Orange peel waste management alternatives to obtain added-value products and energy vectors through the biorefinery concept.

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Abstract.
Orange peel waste (OPW) is a potential raw material to be upgraded in different added-value products and energy vectors applying the biorefinery concept. Therefore, this work evaluates from an energy and economic perspective the production of essential oil, pectin, and biogas as alternatives to valorize OPW residues. The characterization of industrial OPW samples in terms of lignocellulosic composition and proximate analysis was done. Then, the experimental extraction of essential oil and pectin was carried out. Moreover, the remaining solid was used to produce biogas. Instead, the experimental results were used as input data to simulate an OPW biorefinery. The simulation results were used to perform an energy and economic analysis. The experimental essential oil and pectin extraction yields 0.61% w/w and 10.35% w/w, respectively. Biogas production yields 671.67 ml biogas/g VS with a CH_4 content of 66.73%. Moreover, the economic analysis leads to observe that the proposed biorefinery is only feasible at low processing scales. OPW is a potential feedstock to obtain essential oil, pectin and biogas in an energy and economic feasible way at low scales allowing the implementation of small-scale integrated biorefinery systems.
Keywords: *Acid pectin extraction, biogas production, biorefinery concept, economic assessment, energy and analysis, orange essential oil, orange peel waste.*

1. Introduction

Orange peel waste (OPW) obtained from orange juice production is one of the most studied agro-industrial residues in the last years due to the large amounts generated worldwide [1]. This residue comprises about 30% w/w - 50% w/w of the fruit and generates a disposal problem in the food industry [2]. Landfilling and compost are the main alternatives used today by different companies to dispose of this residue. Moreover, OPW has been used to obtain volatile and non-volatile compounds applied in flavorings and cosmetic products [3]. However, different valorization ways are necessary to avoid landfilling disposal-associated problems (e.g., leachate production and organic compounds emissions). Therefore, the integral valorization of OPW ought to be addressed to obtain value-added products and energy vectors derived from the main OPW components through the biorefinery concept. Different biorefinery approaches and valorization ways have been proposed as alternatives to use OPW as raw material. For instance, Patsalou et al., [4] has described the production of essential oil, pectin, and succinic acid using citrus peel waste (CPW) as raw material. These authors conclude that the valorization of CPW is a promising raw material to produce succinic acid as added-value product. Nevertheless, a preliminary economic analysis confirmed that the combined CPW valorization could not be competitive due to the elevated cost of the enzymes in the saccharification stage. In addition, Siles et al., [3] propose the valorization of OPW using combustion, biomethanisation and co-composting. However, the economic feasibility of these alternatives is not ensured due to the high-energy requirements involved in these processes. From these experiences, the importance of the techno-economic and environmental analysis in the overall biorefinery design is highlighted. Therefore, the complete assessment of an OPW biorefinery should involve the three pillars of the sustainability to ensure a good performance of the process [5]. Moreover, the application of experimental data as input to improve the conceptual design of each one of the processing lines in a biorefinery system is desirable. All these aspects are reflected in the biorefinery definition given by Moncada et al., [6]. Therefore, the aim of this work is to evaluate from an energy and economic perspective the production of essential oil, pectin, and biogas as alternatives to valorize OPW residues.

2. Materials and methods

2.1. Experimental procedure

2.1.1. Raw materials

OPW was obtained from the FLP Procesados company, Chinchina Caldas Colombia. OPW used in chemical characterization was immediately frozen at -4°C, dried at 40°C for 24 h until reached a moisture content below 10% (Shimadzu moisture balance MOC-120H). Finally, the samples were milled to 40 mesh (0.4 mm particle diameter) using a knives mill (Gyratory mill SR200 Gusseisen, Redsch GmbH, Germany) to ensure homogeneity and increase surface area [7]. Nevertheless, OPW used as raw material to obtain essential oil, pectin and biogas was cut in small pieces of 2 mm and cooled at 6°C until use.

