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Simulation Approach Through the Biorefinery Concept of the Antioxidants, Lignin and Ethanol Production using Olive Leaves as Raw Material

Juan Camilo Solarte-Toro[a], Juan Miguel Romero-García[b], Juan Carlos López-Linares[b], Encarnación Ruiz Ramos[b], Eulogio Castro[b], Carlos Ariel Cardona Alzate[a,*]

[a]Instituto de Biotecnología y Agroindustria. Universidad Nacional de Colombia Manizales campus. Km 09 vía al Magdalena, 170003 Manizales, Colombia.
[b]Dpt. Chemical, Environmental and Materials Engineering, Center for Advanced Studies in Energy and Environment (CEAEMA), Campus de Excelencia Internacional Agroalimentario (ceiA3). Universidad de Jaén, Campus las Lagunillas, 23071 Jaén, Spain.
ccardonaal@unal.edu.co

Olive leaves is derived from the olive oil production with limited practical applications. This raw material can be used to obtain added-value products through its processing applying the biorefinery concept. Therefore, The aim of this work is to evaluate from a techno-economic and environmental perspective the production of antioxidants, lignin and ethanol using olive leaves as raw material through the use of experimental data and process simulation. For this, a biorefinery scheme composed by an acid extraction stage, organosolv pretreatment and simultaneous saccharification and fermentation process was simulated. This process was performed using experimental data obtained from the main conversion blocks of the proposed scheme assuming a linear scaling. Moreover, the separation and purification of the products were performed using conceptual process design tools. Then, the techno-economic assessment was carried out considering economic indicators of the Spain context for an operating facility with a 10 y life-time. Finally, the environmental evaluation was based in the specific solid, liquid and gaseous emissions calculation. The results showed that 100 g of feedstock can produce 38.24 g of antioxidant extract (phenolic compounds>10 %), 11.82 g of lignin and 3.65 mL of bioethanol. In addition, the techno-economic assessment showed that the proposed biorefinery is profitable when 30,000 t/y are processed with a total project cost of 49.1 M USD, an internal rate of return of 15.22 % and a payout period of 7.27 y. As conclusion, the application of the biorefinery concept to upgrade olive leaves in added-value products is feasible from a techno-economic point of view and the implementation of small scale biorefineries in Jaén (Andalusia, Spain).

1. Introduction

Olive leaves are a lignocellulosic material generated in high amounts during the olive oil production (and olive table production). During the initial olive cleaning process carried out in olive mills (almazaras or in olive table factories), small branches and leaves from harvest are separated by density, this material is named as olive leaves (OL). World production of olives exceeds 18 Mt/y and these are accompanied by 4-7 %w/w of OL (Ruiz et al., 2017a), around 1 Mt/y. In Spain, the annually estimated amount of OL along these industries may exceed 3 kt, with the major production in Andalusia (87.8 % of total) (Manzanares et al., 2017). OL are not used to produce any added-value product and they are disposed in landfills, occasionally removed for animal feed (Romero-García et al., 2016a). Therefore, OL have a great potential to be used as an antioxidants, lignin and ethanol source through the implementation of chemical and biochemical processes (Carvajal et al., 2016).
The extraction of a wide range of bioactive compounds from OL has been investigated (Rahmanian et al., 2015). Bioactive products such as secoiridoids (the major constituent is oleuropein), flavonoids (apigenin, luteolin, together with their 7-O-glucosides) and phenolic compounds (mainly hydroxytyrosol) have been identified (Rodrigues et al., 2015). As lignocellulose-derived biomass materials OL contain a certain proportion of

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carbohydrate polymers and lignin that could be converted into fermentable sugars and other valuable molecules, which in turn would work as precursors for high added-value products such as biofuels, antioxidant compounds and sweeteners. On the other hand, it has been demonstrated that the fuel ethanol prices produced from olive biomass are still not competitive in the worldwide ethanol market (Romero-García et al., 2016b). Therefore, the application of the biorefinery concept to obtain this energy vector and other added-value products could improve this situation (Moncada et al., 2016). Therefore, the aim of this work is to evaluate from a techno-economic and environmental perspective the production of antioxidants, lignin and ethanol using olive leaves as raw material through the use of experimental data and process simulation. The above aiming to elucidate from a qualitative point of view the use of this residue to increase the number of products of the olive tree crop in Spain.

