Bioethanol production using optimized conditions for the sulfuric acid pretreatment of extracted olive tree biomass: Techno-economic evaluation

J.C. Solarte-Toro[1], J.M. Romero-García[2*], J.C. Martínez-Patiño[2], E. Ruiz[2,3], E. Castro[2,3], C.A. Cardona-Alzate[1]

[1]Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia, Manizales campus. Manizales - Colombia. Km 07 vía al Magdalena
[2]Department of Chemical, Environmental and Materials Engineering; [3]Center for Advanced Studies in Energy and Environment (CEAEMA). Universidad de Jaén. Campus Las Lagunillas s/n | 23071 - Jaén (España).
*Presenting author email: jrgarcia@ujaen.es

Abstract

The bioethanol production process has been designed as a stand-alone process. Moreover, the influence of the pretreatment stage optimization on the techno-economic indicators of the bioethanol production using lignocellulosic biomass has been slightly deepened in the open literature. In this way, the aim of this work is to evaluate the economic feasibility of the bioethanol production using olive tree biomass as feedstock in small scale comparing two scenarios with optimal experimental pretreatment conditions that seek different objectives: optimum 1: the highest recovery of fermentable sugars, 164°C, solids loading 15% and sulfuric acid concentration of 5.9%; optimum 2: the highest concentration of fermentable sugars, 160°C, solids loading of 35% and acid concentration of 4.9%. For this, the bioethanol production process was simulated following the influence of the operating conditions in the pretreatment stage. The results shows that lowest price of bioethanol was 2.44 USD/l obtained with optimum 1 conditions. However optimum 2 present lower environmental impact (liquid wastes and CO_2 emissions). In both scenarios, the olive tree biomass use in a standalone process for bioethanol production is not profitable at small scale with the current prices of raw materials (mainly olive tree pruning and enzymes). As conclusion, the raw material costs, depreciation and ethanol production yield have a strong influence in the economic feasibility of the bioethanol production using olive tree biomass. Therefore, the design of this process using the biorefinery concept could allow improving the production of this energy vector through the addition of other processing lines into the process.

Keywords: Acid pretreatment, Bioethanol, Economic evaluation, Olive tree biomass, Optimal experimental conditions

1. Introduction

Nowadays, a renovated interest to reduce the environmental issues caused by the use of non-conventional energy sources as well as to diversify the energy matrix aiming to reach a sustainable development has been aroused at worldwide level [1]. Indeed, the excessive use of fossil fuels such as crude-oil, natural gas and coal to supply 78.4% of the total energy requirements is directly associated with the increasing trend of the net carbon dioxide (CO_2) emissions and the environmental detriment caused by the exploitation of these energy sources [2,3]. For these reasons, the European Union (EU) countries have developed and proposed different strategies to achieve a continuous improvement of urban and rural communities from different perspectives through the correct and efficient management of the renewable resources, which are able in each region, aiming to strength and ensure prosperity, environmental protection and social cohesion at all levels [4]. Among these strategies, the use of renewable energy sources and the implementation of productive processes to obtain a wide variety of products and clean fuels has been one of the main guidelines followed to accomplish the above mentioned objectives. Therefore, the research on the implementation of this type of energy sources is essential to complete the goals proposed for the next years.

In accordance with the above, the renewable energy production in EU countries has grown progressively in recent years. In fact, the energy supplied through the use of renewable resources provided 17% of the total energy demand in 2016, which is in line with the proposed targets for the year 2020 [4,5]. The main types of renewable energy used in the EU countries are the energy derived from biomass and waste, hydropower, wind energy, solar energy and geothermal energy [2,6]. Nevertheless, the use of traditional biomass, biofuels and waste has been the most used type of renewable energy supplying 66.6% of the total energy produced by renewables [7]. This is because of biomass can be transformed into value-added products and energy vectors through biochemical, thermochemical and chemical processes, which involves a series of technologies to extract or upgrade the main biomass components (i.e., cellulose, hemicellulose, lignin, lipids and starch) [8]. Even though, biomass related to the food industry and human or animal consumption has been widely excluded due to the disjunction between food security and biofuels production [9,10]. Thus, the use of residual biomass from agro-industrial processes is the most suitable option to cover the energy demand through the production of energy vectors such as wood pellets, biogas, bioethanol, biodiesel and syngas, which can be obtained in stand-alone processes [11,12].

Bioethanol production has grown in EU countries through the years using as main crops corn (42%), wheat (33%), sugar beet (18%) and other cereals (7%), which supplied 7% of the global bioethanol production at worldwide level. However, the use of wheat and sugar beet has been grown progressively [7]. On the other hand, less than 0.1% of the bioethanol produced came from lignocellulosic biomass obtained from dedicated energy crops (i.e., miscanthus and switch grass). However, the use of other lignocellulosic feedstocks has been widely studied due to their great potential to create more than 300,000 jobs in Europe and cover more than 20% of the total production [13]. Even so, cellulosic ethanol production has not been developed at commercial scale except some facilities located in Italy and other pilot-scale plants and demonstration facilities [13]. This low presence of cellulosic ethanol in the European market can be explained from the technical and economic point of view. Bioethanol production from lignocellulosic materials requires a pretreatment stage to disrupt the lignocellulosic matrix being the most studied and applied the dilute acid pretreatment [14]. Afterward, a saccharification stage using enzymes is necessary to convert the cellulose in fermentable sugars [15]. These process blocks involve from an economic perspective high cost related to the capital investment costs as well as the raw materials costs [16]. In fact, the enzymes costs can influence between 18%-20% the unit cost of bioethanol using lignocellulosic biomass as raw material [17]. For these reasons, different authors have searched and proposed optimal conditions to improve both yields and productivities [18,19]. However, a deep study related to the effect on techno-economic indicators of the bioethanol production process still is evaluated. Therefore, the combination of optimization, simulation and experimental characterization is a strong tool to elucidate the influence of optimized lab-conditions in the overall performance of the bioethanol production process. Moreover, the design of the productive process be designed under the biorefinery perspective aiming to increase the number of processing lines in this process as well as to increase the economic feasibility of projects related to the olive crop residues [20].