2.1.2. Orange peel waste characterization

Characterization has been developed in terms of chemical analysis and proximate analysis. **Table 1** shows the standard methods used in characterization.

Table 1. The standard methods.

CHEMICAL CHARACTERIZATION		
Compound	Method	Ref
Extractives	NREL/TP-510-42619	[8]
Holocellulose	ASTMD1104-56	[9]
Cellulose	TAPPI T203	[10]
Hemicellulose	Subtraction between the holocellulose and cellulose	
Acid insoluble lignin	TAPPI T222	[11]
Total pectin	Yu et al. (1996)	[12]
Fat	Rivas et al. (2008)	[13]
Potein	Macro-Kjeldahl	[12]
Ash	NREL/TP-510-42622	[14]
Moisture	ASTM E871-82	[15]
PROXIMATE ANALYSIS		
Volatile matter	ASTM D1102-84, ASTM E872-82	[16], [17]
Fixed carbon	ASTM E872-82	[16]

2.1.3. Essential oil extraction

The extraction of essential oil was carried out by means of steam distillation. To avoid degradation of the essential oil, the steam was used at 90°C. The time of the extraction was 180 min. From the distillation, an emulsion of water and oil was obtained, which was separated by simple decantation [18].

2.1.4. Pectin extraction

The remaining solid from the essential oil extraction was subjected to the pectin extraction process. The extraction was carried out by means of an acid hydrolysis with citric acid. A pH of 2.8, time of the hydrolysis of 60 minutes with a concentration of sodium hexametaphosphate of 0.7% w/w were used as extraction conditions [18]. The hydrolysis was carried out at 80°C with a wet sample: water ratio 1:20. The mixture was filtered to separate the solid from the liquid. Then, the liquid fraction was centrifuged at 4000 rpm for 15 min to separate remaining solids. Pectin was precipitated with the addition of 98% ethanol (1.5:1, v/v). The mixture was cooled during 20h at 6°C. After, the solution was washed two times with ethanol and dried at 50 °C for 16 h [19].

2.1.5. Biochemical methane potential assay (BMP)

Biogas production was based on the standard method VDI 4630, which reports the use of degassed inoculum obtained from an anaerobic reactor (e.g., UASB). In this case, the inoculum was obtained from the anaerobic reactor located at a coffee processing company in Chinchina, Caldas. The substrate was the remaining solid from the extraction of pectin. The inoculum to substrate ratio in volatile matter basis was 0.4, according to the standard method. The assays were performed by duplicate and a volumetric displacement method was applied to determine the amount of biogas produced [20]. On the other hand, the biogas composition was measured using the Gasboard – 3100P gas analyzer, which reports the composition of CH_4 and CO_2. Finally, a nutrients solution reported by Angelidaki et al., [21] was added to increase the efficiency of the process. A temperature, volatile solids and pH were monitored to evaluate the process yield and efficiency [22].

2.2. Process simulation

2.2.1. Process description

The OPW processing starts with the essential oil extraction. Indeed, the essential oil extraction is performed using a steam distillation process. In this way, a trayed column of five theoretical stages was simulated to remove the main components of essential oil (i.e., D-limonene, β-myrcene, and γ-terpinolene). The second stage of the biorefinery is the pectin extraction. The process flow diagram in this stage is based on the pectin extraction flowsheet described by Casas-Orozco et al., [23]. This process is carried out in a series of two CSTR to achieve a high extraction yield at 80°C. The residence time in the acid extraction process is 60 minutes. Then, the extracted solid is separated from the liquid fraction using a press filter. The liquid fraction from the acid extraction process is mixed with ethanol (95%v/v) to obtain a pectin gel. The ethanol-to-acid hydrolysate is 2:1. Before, the gel is decanted and washed with more ethanol (95%v/v). The rinsed pectin is pressed to remove excess ethanol. Finally, the pressed gel is dried in a convective furnace and milled in a hammer mill. The entire streams with remaining ethanol are pre-heated in a heat exchanger before to be distilled in a trayed column. The recovered ethanol is recycled to the process avoiding the excessive ethanol consumption. The remaining OPW solid is used to produce biogas. For this process, a pretreatment of the solid was not considered due to the effect of the citric acid in the lignocellulosic matrix of the OPW. Therefore, this solid was fed to an anaerobic digester and mixed with an anaerobic inoculum. The process was simulated at mesophilic conditions (i.e., 37°C and 1 atm). The produced biogas is dried using a biogas dryer to increase the calorific value of the biogas.