2. Materials and methods

2.1 Raw materials

The feedstock considered in the calculations of this work is the OL described by Ruiz et al. (2017b). They were obtained from the olive mill "S.C.A. Unión Oleícola Cambil" Jaen (Spain), air-dried to an equilibrium moisture content of approximately 9.5 %w/w and milled to achieve a particle size smaller than 1 cm. The OL was characterized using the National Renewable Energy Laboratory standard biomass analytical procedures (NREL, 2012). The nitrogen content in raw OL as determined by an EA1112 Thermo Finnigan Elemental Analyser and it was converted into protein using the N x 6.25 conversion factor. Starch was measured using the method Total Starch Assay Kit (Megazyme, Ireland). Fat was determined on the material without extractives by soxhlet extraction with hexane for 24 h. The OL composition (% db) was 9.63 glucan; 4.00 xylan; 3.19 arabinan; 1.86 galactan; 0.23 mannan; 16.99 lignin; 43.73 extractives (7.06 glucose; 4.40 phenolics (expressed as gallic acid equivalent (GAE)); 3.55 mannitol); 0.75 acetyl group; 8.44 ash; 8.10 protein; 0.50 starch; 2.47 fat.

2.2 Process description and simulation procedure

The proposed process consists of three main blocks (Figure 1). The first one is an acid extraction performed at 120 °C, 2 %(w/v) H_2SO_4, 60 min and a solid concentration of 15 %(w/v). This process was carried out to remove a large amount of phenolic compounds and xylan. The second block is an organosolv pretreatment at 150 ºC, 60 min with the goal to remove the lignin content using an ethanol–water mixture (50 %v/v) and sulphuric acid (1 %w/v) as catalyst. The solid-liquid ratio employed in this pretreatment was 10 %(w/v). The third one is a simultaneous saccharification and fermentation (SSF) stage was performed to accomplish the ethanol production, at 37 ºC for 72 h and 20 %(w/v) of solids. Commercial Cellic® CTec2 (Novozymes A/S, Denmark) and *Saccharomyces cerevisiae* Ethanol red (Fermentis, France) were used in SSF. Enzyme loading was 15 FPU/g substrate (0.2 g C. CTec2/g substrate) and a cell addition of 0.25 g/L.

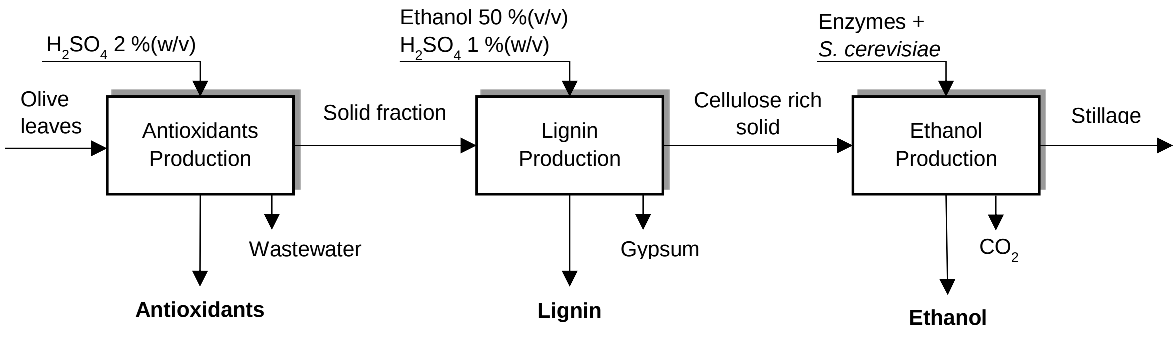

Figure 1: Simplified block diagram of the biorefinery to produce antioxidants, lignin and ethanol

According to the experimental results in the first block 43.6 %w/w of the material is solubilized. In the recovered liquid, there are phenolic compounds (4.3 g GAE/100 g of OL), sugars (mainly glucose, 7.7 g/100 g of OL) and all initial mannitol (3.6 g/100 g of OL). The extracted solid goes to organosolv pretreatment where 35.5 %w/w is solubilized. In the liquid stream, 57.6 %w/w of the initial lignin is recovered. The remaining solid rich in cellulose goes to the final stage of SSF (this solid is washed with water to reduce the ethanol content) where a cellulose hydrolysis yield of 81.2 % is achieved. All the glucose produced is consumed with an ethanol yield of 96.6 % with respect to the theoretical yield.