Spain, as EU country member, has implemented the use of renewable energy to supply part of its energy demand. The most employed renewable energy form is those derived from biomass (45.5%) followed by hydropower [5]. Moreover, the bioethanol production and market has grown slightly in the last years. The main raw materials employed to produce this energy vector are food crop feedstock’s such as wheat and corn [21]. However, this country has a great amount of lignocellulosic waste that could be used as feedstock in a biorefinery context, specially olive-derived biomass, which has a great potential to produce energy vectors and high value-added products such as phenolic compounds [22]. Olive-derived biomass includes different residues such as olive tree pruning (OTP), leaves, stones and dry extracted olive pomace. Olive tree pruning is the agro-industrial residue produced in higher amounts with more than 3 million tons each year in Spain [22], mainly located in specific areas of southern Spain, which easy their use as feedstock in other processes to add value to the olive crop productive chain [23]. Though, this lignocellulosic material has been proposed as a potential feedstock for the production of bioethanol because of its great sugars content providing an opportunity to develop a benefical and appropiate management of this residue. Attending to the above, Martínez-Patiño et al [19] performed an optimization of the acid pretreatment of olive tree biomass with the goal to maximize the concentration and amount of fermentable sugars that can be obtained from it. Two optimal conditions were calculated. The first optimal condition (scenario 1), that ensures the highest recovery of fermentable sugars, has a temperature of 164°C, solids loading 15% and sulfuric acid concentration of 5.9%. Meanwhile, the second condition (scenario 2), that ensures the highest concentration of fermentable sugars has a temperature of 160°C, solids loading of 35% and acid concentration of 4.9%. Nevertheless, these conditions do not ensure the techno-economic feasibility of the bioethanol production using this raw material at pilot or industrial level. Then, the aim of this work is to simulate and to evaluate from the techno-economic point of view the production of bioethanol from olive tree biomass taking into account the above mentioned optimal experimental conditions obtained for the acid pretreatment of this feedstock.

2. Methodology.

2.1. Raw material

Olive tree pruning (OTP) considered in this work is the OTP described by Martínez-Patiño et al [19], which was obtained from an olive crop located in Cambil town in Jaen (Spain). The raw material was air-dried and milled in a knives mill to reduce its particle size until ASTM 40 sieve. Once the lignocellulosic feedstock has been conditioned, the chemical composition analysis in terms of extractives, glucan, xylan, arabinan, mannan, galactan and lignin content was performed. In addition, the total solids an ash content were determined.

These analyzes were carried out using the proposed methods by the National Renewable Energy Laboratory (NREL) [25]. The chemical composition of the olive tree pruning is presented in **Table 1**.

Table 1: Olive tree pruning chemical composition.

Feature	OTP (%w)
Moisture	7.00 ± 0.42
Cellulose (Glucan)	23.59 ± 1.22
Xylan	11.11 ± 0.70
Galactan	2.20 ± 0.10
Mannan	1.78 ± 0.10
Arabinan	2.55 ± 0.17
Lignin	17.21 ± 0.30
- Acid insoluble lignin	14.97 ± 0.30
- Acid soluble lignin	2.24 ± 0.10
Extractives	23.06 ± 0.70
- Glucose	5.30 ± 0.30
- Mannitol	3.35 ± 0.20
- Total phenols[a]	2.88 ± 0.20
Acetyl groups	1.86 ± 0.10
Ash	2.70 ± 0.40

[a]expressed as gallic acid equivalent (GAE)

2.2. Process description.

The bioethanol production process using lignocellulosic biomass has been widely described in literature reports [24]. Nevertheless, a short description of the unit operations and process conditions is done in these works because some differences with other reported processes were included due to the biorefinery perspective given. The simulated bioethanol production process consists of seven blocks, which are: extraction, pretreatment, overliming, saccharification, concentration (i.e., evaporation), fermentation and distillation. These stages were designed taking into account the raw materials characteristics, the schematic process and the experimental results proposed by Martínez-Patiño et al [19] as well as the potential of the raw material to produce other value-added product (i.e., natural antioxidants) according to the hierarchy and sequencing concepts. Thus, the biorefinery design approach described by Moncada et al [26] was used to propose the bioethanol production process thinking about its possible conversion in a biorefinery. The block diagram of the bioethanol production process is presented in **Figure 1.**