1.1.1. Mass, energy and economic evaluation

The proposed OPW biorefinery was analyzed considering the mass and energy requirements of the process. For this, a set of indicators related to mass yields, energy efficiency were calculated [24]. In addition, the renewable energy consumption of the biorefinery derived from the biogas combustion process was 15%, which also can be improved through the co-digestion of different residues. In order to evaluate the economic viability of the proposed biorefinery, an analysis was carried out considering d. The energy requirements (utilities as cooling water, low, mid and high-pressure steam, and electricity) were determined with the package Aspen Energy Analyzer. The cost of the equipment was calculated using the software Aspen Process Economic Analyzer. The capital depreciations, maintenance costs, labor costs, fixed charges, general and administrative costs and the plant overhead were calculated based on the economic evaluation methodology for chemical processes of Peters and Timmerhaus [25]. This analysis was estimated in US dollars for a 10-year period at economic typical conditions of Colombia (annual interest rate of 17%, income tax of 25%), considering the straight-line depreciation method.

3. Results and discussion

3.1. Characterization

The results of the chemical characterization and proximate analysis of OPW are summarized in **Table 2**.

Table 2. Characterization of OPW.

Chemical Characterization (Share %wt. dry)								
Extractives	**Cellulose**	**Hemicellulose**	**Lignin**	**Pectin**	**Protein**	**Fat**	**Ash**	**Moisture**
30.76 ± 1.07	30.38 ± 0.50	9.42 ± 4.36	5.11 ± 2.14	11.13 ± 0.16	4.90 ± 0.20	4.60 ± 1.91	3.64 ± 0.20	77.38 ± 0.15
Proximate analysis (Share %wt. dry)								
Volatile Matter			**Fixed Carbon**		**HHV (MJ/kg)**			
8.15			91.37		11.76			

3.2. Essential oil

The essential oil through steam distillation obtained yield 0.61% w/w. This result is higher than the reported value by Patsalou [4] (0.43% w/w). The main factors to explain the different results are operating conditions of the extraction process such as extraction time and the type of extraction method used.

3.3. Pectin

Reports from the literature indicate pectin yield range of 1% to 20%. Different extracting agents are used for the extraction pectin. Hydrochloric acid, EDTA, citric acid, ethanol, water, tartaric acid stands out to be used as extractive agent. Citric acid is emerging as an excellent compound for the extraction of pectin. Guzel et al. [26] performed pectin extraction at 80 ° C for 60 min pH 1 by conventional extraction. As a result, it was obtained a yield of 11.46%. In this work, a yield of 10.35% was obtained. This reflects a high yield compared to the work done by Guzel.

3.4. Biochemical methane production

The results of TS and VS for the residue that remains after the extraction of essential oil and pectin is 92.37± 0.12 % and 87.87± 0.21 % respectively. 2015 mL of accumulated biogas were produced, with a methane composition of 66.73%, which after the third day stabilized. The yield of biogas was 671.67 mL/gVS (447.82 mL CH_4/gVS). This result is high when compared with the performance given for an OPW without prior pretreatment. Calabro et al. [1] report several yields of biogas production for OPW taking into account a different pretreatment. For the OPW without pretreating it reports a value of 355 mL

CH4/gVS. The presence of essential oil (especially limonene) inhibits the bacteria present in the inoculum which causes a decrease in the production of biogas [27].