The reactions steps in each block of the proposed biorefinery were simulated using a stoichiometric approach, which can be justified from the use of the experimental data obtained and reported in the open literature. On the other hand, all the necessary processes that are required to purify the main products were conceptually designed: i) The rich phenolic compounds stream is neutralized with calcium hydroxide and dried by spray as proposed by Nachman (1998) patent, where almost all phenolic compounds are recovered (95 %) and a natural antioxidants extract is obtained with a purity greater than 10 %. ii)The lignin is recovered through the precipitation process described by Kautto et al. (2013) which is carried out at 50 °C and lowering the ethanol content below 15 %(v/v), where a lignin recovery of 79 % is achieved. iii)The ethanol stream of the organosolv pretreatment together with the SSF product is subjected to a distillation to produce a 50 %(v/v) ethanol stream which is recirculated to the organosolv pretreatment (recovery >99.6 %) (Da Silva et al., 2017). The excess from this stream is subjected to a second distillation and dehydration using molecular sieves to obtain a fuel ethanol (purity> 99.5 %). The process flow diagram of each block into the biorefinery is similar with those reported by Kautto et al. (2013) and (Cardona Alzate et al., 2018). Therefore, the validation of the model can be performed using the process synthesis reported by these authors as well as the yields reported in the above paragraph.

2.3 Techno-economic and environmental assessment

The simulation software employed to perform the proposed biorefinery was Aspen Plus v9.0. The economic evaluation was performed using the simulation tool Aspen Process Economic Analyzer (APEA) v9.0. As a final point, the environmental evaluation was performed calculating the amount of liquid, solid and gaseous emissions that the biorefinery produces (Ruiz-Mercado et al., 2012). All simulation process was performed using the Non-Random Two Liquids (NRTL) and Hayden-O'Connell equation of state (HOC EoS) to describe the behaviour of the liquid and vapor phases presented in each process (Cardona Alzate et al., 2018). It is important to note that experimental data were used to obtain the mass and energy balances of the main processes in the biorefinery (i.e., acid extraction, organosolv pretreatment and SSF process).
The biorefinery is going to be located in the province of Jaén, where there are the largest number of olive mills in Spain (> 23 % of the total) and the highest production of OL (> 36 % of the total) (Manzanares et al., 2017). The size of the analyzed biorefinery has been of 30,000 t, working 8,000 h/y. On the other hand specific parameters regarding to some Spain conditions such as the raw material costs, income tax (25 %), annual interest rate (5 %) and labor salaries, among others, were incorporated in order to calculate the production costs. This analysis was estimated for a 10-year period. The capital depreciation was calculated using the straight-line method. In addition, the capital investment as well as the calculation of the equipment sizing was carried out using the Aspen Process Economic Analyzer tool, which employs the mass flows and the main design variables of the equipment involved in the process (e.g., reactors, distillation columns and so forth) to calculate their size as well as the total cost. Moreover, variables such as construction materials (e.g., stainless steel) also were considered. On the other hand, the utility costs were calculated through the use of the mass flow of steam and cooling water that are necessary to satisfy the energy requirements of the biorefinery. Nevertheless, these flows were calculated once an energy integration using the pinch approach was done using the Aspen Energy analyzer tool considering a minimum temperature difference used to perform the pinch analysis was 10 °C (ΔTmin=10 °C)