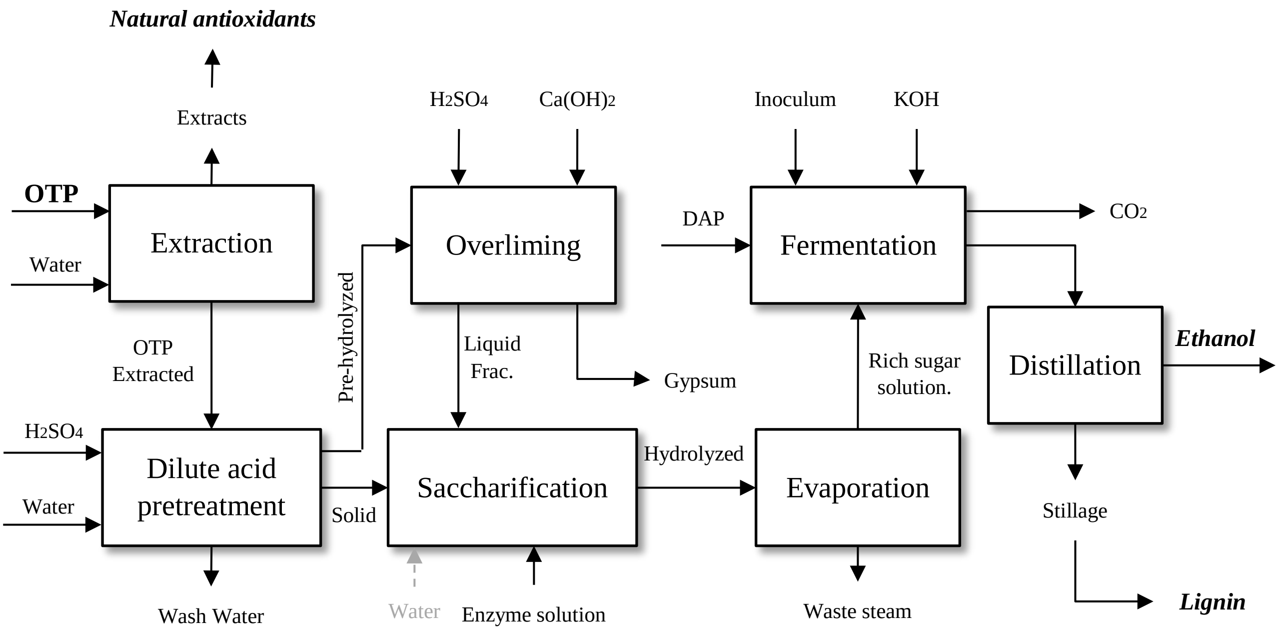


Figure 1: Block diagram of the bioethanol production based on olive tree pruning (OTP).

The first block in the process is the extraction stage. In this, a water extraction was performed using a trayed-column of two theoretical stages to remove water soluble components from the olive tree biomass such as monomeric sugars (e.g., glucose, xylose, arabinose, and mannose), polyols (e.g., mannitol) and phenolic compounds aiming to avoid possible inhibitory effects in the subsequent stages and to take advantage of these components as natural antioxidants of interest in the pharmaceutical, food and cosmetic industry [27–29]. This process was carried out at 2 atm, adiabatic conditions, using heated water at 120 °C to reach 20% solubilization of the loaded solid. Then, the extracted lignocellulosic material was sent to a dilute acid pretreatment stage to disrupt the lignocellulosic matrix into a rich xylose liquor and cellu-lignin fiber. The process conditions (solid-liquid ratio, temperature and acid concentration) of this stage were varied following the two experimental optimums proposed by Martínez-Patiño et al [19]**.** From this stage, the liquid fraction from the pretreatment reactor was detoxified in the overliming block. Here, two processes were carried out: the first one decrease the furfural, 5-hydroxymethylfurfural (HMF), formic acid, acetic acid and phenols (inhibitor compounds) concentration through the calcium hydroxide addition (pH=10). On the other hand, the second process involves the pH adjust to 4.8 using sulfuric acid and the separation of the gypsum formed. The overliming process was carried out at 50°C and 1 atm. Subsequently, the liquid fraction from this stage and the cellu-lignin fiber from the pretreatment block were mixed in the saccharification stage, where the cellulose was degraded to glucose through the use of an enzymatic complex composed of endo-beta-1,4-glucanase, exo-beta-1,4-glucanase and beta-1,4-glucosidase. This process is carried out at pH 4.8 and 50 °C with a solids concentration not greater than 20 %w/v for 72 h [8]. The outlet stream from this stage was sent to a evaporation process aiming to increase the fermentable sugars concentration until 110 g/l and to avoid the oversizing of the following processing stages [33]. Moreover, the concentration stage was considered in the bioethanol production process to maintain always the same initial conditions in the fermentation stage. Then, the fermentation process was carried out using a C_5 and C_6 consuming *Escherichia Coli* MM160 genetically modified [19]. The operating conditions of the fermentation process were 37 °C and 1 atm. In addition, important nutrients (e.g., diamonium phosphate (DAP)) and potassium hydroxide were added to maintain the microorganism growth and the pH control, respectively.

Finally, the distillation stage was designed using conceptual design tools and the process separation scheme proposed by Humbird et al [15]. Thus, two distillation columns and a molecular sieves dehydration process were considered. The first distillation tower is so-called as Beer column, which concentrates the water-ethanol mixture from the fermentation block and removes the entire solid fraction formed during the previous blocks (e.g., biomass). From this, the solid fraction removed, which is rich in lignin, can be upgraded to polymers, fibers, phenols, benzene, toluene, and xylenes (i.e., BTX)compounds [31-33]. The number of theoretical stages considered for this tower was 10 with a reflux ratio around 1.3. The top stream from this tower is condensed and sent to a rectification column to produce an azeotropic ethanol mixture (i.e., 92%w/w) at saturation conditions. Once, the bioethanol has been purified such as possible in the rectification column, this stream is sent to a molecular sieves process were this mixture is vaporized and pressurized to 118 °C and 1.43 atm [34]. Consequently, anhydrous ethanol (>99.5 %w/w) was produced and the water content removed by adsorption [8].