3.5. Mass, energy and economic analysis

The results of the simulation are summarized through the mass flows that have been obtained from each of the products involved in the simulation. **Table 3** shows said mass flows obtained at the simulation level. An annotation that is worth considering is that the mass flow that was considered to perform each of the simulations was 10 ton/h.

Table 3. Mass flows obtained from the simulation process.

Products	Mass flux (Ton/h)
Essential oil	6.1
Pectin	103.5
Biogas	

The energy analysis of the biorefinery was carried out in terms of the consumption of the necessary utilities for the process of transformation of the orange peels in the products proposed. **Table 4** presents the results of the high, medium and low steam consumption, as well as the cooling water and electricity required by the biorefinery.

Tabla 4. Consumption of profits from the biorefinery proposed for the orange peel.

Utility	Flux	Unit	Enthalphy flux	Unit
Electricity	703.53	kW	N.A.	N.A.
Low steam	2.64	t/h	2803.1	MJ/t
High steam	2.36	t/h	2774.1	MJ/t
Average steam	6.00	t/h	2713.1	MJ/t
Cooling water	428.25	m^3/h	20.9	MJ/m^3

The yields obtained in the proposed OPW biorefinery are similar with different results found in the open literature for the products processed in stand-alone way. Therefore, this shows the feasibility of the biorefinery concept to valorize agro-industrial waste. On the other hand, the energy evaluation shows high energy efficiencies in terms of renewable energy use to supply the requirements of the biorefinery. In fact, the overall energy efficiency of the biorefinery was 45%, which demonstrates the need to improve in a energy way the configuration of the biorefinery.

The economic analysis was carried out with the purpose of stipulating if the biorefinery could have economic viability from a preliminary point of view in the Colombian context. In the economic analysis, parameters such as the Net Present Value (NPV), the return period of the investment and the internal rate of return are evidenced. Also, other aspects related to the distribution of costs in the biorefinery, scale analysis, CAPEX and OPEX are analyzed. First, the distribution of the costs associated with the equipment used in the biorefinery is 36% essential oil extraction, 25% pectin extraction and 39% biogas production.

Another of the analyzes involved in the biorefinery is the distribution of costs, which are presented in the diagram in **Figure 1**.

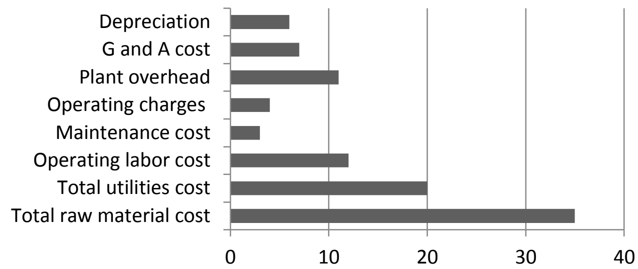

Figure 1. Percentage distribution of the associated costs in the biorefinery (G and A are general and administrative costs).

As shown in **Figure 1,** the results show that the orange peel is one of the most relevant costs in the whole process, being approximately 37% of the total. On the other hand, costs related to services, operation and maintenance and overdesign of the plant are the most important costs within the plant. The distribution presented for this biorefinery has some degree of disparity with other biorefineries published for lignocellulosic residues such as the coffee souk and cane bagasse [28], [29]. This is due to the fact that the amount of equipment used in these biorefineries is very high compared to the equipment considered in the present work, which means that the costs associated with the depreciation of capital are much greater in the published biorefineries. Thus, the distribution of costs makes it possible to elucidate that the largest costs are those associated to all the inputs required for the transfocation of the raw material in the desired products. [6]. Finally, the return on investment to the proposed scale is 8.5 years.

4. Conclusion

The use of orange peel waste under the concept of biorefinery allows the full use of these residues to obtain added-value compounds and energy vectors in a preliminary feasible way. This is reflected in the technical, economic and energetic results of this work.

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