Analysis of a biorefinery with multiple raw materials in the context of post-conflict zones in Colombia: Plantain and Avocado integration in the Montes de María

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Keywords: Avocado, Biorefinery, Multiple Raw Materials, Plantain, Technic, and Economic Evaluation
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Abstract
This work addresses the techno-economic analysis for a multi-feedstock biorefinery system using plantain and avocado residues as raw materials. The experimental procedures were performed to obtain biogas and essential avocado seed oil. Ethanol and food products were obtained by the simulation of the whole biorefinery with reported literature data. The mass and energy balances were obtained using Aspen Plus V.9.0, while the economic assessment was performed using Aspen Process Economic Analyzer.

1. Introduction

Obtaining biofuels from lignocellulosic material has become an alternative with a high potential to replace fossil sources that negatively alter the environment. However, some challenges and difficulties have been identified when developing this type of technology (i.e., biorefineries). Generally, the raw materials to be used do not supply the requirements for processing or are not available in a single region [1]. Additionally, knowing that different products can be obtained from a biorefinery, the complexity can increase. The challenge consists of implementing within the biorefinery concept the use of more than one raw material or the integration of different raw materials [1]. This will allow the process not to depend on the conditions of a single raw material (such as time of cultivation, prices, climate, among others) but can be versatile in using different types of feedstocks. Some authors [2]–[4] have researched this subject and wondered about the interactions between raw materials in each transformation they undergo within the process. Besides, they have noticed that efforts are required to optimize this system, especially from the logistics side. The integration of different raw materials can be facilitated to acquire them because what is sought is to find a single region that provides a variety of desired raw materials. In a country with high biodiversities, such as Colombia, diverse regions rich in different raw materials can be found, such as the Montes de María region, located in the Colombian Caribbean. This area has a high agroindustrial potential which has not been adequately exploited due to the different war actors that intervened in this territory. In this region, the cultivation of plantain and avocado is mainly highlighted.

Plantain cultivation in Colombia is considered one of the most usual economic activities in the country because it serves as subsistence for many producers [5]. This tropical plant is a valuable source of carbohydrates, and that is why the market is mainly focused on obtaining flour, snacks, among other food products [6]. However, the residues of this crop have not been adequately used. Interest has been identified in seeking alternatives for transforming plantain peel, pseudo-stem, and plantain pulp (which is not used for food purposes). One of these alternatives is anaerobic digestion, which consists of transforming organic matter into biogas with the help of microorganisms that perform four stages of transformation [6], [7].

On the other hand, avocado has been considered one of the most versatile and beneficial foods. The main components of avocado are antioxidants [5]. Additionally, the seed (which represents up to 20% of the fruit) is a rich source of carbohydrates, protein, and monounsaturated fats [8], [9]. The potential use of avocado residues (avocado seed, avocado peel, and even avocado pulp that does not have the necessary conditions for food purposes) is the extraction of oil or dyes. These products may have applications in the food or pharmaceutical industry [10]. Also, anaerobic digestion is a promised transformation process. Taking advantage of lignocellulosic residues of these crops in the

Montes de María region, it is possible to propose a competitive, viable and comprehensive biorefinery with multiple raw materials.

It will generate more significant agro-industrial development in the region and benefit the communities that live there since the economy of this area affected by the armed conflict will be recovered through the generation of employment and the recovery of confidence in the productivity of the Colombian fields.

This work aims to evaluate a multi-feedstock biorefinery based on integrating plantain and avocado residues, which are representative raw materials of the Montes de María region in Colombia. A biogas production integrating the raw materials was carried out experimentally and took into account the production of avocado seed oil. Then, the simulation of the biorefinery was complemented with the production of ethanol through the fermentation process (integrating the raw materials). Finally, the biorefinery obtained was analyzed based on techno-economic aspects to estimate the viability of the biorefinery.

2. Materials and methods:

2.1. Raw materials

Plantain and avocado were obtained from the Montes de María region in Colombia (9°34′42″N 75°16′15″O). All the samples were dried at 45°C in a convective furnace until having less than 10% of moisture. Plantain and avocado samples were ground with a knife mill to obtain a particle diameter of 40 mesh [11].

2.2. Chemical Characterization

The chemical characterization of the samples was carried out according to the international standards protocols, in terms of extractives (NREL/TP-510-42619), holocellulose (ASTM D1104-56), cellulose (NREL/TP-510-42620), lignin (TAPPII-T222 om-02), ash content (NREL/TP-510-42722) and moisture content (NREL/TP-510-42621). The characterizations were carried out for each of the waste fractions of both raw materials. The peel, pulp, and mixture were analyzed for the plantain and the avocado, the seed, and peel.