2.3. Simulation procedure and energy analysis.

The mass and energy balances of the bioethanol production process were obtained through the use of Aspen Plus v9.0 software (Aspen Technology Inc. USA). The process was simulated using small scale with a mass flow rate of 90 OTP t/day (wet basis) as feedstock (30,000 OTP t/y, 8000 h/y). As thermodynamic models to describe the liquid and vapor phases as well as to calculate the activity and fugacity coefficients were the Non-Random Two Liquids (NRTL) and the Hayden-O'Connell equation of state (HOC EoS), respectively [8]. Moreover, the lignocellulosic composition of the raw material (i.e., cellulose, hemicellulosic components and lignin) were introduced into the simulation software manually using the thermodynamic properties reported by the National Research Energy Laboratory (NREL) [35].

Once the mass balances of the overall process were obtained, the energy requirements of the bioethanol production process in terms of heating and cooling were calculated. As heat source low (125 °C, 2.46 atm), medium (175 °C, 8.64 atm) and high (250 °C, 38.92 atm) pressure steam were used. Furthermore, demineralized water (20°C) was employed as cooling agent. Thus, the estimation of the energy consumption was performed based on the results of the energy balances obtained from the simulation. In this way, the steam and cooling water needs in heat exchangers, reboilers and condensers were obtained. Finally, the simulation tool Aspen Energy Analyzer v.9.0 was used to perform the pinch analysis of the process using hot and cold streams in the process aiming to reduce the amount of utilities employed in the process, which is directly related to an energy integration [36].

2.4. Techno-economic assessment.

The technical and economic assessment of the designed bioethanol production process involves the calculation of yields, economic parameters and costs associated to the capital and operational expenditures (i.e., CAPEX and OPEX). From the technical point of view, the main parameter that is analyzed is the bioethanol yield, which is expressed as the ratio of the obtained product and the amount of feedstock employed in the process. On the other hand, the main parameter calculated related to the profitability of the process was the production costs which is compared to the current bioethanol market prices. Moreover, the utilities costs, total production costs and the total project capital costs. These costs were calculated using the commercial software Aspen Process Economic Analyzer v9.0 (Aspen Technology Inc., USA) using the mass and energy balances from the simulations. As input data to perform the economic evaluation a 10-years period with an annual interest rate of 5% was considered. In addition, the straight-line method for the capital depreciation calculation and a 25% of tax rate, also were taken into account. The operator and supervisor labor costs were 22.84 USD/h and 24.69 USD/h, respectively, considering the Spain context [37]. Finally, a period of 8000 h per year was taken into account to perform the calculations. The main data used in the economic assessment of the two proposed biorefineries is presented in the **Table 2.**

Table 2. Raw material and utilities costs used in the economic assessment.

Feature	Value	Unit	Reference
Olive tree pruning	40.00	USD/t	
Enzymes	630	USD/t	[15]
Sulfuric acid virgin 100%	73.00	USD/t	[38]
Lime hydrated bulk f.o.b*	65.00	USD/t	[38]
Cooling water	0.04	USD/m^3	[39]
Electricity	0.12	USD/kWh	[39]
LP Steam	4.99	USD/t	[39]
MP steam	5.91	USD/t	[39]
HP Steam	6.79	USD/t	[39]
Fuel	26	USD/MW	[39]

*f.o.b: free on board

3. Results and discussion.

3.1 Process simulation

3.1.1 Ethanol yields

The flows of raw materials and bioethanol produced are shown in Table 3. This shows that almost all flows are greater in the case of the optimum 1 except for the enzymes that is very similar and the potassium hydroxide that is half. Ratio OTP/enzymes near 20 is very similar to reported for different forestry residues [40]. The input that shows the biggest difference is the calcium hydroxide used in the overliming that is close to double, followed by water with a consumption almost 50% higher (> 9000 kg/h) and thirdly the sulfuric acid used in the pretreatment and overliming with 35% higher. The obtained bioethanol yields for the first and second optimal conditions were 110.83 kg bioethanol/t raw material and 97.30 kg bioethanol/t raw material (139.45-122.43 l/t respectively). These yields show that the first optimal conditions, which have the highest amount of fermentable sugars, produces more bioethanol than the second condition. The yields obtained using OTP biomass are very similar to that reported for other lignocellulosic feedstocks such as the forestry residues hog fuel with 100 kg bioethanol/t, higher than, empty fruit bunches (EFB) or sugarcane bagasse (SCB), which are 80.41 kg/t and 59.26 kg/t, respectively (Quintero et al. 2013), and lower than other forestry residues such as, tops and branches or early thinnings with 172 kg/t and 188 kg/t [40] and not lignocellulosic feedstocks such as brown algae with 239.03 kg/t [41].

Table 3. Raw material and products flow.

