the processes was carried out as follows:

2.1.1. Extraction process

This process employs the management of three lines of compounds, including process reactants and raw materials. The first line focuses on CO_2; this reagent is supplied to the process employing sotorage vessels. When the CO_2

leaves the cylinders, it is mixed with a recovery stream generated in the final equipment process; this mixture of CO_2 is cooled until obtaining a liquid phase, which is compressed until reaching the extraction conditions (40°C and 300 bar). Once the CO_2 has reached the extraction conditions, it is fed to the process extractor, where it remains for 60 minutes and then goes through a decompression process through valves. The decompressed CO_2 enters a collector. There is a phase separation at ambient conditions, where this phase separation is used to recover the CO_2 and recirculate 90% of the flow entering the collector. The second line refers to the circulation of ethanol throughout the extraction process. The ethanol is pumped into the process, where it is mixed with recirculated ethanol. The resulting mixture is fed into the extractor, where it reaches the extraction conditions, corresponding to 40°C and 300 bar. Once the extraction process is finished, it is decompressed and reaches a collector, where it is removed in the liquid phase, being mixed with the extract of the material used. Finally, the third line shows the flow of the raw material used throughout the process. Initially, the raw material is milled and then dried at 75°C as reported by (Saavedra et al., 2017), using air as the service fluid. Once the raw material is dry, it is taken to the extractor, where the bioactive compounds are extracted from it through the action of the solvent and co-solvent used. The material is depressurized and separated from the liquid and gas streams in the collector. The described scheme is presented in Figure 2.

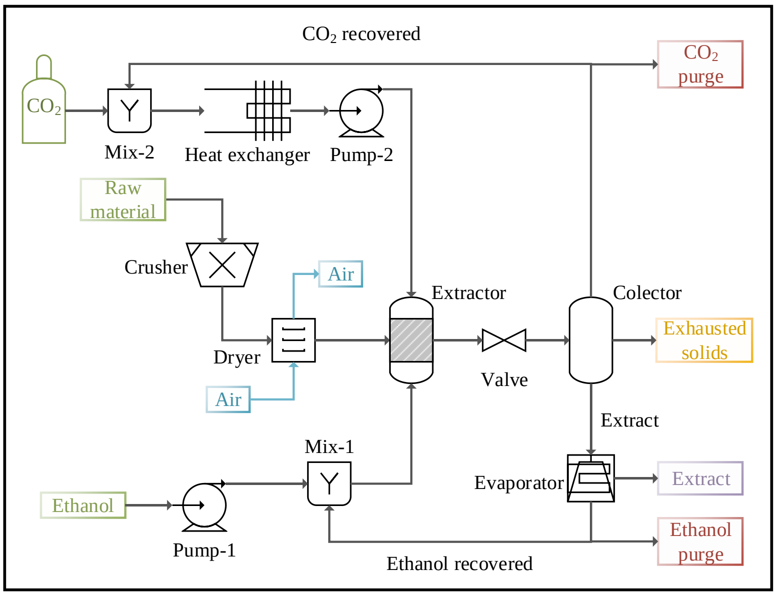

Figure 2. Flow diagram for supercritical fluid extraction simulation

2.1.2. Cogeneration

The cogeneration is done using a post-extraction exhausted solids gasification process. The work of (Puig-Gamero et al., 2018) is the basis for the design of the process. A pressurized gasification process at 30 bar was considered. The gasifying agent is air, fed at a molar ratio of 1.2 to the exhausted solid. The main products of this process are CO_2, CO, CH_4, H_2S and $NH_{3\,(syngas)}$. The resulting gas is passed through a turbine and an engine to take advantage of its high energy value. The resulting energy stream can be used to supply the energy demand in the supercritical fluid extraction process.

2.2. Economic assessment

The economic analysis is highly relevant to compare possible scenarios for two different waste generated from avocado. In this work, the mathematical models reported by (Ulrich and Vasudevan, 2006) are used to estimate the costs associated with the process profits. Labor costs were calculated from the information reported by (Peters and Timmerhaus, 1991); depreciation was estimated through the straight-line method. Finally, the costs associated with the equipment were determined using the Aspen Process Economic Analyzer software (Aspen Technology Inc.). From all the information calculated, it is possible to estimate the Net Present Value (NPV) of the processes under the Colombian context for ten (10) years.

3. RESULTS AND DISCUSSION

3.1. Technical assessment

In scenarios 1 and 2, the flow used is 1,256.71 kg/h. The value corresponds to the proportion of peel present in 5% of the annual production of avocado (73,391.85 ton/year); it was found that this allowed the production of 279.46 kg/h of extract. The information presented shows that from the avocado peel, 0.22 kg per kg of processed peel can be obtained. Regarding the energy produced from the avocado peel, it is possible to obtain 0.11 kWh per kg of raw material. In scenario 2, the energy obtained from the gasification process can supply the energy demand presented mainly by the pumps of the process. In the avocado seed, it allowed obtaining 0.23 kg of extract per kg of processed raw material. Considering that the feeding flow of the avocado seed is 1,675.61 kg/h, 0.10 kWh can be generated per kg of raw material. In both integral biorefinery schemes (scenarios 2 and 4), the extraction scheme presented in Figure 2 must consider the energy feed from the cogeneration process. The final scheme for integral biorefinery cases takes the form of the scheme presented in Figure 3. Under both processing schemes, considering both the peel and the seed of the avocado, it is possible to transform 45% of this fruit. It should be considered that this percentage corresponds to the amount of waste generated by the consumption or processing of avocado. Thus, when considering both exploitation schemes, mainly those focused on integral biorefineries, it is possible to process 2,932.32 kg/h of avocado waste from 8,378.07 kg/h. This flow corresponds to 5% of the annual avocado production. Thus, integral biorefineries are projected as a promising alternative from a technical perspective to use waste.