2.3. Anaerobic digestion performance

The anaerobic digestion performance was carried out through the biochemical methane potential (BMP). Activated sludge was used as inoculum, and the VDI 4630 German standard method was followed. For this, it was ensured that for every 500 ml of digestion volume, the inoculum should provide between 7.5-10 g of volatile solids. Besides, the ratio of the volatile solid of the raw material and inoculum should be less than 0.5. An adequate rate was found between the raw materials to carry out the procedure, following the process described by Piedrahita, S. 2021. For preparing the solution, 1 ml of macronutrient solution and 0.4 ml of Macronutrient solution were added per 100 ml of digestion volume, according to Angelidaki et al. 2009 [12]. The volume needed to complete the digestion was filled with water.

Table 1 shows the composition of the macro and micronutrient solution. Finally, the experiment was left at 37°C for 25-30 days. The biogas produced was measured through a portable gas analyzer (Gasboard – 3100P portable infrared syngas analyzer).

Table 1. Nutrients used for the preparation of the medium for anaerobic digestion.

COMPOUND	FORMULA	CONCENTRATION (g/L)
MACRONUTRIENTS SOLUTION		
Ammonium chloride	NH_4Cl	100
Sodium chloride	$NaCl$	10
Magnesium chloride hexahydrate	$MgCl_2 \cdot 6H_2O$	10
Calcium chloride dihydrate	$CaCl_2 \cdot 2H_2O$	5
Dipotassium hydrogen phosphate trihydrate	$K_2PO_4 \cdot 3H_2O$	200
MICRONUTRIENTS SOLUTION		
Zinc Chloride	$ZnCl_2$	0.05
Ferrous chloride tetrahydrate	$FeCl_2 \cdot 4H_2O$	2
Aluminum chloride	$AlCl_3$	0.05
Cobalt Chloride hexahydrate	$CoCl_2 \cdot 6H_2O$	0.05
Boric acid	H_3BO_3	0.05
Ammonium molybdate tetrahydrate	$(NH_4)_6MO_7O_{24} \cdot 4H_2O$	0.05
Ethylenadiaminetetraacetic acid	$C_{10}H_{16}N_2O_8$	0.5
Hydrochloric acid	HCl	1 ml

2.4. Essential oil from avocado seed

The extraction of essential oil was carried out using steam distillation. Steam distillation allows recovering volatile compounds with a high boiling point of solid matrices using saturated or superheated steam as a separating agent [13]. This process is used to extract essential oil from plants [14]. The process consists of using the steam generated when boiling of the water occurs as an extracting agent to vaporize or release the volatile compounds of the samples. The compounds absorb heat, thereby transferring them to the vapor where they diffuse. Subsequently, the vapor phase is condensed and collected in an Erlenmeyer. Figure 15 shows the scheme of the extraction of essential oil by steam distillation. The steam was worked at 90 °C to avoid degradation of the essential oil. From the distillation, an emulsion of water and oil was obtained. The oil is in the upper and hydrosol (water with some hydrolyzed compounds) in the lower phase of the decanter. This type of assembly allows dry steam distillation. The emulsion obtained in the extraction was separated by simple decantation [15]. Hexane was added in a 1:10 ratio to obtain better visibility of the phases formed, and the hexane was contacted with the emulsion for 10 min. The contact was made by stirring the mixture in a separatory funnel. The resulting emulsion stood for 10 min and was decanted. The hexane-essential oil solution corresponds to the light phase. Finally, hexane evaporated at 68 °C. The temperature was controlled in order not to degrade the essential oil.