Feature	Optimum 1 (Solids loading 15%)		Optimum 2 (Solids loading 35%)	
	Raw materials (kg/h)	Products (kg/h)	Raw materials (kg/h)	Products (kg/h)
Olive tree pruning	3750.00		3750.00	
Water	28634.53		19549.99	
Sulfuric acid	261.40		193.82	
Calcium hydroxide	187.57		109.48	
Enzymes	219.03		221.93	
Diamonium phosphate	3.20		2.81	
E. coli MM160	4.99		4.38	
Potassium hydroxide	14.20		30.53	
Protein	11.39		10.00	
Bioethanol		415.61		364.87

3.1.2 Water consume and liquid waste

The optimum 1 consumes more water than the optimum 2 (i.e. 68.89 kg water/kg bioethanol and 53.58 kg water/kg bioethanol), the biggest difference is in the pretreatment stage with more than 10,000 kg/h (Table 4). If the extraction stage is not considered, the values are 41.08 kg water/kg bioethanol and 21.89 kg water/kg bioethanol, this last value similar to those reported for corn stover 15.08-25.48 kg water/kg bioethanol [42]. In the case of optimum 2 there is a water consumption in the saccharification stage to adjust to the maximum solid-liquid ratio used of 20 %w/v [43]. In the same way, the specific liquid waste generated by using a low solids loading is high. Concretely, the optimal with a solids loading of 15% produces 60.67 kg effluent/kg bioethanol and the optimal condition with a solids loading of 35% produces 46.88 kg effluent/kg bioethanol, a 77%. In the case of optimum 1, the largest effluent is produced in the evaporation stage, approx. 8000 kg/h, more than 40 times higher than that produced in the optimum 2. For this latter, the highest effluent is produced in the distillation stage, 5551.20 kg/h, lower than that produced in optimum 1, representing less than 83%. In the pretreatment stage, a greater effluent is produced in the optimum 2 due to the washing of the solid since there is a greater recovery of it (see Table 4). In summary, optimum 1 produces almost 50% more liquid waste than optimal 2.

Table 4. Water consume and liquid waste for the different process stages.

Feature	**Optimum 1 (Solids loading 15%)**		**Optimum 2 (Solids loading 35%)**	
	Water consume (kg/h)	**Liquid waste (kg/h)**	**Water consume (kg/h)**	**Liquid waste (kg/h)**
Extraction	11559.90	7650.54	11559.90	7650.54
Pretreatment	17074.63	2854.15	7015.72	3718.89
Overliming				
Saccharification			974.37	
Evaporation		7999.73		183.19
Fermentation				
Distillation		6712.88		5551.20
Total	28634.53	25217.29	19549.99	17103.81

3.1.3 Utilities (heating+cooling)

The optimum 1 with the lowest load of solid (15%) has the highest specific consumption of utilities (heating+cooling) with 59.55 kW/(kg bioethanol/h) more than twice the case with high load (28.05 kW/(kg bioethanol/h)). This behavior is similar to that found by Rodriges et al [44] evaluating different pretreatments with corn stover. The stage with the highest consumption of utilities in optimum 1 is evaporation, due to the low concentration of sugars in the liquor produced, representing more than 50% of the total consumed utilities, followed by the pre-treatment stage with 23.57% for the highest mass treated (Table 5).

On the contrary, the evaporation stage in optimum 2 does not reach 15% of its total consumed of utilities, and with respect to optimum 1 less than 12%. As for the distillation, it presents similar values in both optimums, being higher for the case with 35% solid. In this optimum, distillation is the stage with the highest consumption of utilities, over 38%, followed also by pretreatment as it happened in the optimum 1, representing almost 23% of the total, a value very similar to the optimum 1. The decrease in consumption of utilities in the distillation stage due to an increase in the sugars concentration in the liquor is much lower than the increase in the utilities to carry out said concentration in the evaporation stage, this is in agreement with other authors [45].

The process energy integration in both cases allows a very significant utilities saving, around 35%, being slightly higher in the case of the optimum 2 (Table 5). With energy integration, the specific consumption of utilities is reduced, remaining at: 39.23 kW/(kg bioethanol/h) optimum 1 and 18.01 kW/(kg bioethanol/h) optimum 2, less than half the optimum 1. This last value is of the order of the obtained for hog fuel in which, as mentioned previously, had a very similar yield of bioethanol [40].

Table 5. Heating and cooling for the different process stages.

Feature	**Optimum 1 (Solids loading 15%)**		**Optimum 2 (Solids loading 35%)**	
	Heating+cooling (kW)	**%**	**Heating+cooling (kW)**	**%**
Extraction	2148.86	8.68	2148.94	20.99
Pretreatment	5833.58	23.57	2344.91	22.91
Overliming	266.07	1.08	142.77	1.39

Saccharification	37.16	0.15	70.22	0.69
Evaporation	12654.45	51.13	1485.90	14.52
Fermentation	152.93	0.62	148.00	1.45
Distillation	3656.26	14.77	3895.64	38.06
Total	24749.32	100.00	10236.38	100.00
With energy integration	16304.52	65.88	6572.25	64.20

3.1.3 Carbon dioxide emissions

On the other hand, a high carbon dioxide emissions from the fermentation stage and steam production are expected from the first optimal condition due to the higher amount of sugars that are fermented and liquid employed in the process. In accordance with the above results, the first optimal condition has the highest environmental impact, which can be seen as a drawback. The specific emissions of CO_2 are 7.91 and 4.22 kg/kg bioethanol, for optimum 1 and 2 respectively (close to double). The stage with the highest emissions in optimum 1 is evaporation, due to the high energy requirement for the concentration of the liquor produced, representing more than 44% of the total emissions produced, followed by the pre-treatment stage with 20.58% for the largest mass treated (Table 6). On the contrary, the evaporation stage in the optimum 2 does not reach 11% of its total consumed of utilities, and with respect to the optimum 1 less than 11%. Regarding distillation, it presents similar values in both optimums, being higher for the case with 35% solid. In the optimum 2 the distillation is the stage with the highest emissions, more than 29%, followed by the fermentation stage, representing almost 24% of the total, where the CO_2 is formed in the fermentation of the sugars (Table 6). The energy integration of the process in both cases allows a very significant reduction in emissions, being higher in the case of optimum 1 (> 30%, optimum 2 >25%). With energy integration, the specific emissions of CO_2 are reduced to remain at: 5.54 kg/kg bioethanol in optimum 1 and 3.07 kg/kg bioethanol in optimum 2, 55% of the value of optimum 1.