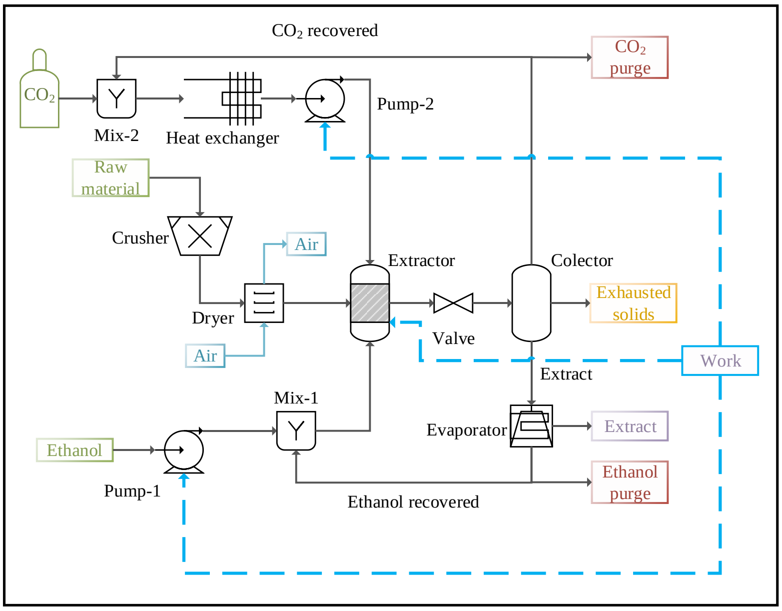

Figure 3. Flow diagram for integral biorefinery (SFE + cogeneration)

3.2. Economic assessment

Concerning the economic aspect, some important data should be considered. Among these data are the NPV, the distribution of costs, the minimum scale of processing, and the return period.

3.2.1. Net present value

It is used to evaluate long-term investment projects, allowing to evaluate if the investment made fulfills a specific objective (i.e., to maximize the investment). The variation of the NPV as a function of time is shown in Figure 5. it can be seen that all the scenarios have a positive VPN, indicating that through the investment in the processing schemes described, it is possible to maximize the investment. Therefore, the processes are projected as alternatives for improving the economic conditions of a specific region by the waste valorization. Among the factors that lead to present different values of NPV for each scenario are the total costs, which presented values of 5.23, 5.38, 5.62, and 6.74 mUSD/year in scenarios 1, 2, 3 and 4, respectively. Factors such as the scale of processing and the addition of a new processing stage (cogeneration) led to the differences between the total investment costs of each of the scenarios.