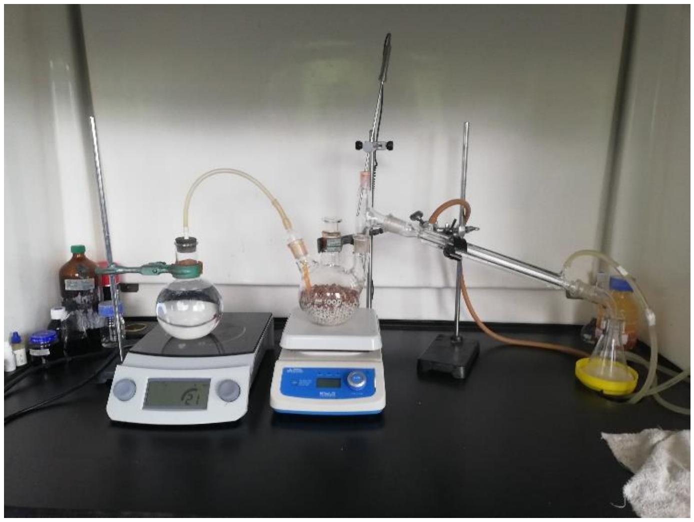

Figure 1. Experimental extraction of avocado seed oil

2.5. Simulation procedure.

The characterization and experimental results served as input data for the simulation of biorefinery with multiple raw materials. Figure 2 shows the proposed scheme for the multi-feedstock biorefinery. Plantain and avocado residues that are not pulp are entered into drying and milling processes to obtain the fractions of starch and lignocellulosic compounds present in them. These processes consist of dryers, mills, heat exchangers, filters, and a starch extraction section consisting of a wash with ascorbic acid, followed by a decanter and a filter. Meanwhile, the pulp of both raw materials is directed to specific processes of obtaining food such as snack and flour (for plantain pulp), guacamole, and packed pulp (for avocado pulp). The avocado seed has a special treatment in which the essential oil is extracted to be considered a biorefinery product. Lignocellulosic and starch-rich streams and residues from avocado seed oil extraction undergo anaerobic digestion and fermentation processes. The fractions of these residues that are directed to each process are explained later. In the fermentation section, the raw material stream is pretreated to ensure greater accessibility in the fermentation process to the raw material molecules. This process consists of stages of acidic and enzymatic hydrolysis, and the sugar platform is obtained. Then, the stream is taken to a fermentation process to obtain ethanol as a product of this biorefinery.

On the other hand, the anaerobic digestion process is carried out with the indicated raw material fraction. It carries out four stages (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) through the action of microorganisms. Finally, two products are obtained (biogas platform and digestate). The biogas undergoes a cogeneration stage to obtain electricity and steam as bio-engineering products, while the digestate serves as fertilizer.

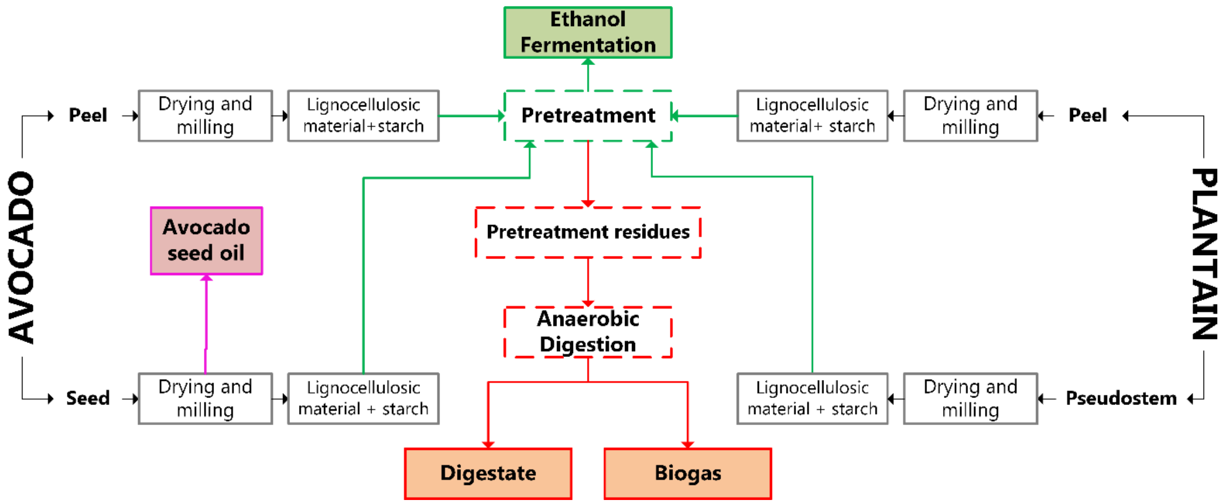

Figure 2. Multi-feedstock biorefinery scheme proposed.

2.5.1. Mass and energy analysis

Aspen Plus V.9 commercial software was used to determine the material and energy balances of the process. The mass analysis was performed for the proposed biorefinery for following up the transformation of the integrated raw materials towards value-added products. Different indicators such as mass and energy were analyzed to compare the data with literature and have global data on these balances.

2.5.2. Economic analysis

Additionally, the operational and capital costs of the biorefinery were calculated, assuming an annual interest rate of 12.1% (Colombian context), a straight-line depreciation method, and a tax rate of 33%. The prices used in this analysis (such as raw material, reagents, and labor wages) were taken under Colombian conditions.