Table 6. Carbon dioxide emissions for the different process stages.

Feature	Optimum 1 (Solids loading 15%)		Optimum 2 (Solids loading 35%)	
	Steam production ($kg CO_2/h$)	Fermentation ($kg CO_2/h$)	Steam production ($kg CO_2/h$)	Fermentation ($kg CO_2/h$)
Extraction	316.08		316.08	
Pretreatment	676.67		235.16	
Overliming	0.14		0.08	
Saccharification	8.80		16.62	
Evaporation	1453.11		159.24	
Fermentation		416.00		365.22
Distillation	416.40		446.71	
Total	2871.18	416.00	1173.88	365.22
With energy integration	1884.49	416.00	754.22	365.22

3.2. Techno-economic assessment.

The economic evaluation of the both scenarios is showed in Table 7. From this, it is possible to observe that the production total cost of the optimum 1 is more than 14% higher than the optimum 2 with a value of 10.75 million USD/y, and that the two more representative costs can be attributed to the raw material and depreciation, around 31% y 18% respectively. These two costs have been reported as more influential factors in the production of bioethanol [46].In both scenarios the variable costs distribution is similar. However, in the case of optimum 1, the third cost is utilities followed by operating labor (17.30% and 13.41%) while for optimum 2 this order is reversed (11.50% and 15.53%). The utilities costs in the optimum 1 is 72% higher than the optimum 2 due to the amount of liquid that is used in this process. In fact, the process with a solids loading of 15% consumes more than de double of the energy than the scenario with a solids loading of 35%. When is realized the process energy integration in both cases the annual production cost is reduced but more significantly in the optimum 1 with a reduction of more than 4% while in the optimum 2 it does not reach 2%. Despite this greater reduction, the optimum 1 still has the highest production cost with 10.29 million USD/y, almost 12% higher than the value of the optimum 2. Moreover, the total project capital costs of scenario 1 an scenario 2 were 24.51 million USD and 22.16 million USD, more than 10% higher in the case of optimal 1 which initially could suggest that a high solids loading in the pretreatment stage must be used. These cost are low compared with the data reported by Humbird *et al.* (2011) for a facility that only produces bioethanol from corn stover. Nevertheless, this difference between the reported and the obtained data is attributed to the process scale, which is very low in this work. Compared to a closer scale 80000 t/y the value is quite similar with 29.9 million USD [41].

Table 7. Techno-economic assessment results.

Feature	Optimum 1 (Solids loading 15%)		Optimum 2 (Solids loading 35%)	
	Thousands USD/year	(%)	Thousands USD/year	(%)
Raw materials	3187.97	29.67	3074.34	32.72
Utilities	1858.76	17.30	1080.51	11.50
Operating labor	1440.72	13.41	1440.72	15.33
Maintenance	379.00	3.53	256.00	2.72
Operating charges	360.18	3.35	360.18	3.83
Plant overhead	909.86	8.47	848.36	9.03
G and A costs*	648.02	6.03	563.17	5.99
Depreciation	1960.50	18.25	1772.78	18.87
Total production cost	10745.01	100.00	9396.05	100.00
Total production cost^{a}	10287.67	95.74	9209.41	98.01
Total Project Capital Cost (Million USD)	24.51		22.16	
Bioethanol cost (USD/l)	2.55		2.54	
Bioethanol cost^{a} (USD/l)	2.44		2.49	

*General and Administrative costs. ^{a}With energy integration

The bioethanol production cost for both scenarios was almost the same if energy integration is not done, being lower in the case of the optimum 2 with a value of 2.54 USD/l. However, with energy integration, the optimum 1 has the lowest value with 2.44 USD/l since the value has been reduced by 0.11 USD/l while in the case of the optimum 2 it has only reduced by 0.05 USD l where the utilities cost had a lower influence on final value. In any case, the value obtained under the conditions studied (small scale, current prices of raw materials (olive pruning, enzymes), etc.) is greater than the current market value of bioethanol that can be of the order of 0.52 USD/l [47]. The above values are in the order of those found for other pretreatments with corn stover in different conditions: 1.78-2.46 USD/l for LHW and 1.80-3.56 USD/l for AFEX but with a much larger plant size, higher than 2000 t/day [44]; and higher than for different forestry residues pretreated with steam explosion 0.77-1.52 USD/l also with higher plant size 600 t/day [40].

The bioethanol production cost has the main cost in raw materials (around 30%) and within these in both scenarios the order of the three majority is OTP, enzymes and water, among which accumulate more than 86% (**Figure 2**). The first two, OTP and enzymes, represent more than 72% of the cost of raw materials, with values higher than 37% and 34% respectively. The cost of bioethanol has been correlated with the price of the feedstock and the cost of the enzyme [46], the largest contributor. The costs of these last two would be necessary to reduce it, in the case of the OTP looking for an optimal location of the plant, which could reduce the logistic costs (production and transport), while for the enzymes in recent years they have been reduced much the cost of production of them and also increases its enzymatic capacity so it could also lower the dosage [48].