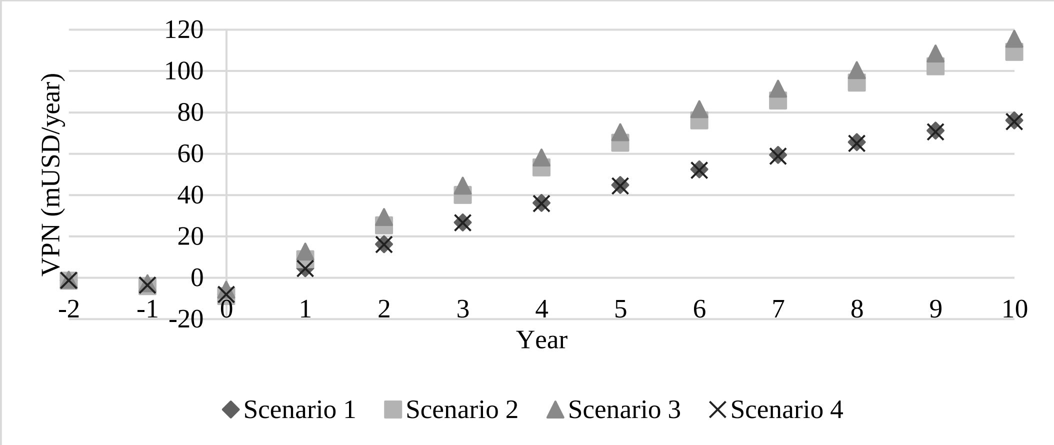

Figure 4. VPN obtained for each scenario analyzed

3.2.2. Distribution of costs

The costs associated with the process are distributed as follows. (*i*) Raw material costs; these costs represent between 56 and 72% of the total costs in the different scenarios. Raw material costs related to the acquisition costs of raw material, CO_2 and ethanol correspond to 53, 18 and 29%, respectively. Among the scenarios analyzed, those with the highest percentages regarding raw material costs are the scenarios corresponding to avocado seed. The main reason is the amount of raw material processed in these scenarios. *(ii)* The costs associated with depreciation are the ones that present the highest contribution to the total cost. *(iii)* The labor costs, maintenance costs and general fixed costs present less than 10% of total costs. The Cost distribution for scenarios 1, 2, 3 and 4 are presented in Table 1. From the process-associated costs, it is possible to estimate the production cost of one kg of extract for each scenario. Thus, the cost of 1 kg of extract for each scenario is 2.14, 2.20, 1.65 and 1.98 USD, respectively. They show that the use of avocado seed allows obtaining an extract of this residue at a lower cost compared to the peel. Being a determining factor the composition of the avocado as a fruit.

Table 1. Distribution of the cost for each scenario

Item	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Raw Materials	57.99	56.37	72.03	60.02
Utilities	3.07	5.75	1.28	6.74
Maintenance	9.18	8.93	6.17	7.87
Labor	1.18	1.15	1.10	0.92
Fixed & General	5.80	5.64	3.95	4.95
Plant Overhead	5.42	5.27	3.80	4.60
Capital Depreciation	17.37	16.90	11.67	14.90

3.2.3. Minimum processing scale

This parameter indicates the minimum amount of raw material to be processed to recover the investment in the project lifetime (i.e., where the NPV is zero). For the analyzed conditions of this work, the minimum processing scales for scenarios 1, 2, 3, and 4 correspond to 18.6, 18.6, 8.29, and 15.92 kg/h, respectively. The addition of the cogeneration stage for avocado peel does not have a considerable impact on the costs of the process. In the case of seeds, there is an effect on process costs, reflected in the minimum flow of raw material that must be processed to recover the initial investment.

The results concerning this factor are presented in Figure 5. The dependence of the raw material flow and the payback period can be seen. When using raw material flows close to the minimum, the payback period is around nine years. If raw material flows of 60 kg/h are considered, the payback period decreases to two years. When using larger flows, the payback time starts to decrease to only months. From 600 kg/h, the payback time is eight months. This analysis identifies the viability of the process for those regions where high flows of avocado residues are present.

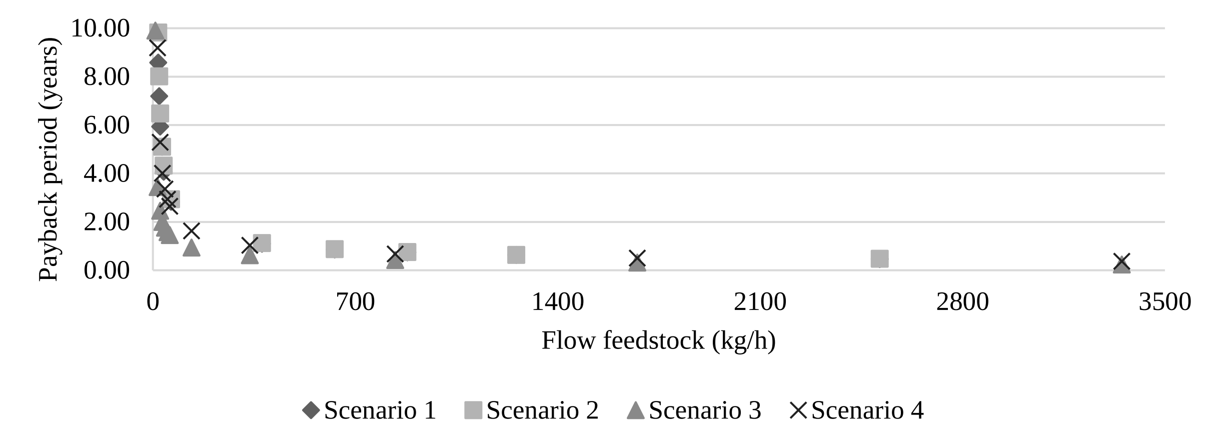

Figure 5. Payback period vs. Flow Feedstock

CONCLUSION.

Avocado residues are projected as promising raw materials for obtaining bioactive compounds employing supercritical fluid extraction processes. However, this process generates an exhausted solid with a high potential for transformation, e.g., cogeneration processes. The implementation of an additional processing step uses the valorization concept through biorefineries. This concept provides better results than those obtained in stand-alone processes (extraction stage with supercritical fluids). The use of the residues obtained in the initial stages of the process allows advancing in integral biorefineries. The integral biorefineries based on extraction with supercritical fluids and cogeneration allow the integral utilization of avocado residues (peel and seed).

In this work, the economic feasibility of extracting bioactive compounds from avocado wastes using supercritical fluid extraction is demonstrated. The highest production cost is presented for scenario 2 (2.20 USD/kg). In contrast, the lowest is provided by scenario 3 (1.65 USD/kg). Both costs are lower than those of these extracts on the market. The above shows the economic potential obtained from the integral use of these wastes.

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