3. Results and discussion

3.1. Characterization of the raw materials fractions

The results of the characterization of the raw materials are shown in Table 2, where the high potential of the raw materials to be transformed through processes such as anaerobic digestion, fermentation, and oil extraction is appreciated. More than 900 ml of biogas per g of VS was obtained during the experimental part, integrating the residues of avocado and plantain. Comparing these results with those reported by Khan et al. 2016 [16], where they used only plantain peel during 35 days of the experiment, approximately 12% of methane was obtained five days less. On the other hand, avocado seed oil extraction was performed, obtaining results similar to those reported in the literature (about 500 g of essential oil per kg of dry raw material) [17]. Finally, the results of the biorefinery simulation allowed obtaining the material and energy balances of the process and the capital and operational costs associated with it. It could be concluded that raw material and labor costs were the most representative within capital costs. It was also possible to find the minimum processing scale of the proposed biorefinery.

Table 2. Chemical characterization results (wet basis)

Component	Plantain peel	Plantain pseudostem	Avocado seed	Avocado peel
Moisture	8,07	82,86	11,26	7,53
Extractives	40,99	3,22	33,10	24,43
Cellulose	14,33	6,96	8,52	21,02
Hemicellulose	12,54	3,22	38,37	27,73
Lignin	9,63	2,38	4,71	4,86
Lipids	n.d	n.d	1,79*	13,24*
Ash	14,45	1,36	2,26	1,20

n.d Not determined. *Data from [18]

As shown in Table 2, avocado residues are rich in hemicellulose, which can originate C5 sugars (xylose) that can be potentially transformed by anaerobic digestion to obtain biogas and that benefits the C/N ratio [19]. Additionally, the high content of extractives soluble in water and ethanol gives an idea about the content of polyphenolic compounds that may be contained in avocado seed oil [20]. The lipids in the avocado residues are also part of the compositions that benefit obtaining biogas and fertilizer. On the plantain residues, the high cellulose content (mainly for the plantain pseudostem) indicates that a good performance is possible to obtain ethanol. Additionally, these residues especially have a low lignin content that favors the cellulose to be much better accessed for its transformation, so it is expected that high yields will be obtained in the different processes for obtaining value-added products.

3.2. Simulation results

3.2.1. Technical analysis

The avocado seed oil extraction data and the conditions of the anaerobic digestion process were obtained from authors who reported these results in single-material biorefineries. In the conditions for obtaining avocado seed oil, the yields reported by [18] were managed. In the simulation, the productivity of 0.13 kg/h of oil was obtained, which indicates a yield of 6.99 kg/g of the avocado seed. These results are not satisfactory compared with other literature data, such as [21], [22]. Additionally, essential oil extraction results have been reported with high yields for the avocado pulp but low in the seed of this fruit [23].

On the other hand, the novel PSM model [24] was used to simulate the stages of anaerobic digestion. Table 3 shows the reactions taken into account for the raw material compositions obtained in the immediately previous stream in the simulation. Stoichiometric and kinetic type reactors were used for modeling. Obtaining biogas through the co-digestion of waste indicated productivity of 8.41 kg/h of biogas with a methane mass composition of 0.43, and having an overall yield of 16.21 kg/g of processed material (waste of the pretreatment and fermentation processes of the stage of obtaining ethanol). However, the digestate obtained, which can be used as a fertilizer, had productivity of 40.59 tons/h due to the significant amount of dilution required for the biogas production process. The yield of this product was 0.78 kg/kg of material processed at this stage.

Table 3. PSM model reactions used to simulate the anaerobic digestion in Aspen Plus.

Anerobic digestion stage			
	Hydrolysis		**Extent of reaction**
1	Cellulose	$(C_6H_{10}O_5)n + H_2O \rightarrow n(C_6H_{12}O_6)$	0.4 ± 0.1
2	Cellulose	$C_6H_{10}O_5 + H_2O \rightarrow 2C_2H_6O + 2CO_2$	0.6 ± 0.0
3	Hemicellulose	$C_5H_8O_4 + H_2O \rightarrow 2.5C_2H_4O_2$	0.5 ± 0.2
4	Hemicellulose	$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5$	0.6 ± 0.0
5	Xylose	$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O$	0.6 ± 0.0
6	Ethanol	$2C_2H_6O + CO_2 \rightarrow 2C_2H_4O_2 + CH_4$	0.4 ± 0.1
7	Extractive	$CH_5N + 0.5H_2O \rightarrow 0.25CO_2 + 0.75CH_4 + H_3N$	0.6 ± 0.2
	Acetogenic		**Kinetic constant**
9	Propionic acid	$C_3H_6O_2+0.06198H_3N+0.31433H_2O \rightarrow 0.06198C_5H_7NO_2+0.9345C_2H_4O_2+0.660412CH_4+0.160688CO_2+0.00055H_2$	$1.95x10^{-7}$
10	Isobutyruc acid	$C_4H_8O_2 + 0.0653H_3N + 0.8038H_2O + 0.0006H_2 + 0.5543CO_2 \rightarrow 0.0653C_5H_7NO_2 + 1.8909C_2H_4O_2 + 0.446CH_4$	$5.88x10^{-6}$
	Methanogenic		**Kinetic constant**
11	Acetic acid	$C_2H_4O_2 + 0.022H_3N \rightarrow 0.022C_5H_7NO_2 + 0.945CH_4 + 0.066H_2O + 0.945CO_2$	$2.39x10^{-3}$
12	Hydrogen	$14.4976H_2 + 3.8334CO_2 + 0.0836H_3N \rightarrow 0.0836C_5H_7NO_2 + 3.4154CH_4 + 7.4996H_2O$	$2.39x10^{-3}$