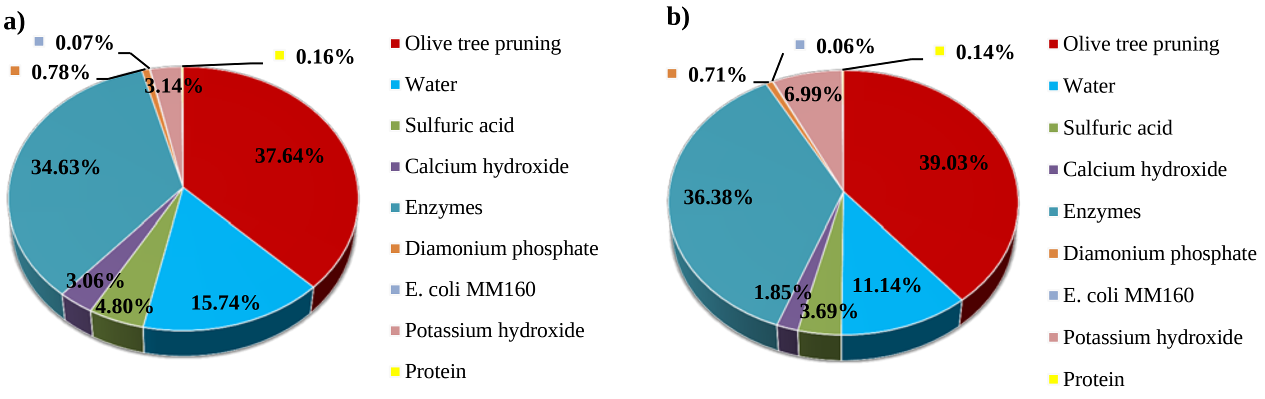


Figure 2. Distribution of raw materials cost: **a)** Optimum 1 (Solids loading 15%). **b)** Optimum 2 (Solids loading 35%).

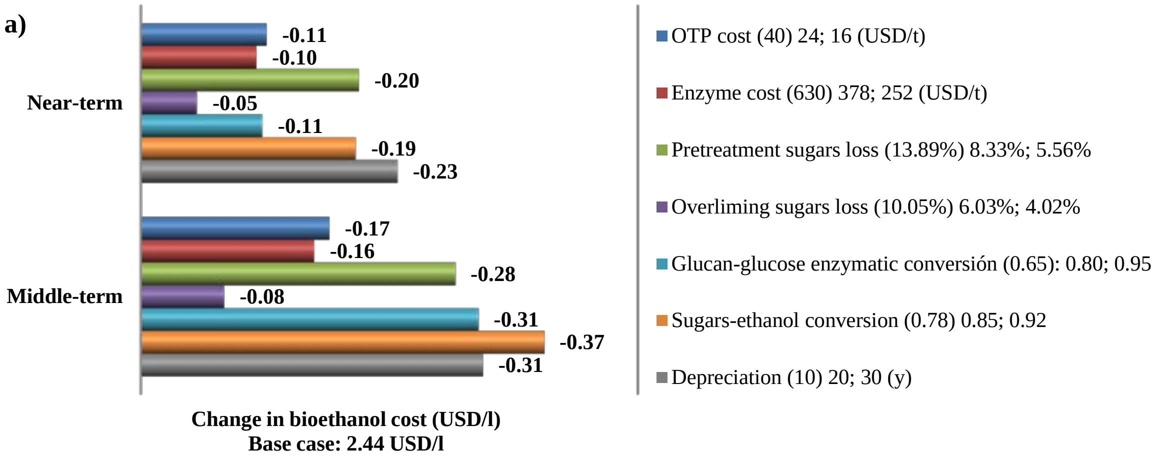
3.3 Sensitivity analysis

A sensitivity analysis of the production cost of bioethanol has been carried out in which the influence of 7 key parameters has been studied. On the one hand there would be the costs of raw materials with greater influence such as OTP and enzymes. On the other hand, there would be sugar losses in the pretreatment and overliming stages and conversions in saccharification (Glucan-glucose enzymatic conversion) and fermentation (Sugars-ethanol conversion), the last four relative to the ethanol production yield. Finally the depreciation since it was shown as the second most representative cost after the raw materials (Table 7). For each of these parameters, two values have been studied, classifying them into near and middle time according to the proximity in which they could be achieved [49]. For the case of near-term, a reduction of 40% with respect to the base case values has been proposed in the parameters "OTP cost", "enzyme cost", “pretreatment sugars loss” and “overliming sugars loss”; an increase in the conversions in the saccharification (Glucan-glucose enzymatic conversion) and the fermentation (Sugars-ethanol conversion) up to values of 0.8 and 0.85 respectively, and finally an increase in the life of the plant until 20 years for the calculation of depreciation. On the other hand, a reduction of 60% has been proposed for middle-term with respect to the base case values in the parameters "OTP cost", "enzyme cost", “pretreatment sugars loss” and “overliming sugars loss”; an increase in the conversions in saccharification and fermentation to values of 0.95 and 0.92 respectively, and finally an increase in the life of the plant up to 30 years for the calculation of depreciation.

