

**Analysis of biorefinery platforms based on technical characteristics of the raw materials:
a comparison between orange and plantain peels waste**

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Abstract

Fermentable sugars are considered a product platform. Different metabolites such as alcohols, organic acids, biomaterials, and biomolecules can be obtained from this. The production of fermentable sugars has been extensively studied to obtain higher yields. However, few studies determine the best route in technical, energy, and economic terms. In this work, two raw materials (orange peel waste and plantain peel) of great interest for fermentable sugars production were studied. The conceptual design and optimization methodology were used for this purpose. The material and energy balances were obtained using the Aspen Plus V.9.0 software for the conceptual design. Besides, the investment costs of each process unit were obtained by the Aspen Economic Analyzer V.9.0 software. Balances and costs were the input to the mathematical development of optimization. A superstructure was established for this purpose. GAMS software was used. The economic results of the optimal biorefineries schemes showed a non-feasibility performance, represented numerically in the NPV. Nevertheless, comparing the two raw materials and the schemes, it is possible to conclude that the best raw material to produce sugars as platforms products is OPW.

Keywords: Biorefinery Platforms, Optimization, Orange peel waste, Plantain peel waste, Technical and Economic Assessment

1. Introduction

Lignocellulosic biomass has a high potential as a renewable source, and there is currently an interest in developing alternatives for processing it. Fermentable sugars can be an interesting platform that can be obtained through this type of biomass because the lignocellulosic matrix

is rich in cellulose and hemicellulose, which after certain processes, can produce C5 and C6 sugars [1]. Under the concept of biorefinery, this process has high potential and great interest due to the sustainable use of by-products. However, challenges have been identified when establishing an analysis methodology to identify the best raw material for the process, in technical and economic aspects based, for example, on its composition, prices in the market, availability of the raw material, and technologies for transformation.

Orange peel waste (OPW) is a valuable lignocellulosic residue that represents about 50 % of the orange fruit, and it is for this reason, alternatives have been sought for its transformation. Fermentable sugars can be obtained by enzymatic hydrolysis of the cellulose and hemicellulose present in the residue and from the pectin, which can be previously extracted from the orange peel [2], [3]. On the other hand, plantain peel waste is also an important residue from the plantain crop. In Colombia, this fruit is representative and serves as a tool for developing the regions and the farmers. That is why it is crucial to search for transformation processes that help strengthen the economic chain of this crop. Some authors have produced fermentable sugars from this raw material and have used them as platforms to obtain various products [4], [5], to obtain these sugars from the plantain peel, cellulose, and hemicellulose undergo an enzymatic hydrolysis process [6]. Considering that it is necessary to evaluate the potential of raw materials in a process, process simulation is essential. The process simulation considers all the corresponding stages, including the necessary pretreatment and the interaction of the key components that define the process conditions. All this under the context of a viable biorefinery allows the concluding consideration of the feasibility of raw material compared to another to be used for this purpose.

This work aims to establish which of the raw materials (orange peel waste and plantain peel waste) provides more accessible sugar production costs under biorefinery. Besides, each analysis of the biorefineries will be performed after a general optimization of the process to have the best processing routes and thus be able to compare them with each other.

2. Methodology

The conceptual design methodology is implemented to find a superstructure that combines different types of variables, which must satisfy the objectives of the biorefinery. The methodology proposed by Aristizábal et al. [7] was applied. The conceptual design allows for obtaining the material and energy balances of the established processing units. The simulation of the proposed processing units was carried out using the Aspen Plus V9.0 software. Likewise, the conceptual design requires data from various sources, development, and evaluation of all the alternatives to structure the biorefinery theoretically.