Finally, the productivity of ethanol from the integration of the residues was 2.65 kg/h, and a yield of 0.38 kg/kg glucose. The mass and energy indicators are showed in table 4.

Table 4. Mass and energy indicators for the proposed biorefinery with multiple raw materials

Indicator	**Value**
Ethanol yield	0.38 kg/kg glucose
Biogas yield	16.21 kg/g of processed material
Essential Oil yield	6.99 kg/g of avocado seed
Fertilizer yield	0.78 kg/kg of processed material
Energy consumed	13,6 MJ/kg residues

3.2.2. Economic assessment

For the economic analysis, the prices of raw materials, reagents, and products shown in Table 5 were considered. Additionally, the total capital cost was 17.21 mUSD. The preliminary economic results of the entire biorefinery system are shown in Table 6. According to preliminary calculations, the profit margin was positive, indicating that the biorefinery products offered in the market are capable of supplying the production costs of the proposed scheme. If process conditions such as stream optimization, use of process waste, more energy integrations, and even process returns are improved, this result may be further improved. Considering the profit margin results, the stand-alone process based on plantain peel to obtain ethanol reported by Parra et al. 2017 [25] resulted in a profit margin of 0.44. A profit margin of 1.26 was calculated when essential oil from citronella as a stand-alone process is obtained using the supercritical CO_2 extraction technique reported by Moncada et al., 2014 [26].

By comparing the preliminary results obtained for the biorefinery with multiple raw materials together with traditional biorefineries in which there is no integration, it can be concluded that it is necessary to complement the economic analysis with a projection of costs for at least 20 years and thus be able to determine the viability of the biorefinery. An example of this is the calculation of the Net Present Value (NPV), which gave viability for the case reported by the biorefinery based on obtaining biogas from the banana peel Martínez-Ruano et al. 2018 [19].

Table 5. Cost of utilities, reagents, products, and raw materials for the biorefinery

Item	Cost (mUSD)	Item	Cost (mUSD)
UTILITIES		**REAGENTS**	
LP-steam	0,002	Water	1,882
MP-steam	14,833	H2SO4	0,287
Cooling water	4,361E-05	Inoculum	0
Electricity	0,026	Enzyme	0,0244
PRODUCTS		**RAW MATERIALS**	
Oil	0,006	Avocado seed	0,184
Biogas	0,045	Avocado peel	0,082
Digestate	21,338	Plantain peel	0,008
Ethanol	0,041	Plantain pseudostem	0,011

Table 6. Economic data results

Parameter	mUSD/y
Revenues	21,430
Raw material	0,285
Reagents	3,387
Utilities	14,862
Capital investment	1,033
TOTAL	19,567
Profit	1,863

4. Conclusion

The results demonstrate the potential of integrating avocado and plantain residues as raw materials to produce biogas, ethanol, and essential oil from an avocado seed. As a general conclusion of this work, proposing a biorefinery with multiple raw materials allows obtaining a vision of the agro-industrial potential of a single region, empowerment economically and socially the affected regions with new opportunities for development and reconstruction. In addition, the emerging possibility for providing new processing alternatives for the residues of these crops can be valuable because it allows seeing opportunities to obtain value-added products.

5. Acknowledgments

The authors express their gratitude to the research program entitled “Reconstrucción del tejido social en zonas posconflicto en Colombia” SIGP code: 57579 with the project entitled “Competencias empresariales y de innovación para el desarrollo económico y la inclusión productiva de las regiones afectadas por el conflicto colombiano” SIGP code 58907. Contract number: FP44842-213-2018.

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