3. Results and discussion

3.1 Process simulation and economic assessment

The productivity of antioxidants, lignin and bioethanol from the simulation of the proposed biorefinery were 31.44 t/d, 9.72 t/d and 2.37 t/d with a mass yields related to the feedstock of 0.38, 0.12 and 0.03. The antioxidants stream has a 10 % (w/w) of phenolic compounds, where oleuropein and hydroxytyrosol are the main components. On the other hand, the ethanol and lignin were obtained with a purity of 99.5 % (anhydrous ethanol) and 65 %, respectively (Romero-García et al., 2014). The low purity of the lignin stream can be explained due to the precipitation of other components that are presented after the organosolv process. In addition, this result also can be attributed to the 79 % of the soluble lignin precipitation that was considered according to the operational conditions of this step (T=50 °C and P=1 bar) (Kautto et al., 2013). Finally, the ethanol purity was accomplished through the use of molecular sieves.
The above mentioned results indicated that antioxidants have a high production capacity in comparison to the lignin and bioethanol. This can be attributed to the relatively high amount of extractives content of the OL that accounts to 40 % of its dry basis. This fact is interesting because commonly potential antioxidants sources are food residues such as Andean blackberry, capulí cherry peel and banana. Passion fruits have lower amounts of cellulose and hemicellulose in their structure, which difficult the obtainment of other type of products (Vasco et al., 2008). Moreover, the ethanol yield from the saccharification and fermentation process is lower than the data reported by (Ballesteros et al., 2002), with a maximum ethanol production of 11.90 g/L. Finally, an energy analysis of the biorefinery scheme shows that the most energy demanding stage is the ethanol production focused mainly in the ethanol purification followed by the organosolv pretreatment and the acid extraction

process. Once an energy analysis of the whole process was performed and the pinch approach was used to design a heat exchanger network, the energy savings were estimated on 13.22 %. Thus, the whole process consumes 2,612 kg/h of middle pressure steam, $3.49x10^4$ kg/h of low pressure steam and $3.51x10^6$ kg/h of cooling water.
The economic assessment of the proposed biorefinery was performed using the mass an energy balances obtained from the simulation. The considered mass flow of OL in dry basis was 3,425 kg/h. The OL processing to produce antioxidants, lignin and bioethanol is mainly affected by the raw materials costs, utilities costs, operating labor costs and the depreciation costs, which accounts more than 70 % of the total cost of the biorefinery. In this way, the operational expenditures (OPEX) of this process was about 8 M USD, which, considers the direct variable costs and the costs of the indirect manufacturing materials. This cost is lower in comparison with other biorefineries reported in the literature (Moncada et al., 2014). Moreover, the total capital investment of the biorefinery was calculated as the total direct cost of each one of the used equipment in the biorefinery. Thus, the calculated total capital investment was 22.80 M USD, which is lower in comparison with the processes reported by Ghanta et al (2013). Nevertheless, the calculated costs (i.e., OPEX and Investment) are directly related with the plant capacity and availability of the raw material. Finally, the total project capital cost of the biorefinery was 49.10 M.USD, which is a comparable result with the reported data by (Cardona Alzate et al., 2018). The above mentioned values were calculated using the information showed in Table 1 and the obtained data for the equipment costs determined by the software Aspen Process Economic Analyzer v9.0. However, these results could have an uncertainty between 30 % and 50 %, depending on the correlations for the equipment sizing. Finally, the plant overhead feature showed in Table 1 allows to estimate that the plant capacity of the biorefinery can be increased. The above can be supported due to the plant overhead share in biorefineries of lignocellulosic materials varies from 1 % to 5 %.

Table 1: Annualized costs and economic metrics for the proposed biorefinery

Feature	Thousands USD/y	Share (%)
Raw materials	2,053	13.81
Utilities	2,400	16.14
Operating labour	2,084	14.02
Maintenance	1,320	8.88
Operating charges	521	3.50
Plant Overhead	1,702	11.45
G and A cost*	862	5.80
Depreciation	3,928	26.42
Total cost	14,872	100
Internal rate of return (%)	15.22	
Profitability index	1.16	
Payout Period (years)	7.27	
NPV (M USD)	25.55	