Furthermore, the total capital investment and operating costs were obtained at this stage. Aspen Economic Analyzer V.9.0 software was used for obtaining these costs. The superstructure of each biorefinery is defined to select the best route in economic terms. **Equation 1** shows the objective function to be developed in terms of the product sales (S^{Prod}), raw material cost (C^{RM}), reagent cost (C^{Reac}), utility cost (C^{Util}), and investment cost (C^{Invs}).

$$Z = S^{Prod} - C^{RM} - C^{Reac} - C^{Util} - C^{Invs} \quad \text{Eq 1}$$

The economic parameters of the objective function are given by:

$$S^{Prod} = \sum_k \sum_i Pr_k^P * f_{i,k}^{Reac} \quad \text{Eq 2} \quad C^{RM} = Pr^{RW} * f^F \quad \text{Eq 3}$$

$$C^{Reac} = \sum_k \sum_i Pr_k^{Reac} * f_{i,k}^{Reac} \quad \text{Eq 4} \quad C^{Util} = \sum_k \sum_{util} Pr_k^{Util} * (f^F * \alpha_k^{Util}) \quad \text{Eq 5}$$

$$C^{Invs} = \left[C^{Cap} + C^{Man} * \left(\frac{(1+i)^n - 1}{i * (1+i)^n} \right) \right] * \left(\frac{i * (1+i)^n}{(1+i)^n - 1} \right) \quad \text{Eq 6}$$

$$C^{Cap} = \sum_k Pr_k \quad \text{Eq 7} \quad C^{Man} = C^{Cap} * 0.6 \quad \text{Eq 8}$$

Where, the superscripts $P, F, Reac, RW, Util, n$ are product, feedstock, reactants, raw material, utilities (Low-Pressure Steam, electricity, or cooling water), return of investment respectively. Pr is price or cost. f is component flow (kg/h). i is the interest rate, the subscripts i, k are component and unit, respectively. α is the relationship between the flow of utility and the flow of raw material. Possible scenarios that meet the proposed objectives are described below. The objective function is fed from the material balances (input and output flows) of each process unit. For this, it is necessary to develop a mathematical model. The mathematical model was solved using the GAMS software under a Mixed-Integer Nonlinear Program (MINLP) approach.

2.1. Orange peel waste biorefinery

Fermentable sugar production from OPW has been extensively studied. The essential oil and the pectin fractions of OPW have been proposed as alternatives for generating more products. Based on this, the concept of biorefinery develops. Furthermore, the limonene present in the essential oil is considered an inhibitor in the production of metabolites by fermentation. For this reason, before fermentable sugar production is advisable to remove limonene.

On the other hand, pectin is a biopolymer made up mainly of galacturonic acid, and to a lesser extent, sugars such as arabinose, maltose, and glucose. In this work, two possible routes are initially considered. In all the possibilities analyzed, the production of biogas and fertilizer from the remaining solid is considered. The methodology proposed by Rajendran et al. [8] was applied to obtain the yields. **Figure 1** shows the proposed superstructure.

The first route was to remove the OPW essential oil by distillation [9]. The liquor from this unit could be used to purify the essential oil or released as a liquid stream. Three alternatives for the production of fermentable sugars are proposed with the remaining solid. The first alternative is to perform hydrolysis with hydrochloric acid to solubilize the OPW pectin [9]. The liquor obtained was done either by pectin production, adding ethanol, or considering liquor as waste.

On the other hand, the solid was feed to enzymatic hydrolysis of cellulose [9]. The liquor contains C6 fermentable sugars. The solid obtained was used for the production of biogas and fertilizer. The second alternative was done the enzymatic hydrolysis of OPW pectin and cellulose [10]. The remaining solid was taken to biogas and fertilizer production. Finally, the third alternative was the enzymatic hydrolysis of cellulose [11]. The remaining solid was used for biogas and fertilizer production. The second route was the acid hydrolysis of OPW with hydrochloric acid [12]. This unit guarantees the solubility of the essential oil; thus, two alternatives were proposed with the generated liquor. The first was pectin purification, and the second was to take the liquor as residue. The resulting solid was fed to the cellulose enzymatic hydrolysis unit [12]. The liquor contains C6 fermentable sugars, and the resulting solid is taken to the production of biogas.

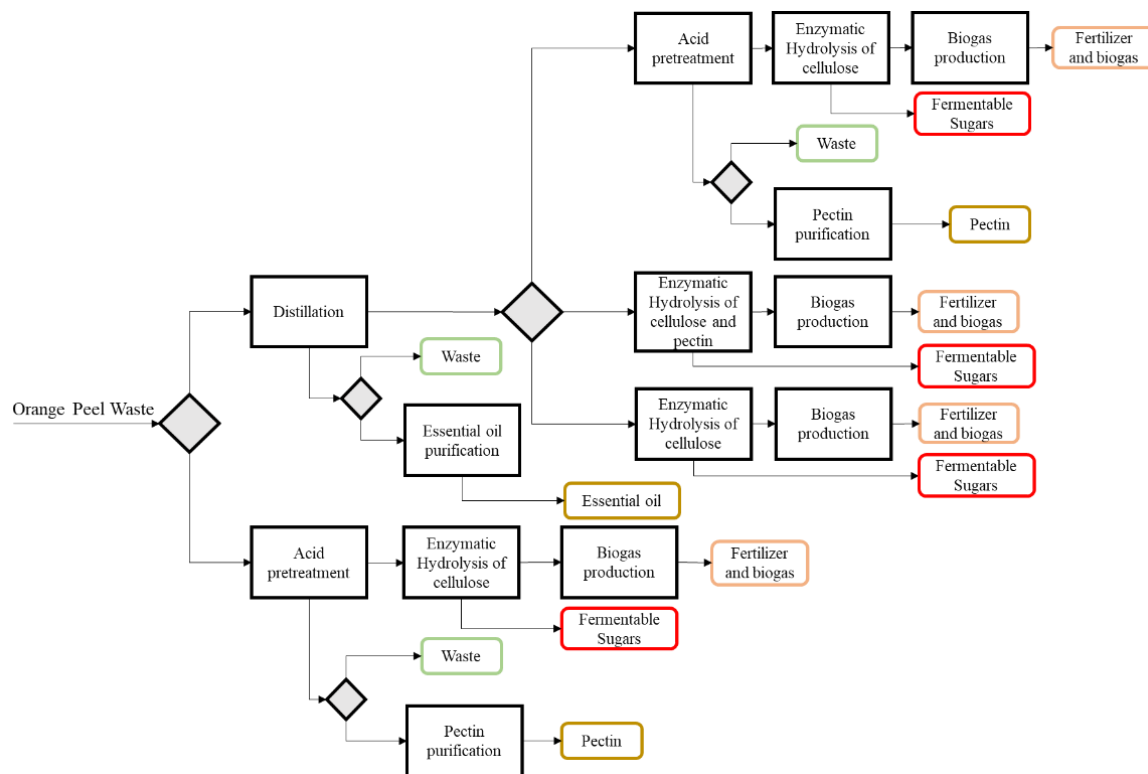


Figure 1. Super-structure OPW Biorefinery

2.2. Plantain peel biorefinery

Many studies have shown and focused on the potential of obtaining value-added products from lignocellulosic biomass. One of the most abundant raw materials in tropical and highly biodiverse regions such as Colombia is plantain, and the primary residue of this crop is plantain peel. For this scheme, a multi-product biorefinery was planted (**Figure 2**).