*General and Administrative costs

In addition, the feasibility of the OL based biorefinery was demonstrated through the calculation of the metrics mentioned in Table 1, using the cash flows obtained from the economic assessment and the expected products sales in the Spain context. In this way, the simulated biorefinery is feasible according to the profitability index, which is greater than the unity and the initial investment in the project will be recovered in the eighth year of the lifetime of the biorefinery. This statement is evidenced in the pay-out period, which is 7.27 y. Finally, the variance of the net present value (NPV) in the lifetime of the project is showed in Figure 2.
In this, the NPV of the biorefinery is negative in the first seven years of the lifetime of the project. However, a positive economic margin from the product sales is obtained in the eighth year. In the end of the lifetime of the process, the revenues of the facility are 25.55 M USD, which is higher in comparison with the biorefineries presented by (Cardona Alzate et al., 2018) in spite of the plant capacity. Even so, this value remains lower when this value is compared with the NPV reported by Moncada et al. (2014) for a sugarcane based biorefinery in the Colombian context.

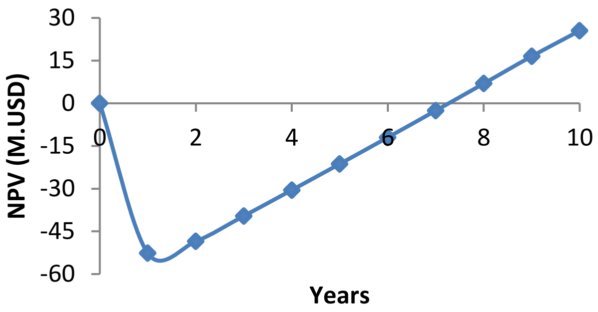

Figure 2: Net Present Value of olive leaves biorefinery with a feedstock mass flow of 3,425 kg/h in dry basis

3.2 Environmental assessment

The environmental assessment of the OL based biorefinery was performed considering the solid, liquid and gaseous emissions of the process. In this case, the solid residues are only associated to the calcium sulphate, which is formed in the acid extraction process. The mass flow of this residue is 1,371.81 kg/h with a moisture content of 45 %(w/w). This compound was considered as a residue because a conditioning process (i.e., drying and milling) is necessary to convert the gypsum in a co-product of the biorefinery. On the other hand, the gaseous emissions are associated with the carbon dioxide (CO_2) produced in the SSF process. The calculated mass flow of this gas was 501.69 kg/h, which has a global warming potential (GWP) of 0.2766 kgCO_2/kg of product. This value is relatively low in comparison with the global warming potential generated by the standalone bioethanol production from corn, which varies from 0.03 to 2.34 (Kraatz et al., 2013). Finally, the liquid emissions are the main residues that are produced in the biorefinery. The total amount of liquid waste (wastewater+stillage) that is generated in the biorefinery was 33.5 t/h, which is associated with the water requirements of the acid extraction and organosolv pretreatment. This amount of water is higher than the amount of waste water produced in the bioethanol production process at industrial level. Other environmental indicators related with the hazardous materials management into the biorefinery were calculated according to the GREENSCOPE methodology (Ruiz-Mercado et al., 2012). These indicators can be found in Table 2.

Table 2: Environmental indicators calculated for the biorefinery

Indicator	Value	Units
Specific liquid waste	18.31	kg waste water/kg products
Specific solid waste	0.76	kg gypsum/kg products
Global warming potential	0.28	kgCO_2/kg product
Specific hazardous raw materials input*	0.54	kg hazardous material/ kg product

The environmental analysis reflects that the main problem associated to the implementation of an olive based biorefinery is the water use. Therefore, the solid to liquid ratios of the acid extraction process and organosolv pretreatment must be decreased aiming to reduce the amount of the water requirements. In this way, a mass integration of different streams into the biorefinery could be applied.

4. Conclusions

Olive leaves are potential lignocellulosic feedstocks that can be employed to produce different high added-value products such as antioxidants, lignin and bioethanol through the implementation of the biorefinery concept. The results from the techno-economic analysis showed that the proposed biorefinery scheme was profitable at the studied process scale. Moreover, the environmental results suggest low solids and gaseous emissions. However, the high specific liquid waste production might be a problem that can be deeply studied to optimize the water used in a biorefinery system with an organosolv pretreatment. Finally, the use of experimental data coupled to simulation tools allows to obtain interesting results related with the prefeasibility analysis of a process.

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