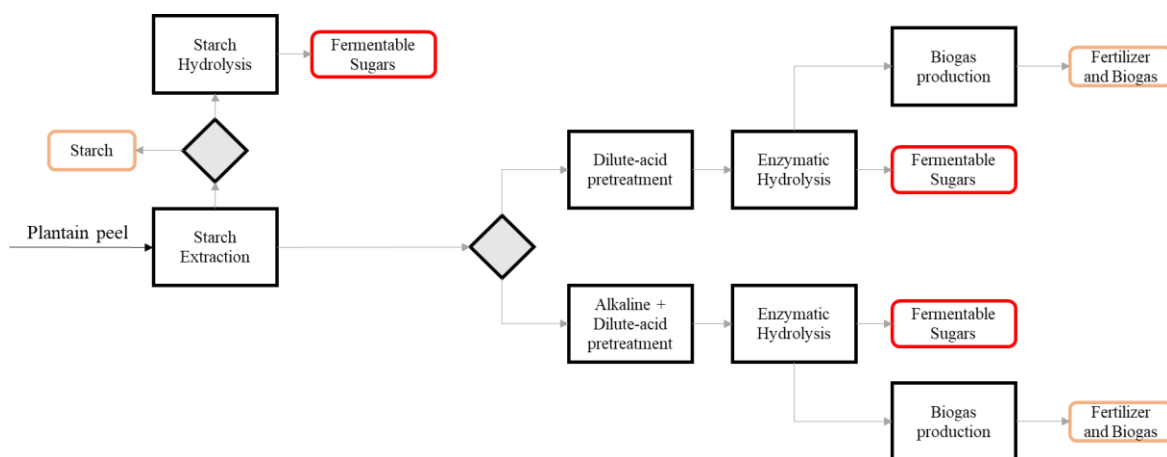


Figure 2. Structure Plantain peel Biorefinery

Plantain peel stream undergoes a starch extraction process on a wet basis. The action of ascorbic acid promotes this extraction because it can pause the degradation of lignocellulosic material present in the feedstock[13]. Then, two possible routes were given. The first was to sell the starch, and the second was to subject it to enzymatic hydrolysis in which fermentable sugars were obtained [14]. After those steps, the drying process was carried out to remove moisture from the process stream. Then, the stream can be submitted to dilute-acid hydrolysis or alkaline hydrolysis. Dilute-acid hydrolysis is a process in which a polyprotic acid (i.e., sulfuric acid) is used to catalyze the division of cellulose and hemicellulose into their respective monomers. By contrast, in alkaline hydrolysis, a basic compound is used as a catalyst. The operating parameters depend on the substance and the concentration with which the process will be carried out. In the dilute-acid hydrolysis stage, the stream that could not be transformed go to the lignin precipitation process from black liquor. Here, the formed product can be established as waste or fed to the anaerobic digestion process.

In contrast, the hydrolyzed stream undergoes enzymatic hydrolysis, in which the beta 1,4 glycosidic bonds of cellulose were hydrolyzed to obtain sugars [15]. In performing alkaline hydrolysis, the hydrolyzed stream went then to dilute-acid hydrolysis to perform better in the pretreatment stage. Then, the enzymatic hydrolysis process was carried out, and an unprocessed stream entered directly into the anaerobic digestion process.

The technical analysis was carried out through the mass and energy evaluation of the optimized scheme to transform the two raw materials into fermentable sugars. Both analyzes were carried out in terms of indicators to make a comparison between the optimized biorefineries. The indicators used in this work are shown below (Table 1):

Table 1. Mass and energy indicators.

Mass indicator	Ref.	Mass indicator	Ref.
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<u>Product yield</u> $Y_P = \frac{\dot{m}_{Product,i}}{\dot{m}_{Raw\ material}}$	[16]	<u>Reaction mass efficiency</u> $RME = \frac{\dot{m}_{Product}}{\sum \dot{m}_{Products\ inputs}}$	[17]
<u>Annual Productivity</u> $P_P = \frac{M_p}{M_{Raw\ material} * Wp}$	[18]	<u>Carbon conversion efficiency</u> $CCE = \frac{\dot{m}_{C\ in\ Biogas}}{\sum \dot{m}_{C\ in\ exhausted\ solid}}$	[19]
Energy indicator	Ref.	Energy indicator	Ref.
<u>Specific energy consumption</u> $S_{EC} = \frac{\dot{Q} + \dot{W}}{\dot{m}_{Raw\ material}}$	[20]	<u>Overall energy efficiency</u> $\eta = \frac{\dot{m}_{Biogas} * LHV_{Biogas}}{(\dot{m}_{OPW} * LHV_{OPW}) + \dot{Q} + \dot{W}}$	[20]
<u>Self-generation index</u> $SGI = \frac{(\dot{m}_{Biogas} * LHV_{Biogas}) * \eta_{Conversion}}{\dot{Q} + \dot{W}}$			[21]

Where, $\dot{m}_{product,i}$: mass flow of product, (i) [kg/h], $\dot{m}_{Raw\ material}$: mass flow of raw material, [kg/h], M_p : mass of the product (i) obtained in a specific Wp , [kg/h], $M_{Raw\ material}$: mass of Raw material obtained in a specific Wp , [kg/h], Wp : the working period of the biorefinery, $\dot{m}_{Product}$: mass flow of product, [kg/h], $\sum \dot{m}_{Product\ inputs}$: the mass flow of inputs to the production process, [kg/h], $\dot{m}_{C\ in\ Biogas}$: mass flow of carbon in biogas, [kg/h], $\sum \dot{m}_{C\ in\ exhausted\ solid}$: mass flow of carbon in exhausted solid, [kg/h], \dot{Q} : Thermal requirements of the biorefinery, [MJ/h], \dot{W} : Power requirements of the biorefinery, [MJ/h], $\eta_{Conversion}$: efficiency of biogas conversion technology (e.g., cogeneration system).

Finally, the optimized schemes were compared in economic terms. The comparison of the biorefineries was made considering fixed and variable costs. This analysis was performed in US dollars and the economic context of Colombia (annual interest rate of 12.1 % and income tax of 33 %). Furthermore, the optimal schemes were analyzed on the same low-scale considering the production in depressed zones of Colombia (140 kg/h). The economic viability was analyzed from the net present value (NPV).

3. Results and discussion

3.1. Optimization results

Figure 3 and **Figure 4** show the optimized flowsheet diagrams for OPW-based biorefinery and plantain peel-based biorefinery, respectively. As can be seen, the OPW biorefinery begins with the distillation stage. The resulting stream is taken to the enzymatic hydrolysis process of the cellulose and pectin contained in the stream to result in fermentable sugars. The residues obtained are taken to anaerobic digestion to obtain fertilizer and biogas. In the plantain peel biorefinery case, the residue undergoes the starch extraction process, which will be one of the by-products of the process. The stream is rich in lignocellulosic material undergoes a pretreatment process with dilute acid and then an enzymatic hydrolysis step in which fermentable sugars are obtained. The carbohydrate-rich residues from these stages are finally taken to anaerobic digestion to obtain biogas.

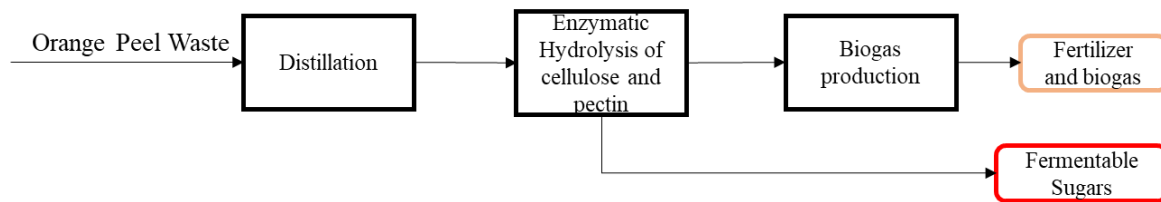


Figure 3. Scheme of the optimal OPW biorefinery

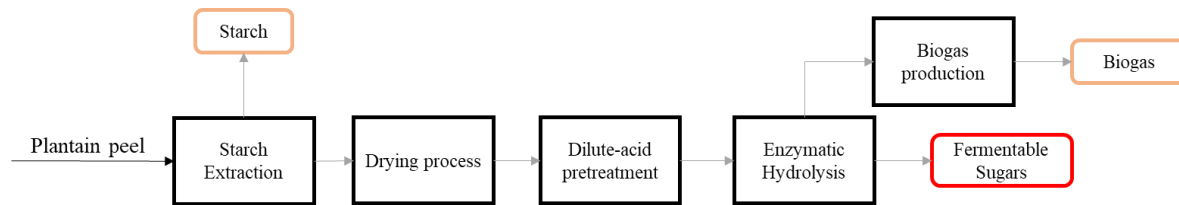


Figure 4. Scheme of the optimal Plantain peel biorefinery

3.2. Technical assessment

As a summary of the technical analysis, the results for each optimized biorefinery's mass and energy indicators are shown in **Table 2**. The route for the OPW biorefinery showed productivity of 541.03, 44.44, and 3,683 kg/h of fermentable sugars, fertilizer, and biogas, respectively. During this process, the fermentable sugars were brought up to a 40 g/L, which is the concentration required in the market. The fertilizer obtained was achieved with 20-25% moisture, and the resulting biogas is rich in methane and CO₂. The yields of fermentable sugars, fertilizer, and biogas for this biorefinery were 3.86, 0.32, and 0.03, respectively. On the other hand, in the case of the optimized biorefinery based on plantain peel, the

productivity of fermentable sugars, starch, and biogas were 19.84, 2.99, and 0.36 kg/h, respectively, obtaining a yield of 0.14 for fermentable sugars also concentrated at 40 g/L, 0.02 for the conventional extraction of starch from the plantain peel and finally a yield of 0.03 for the biogas.

It is possible to notice the high performance that the process for obtaining fermentable sugars is presented in the OPW scheme. It makes it the best residue of the cases studied to obtain sugars under the concept of biorefinery. Additionally, the biogas yields were similar, indicating that the residues obtained from the process streams and used had compositions that allowed adequate assimilation by anaerobic microorganisms.

Table 2. Technical indicators obtained from the optimized biorefineries schemes.

Indicators	Optimized OPW biorefinery	Optimized Plantain peel biorefinery
Mass Indicator		
Fermentable sugars yield	3.86 kg/kg OPW	0.14 kg/kg Plantain peel
Biogas yield	0.03 kg/kg OPW	0.03 kg/kg Plantain peel
Fertilizer yield	0.32 kg/kg OPW	-
Starch yield	-	0.02 kg/kg Plantain peel
Reaction mass efficiency	11.24 %	5.92 %
Annual Productivity	0.053 %	0.002 %
Energy Indicators		
Specific energy consumption	3.21 MJ/kg OPW	0.52 MJ/kg Plantain peel
Overall energy efficiency	5.14 %	1.59 %
Self-generation index	13.58 %	9.98 %

3.3. Economic assessment

The economic results of the optimized biorefineries showed a non-favorable behavior for the NPV. For both cases, 20 years of the project were analyzed, showing that the NPV for that year is **-13.52** and **-18.92** mUSD for OPW and plantain peel-optimized biorefineries. The costs that most influenced the determination of the cost of production in both cases were raw materials, reagents, and utilities (about 65 % for the OPW biorefinery and approximately 78 % for the plantain peel biorefinery). As expected, the capital costs for the OPW-optimized biorefinery were higher than those obtained for the plantain peel biorefinery. Comparing the different processing stages (distillation for the OPW biorefineries and starch extraction for

the plantain peel biorefinery), it is notable that the equipment and requirements for utilities and energy supplies are very different, causing the distillation process to be more expensive.

Additionally, the economic profit for both schemes had a negative value, which means that the schemes are not profitable at the established 140 kg/h scale. However, this behavior can be improved by considering a higher processing scale. Even high scales may favor different optimized schemes than those resulting in this study.

4. Conclusions

The optimization methodology applied to the design of biorefineries was developed in this work. It could be shown that the optimized biorefinery schemes showed high productions of fermentable sugars, which are platform products widely used in biotechnological processes since they allow obtaining various value-added products. The best raw material with the best performance in the analysis was OPW, with a production yield of fermentable sugars (3.86 kg/kg) higher than the obtained from plantain peel biorefinery (0.14 kg/kg).

As future works, the authors propose that the optimization methodology can be applied again in these systems. The optimization objective allows determining the optimal routes with optimal processing scales in which profitability of the biorefinery is obtained and high yields of the products by-products of it. Another analysis that can be included in this work is polluting emissions to the environment, which could be an additional optimization function.

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