The results obtained for the two optimum are shown in **Figure 3**. For the case of "near-term" in the optimum 1 the parameter that allows the greatest reduction is depreciation with a value of 0.23 USD/l followed very closely by “pretreatment sugars loss” and “sugars-ethanol conversion” with 0.2 and 0.19 USD/l respectively (**Figure 3**(a). For optimum 2, those 3 parameters are also that offer the greatest reductions but the order is different and with higher values (“pretreatment sugars loss”, “depreciation”, “sugars-ethanol conversion”, with 0.27, 0.24 and 0.20 USD/l respectively) (**Figure 3**(b). In both optimums if the cost of OTP and enzymes is showed together would present the second largest reduction with values 0.21 and 0.25 USD/l for optimal 1 and optimal 2 respectively.

For the case of "middle-term" with respect to "near-term" the order of the parameters is altered in the reduction that could be achieved. For optimum 1 now the parameter that achieves the greatest reduction is “Sugars-ethanol conversion” (0.37 USD/l) with three other parameters with very similar values, depreciation, “glucan-glucose enzymatic conversion” and “pretreatment sugars loss” (0.31, 0.31 and 0.28 USD/l) to which could be added the sum of the costs of OTP and enzyme (0.33 USD/l). For optimum 2, “pretreatment sugars loss” is maintained with the highest reduction (0.39 USD/l), but the order of the other parameters changes, resulting in “sugars-ethanol conversion” below (0.37 USD/l) and “glucan-glucose enzymatic conversion” and depreciation very close (0.33, 0.32 USD/l); the sum of cost of OTP and enzymes would tie in the second place. In all cases the “overliming sugars loss” has the lowest reductions.

Finally, if all the reductions obtained for the case of "near-term" could be achieved, reductions higher than 40% would be achieved, with values of the ethanol production cost of 1.44 and 1.37 USD/l for optimum 1 and optimum 2 respectively, still far from the current market value. On the other hand, making the same consideration for "middle-term" the reductions are close to duplicating the previous ones, leaving values of 0.77 and 0.63 USD/l for optimum 1 and optimum 2, already in the order of the current values of the market. It should be noted that optimum 2 is more affected by all the parameters studied since the greatest reductions are obtained in both scenarios and therefore the lower costs of bioethanol production.



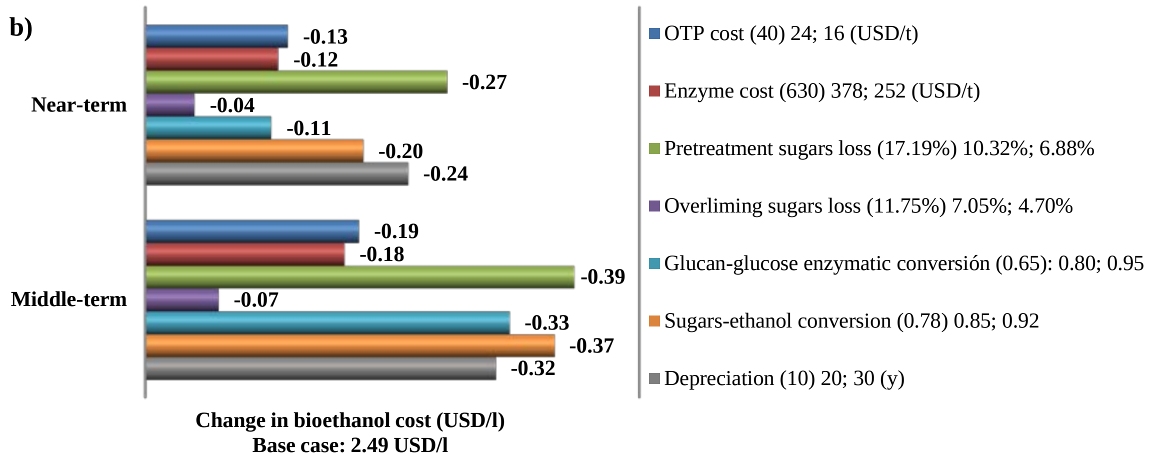


Figure 3. Results of the sensitivity analysis for the key process parameters in near and middle term (base case values between parentheses). **a)** Optimum 1 (Solids loading 15%). **b)** Optimum 2 (Solids loading 35%).

4. Conclusions.

The techno-economic analysis presented has allowed to compare two scenarios with optimal experimental pretreatment conditions that seek different objectives (optimum 1: the highest recovery of fermentable sugars; optimum 2: the highest concentration of fermentable sugars) whose main difference is in the solid loading (15%, 35%) and see the viability of bioethanol production from OTP at small-scale. It is possible to observe that with the optimum 1 (low solid loading) the lowest value of bioethanol production cost is obtained, on the other hand, with the optimum 2 (high solids loading) could be used in bioethanol production process with the aim to decrease its environmental impact (liquid wastes and CO_2 emissions) and improve the economics of the process in terms of utilities. However, without matter the evaluated condition, the olive tree biomass use in a standalone process for bioethanol production is not profitable at small scale and with the current prices of raw materials (mainly olive tree pruning and enzymes).

The sensitivity analysis of 7 key parameters related to the price of the raw materials ("OTP cost", "enzyme cost"), the ethanol production yield (“pretreatment sugars loss”, “overliming sugars loss”, “glucan-glucose enzymatic conversion” and “sugars -ethanol conversion”) and depreciation, at near and middle time, has shown that middle-term the cost of bioethanol production would be very close to the current market value. This analysis has also shown that the optimum 2 has more sensitivity to the parameters studied, obtaining in both scenarios, near and middle term, the lowest values of bioethanol production cost, still higher than the current market value. A biorefinery scheme should be proposed with the aim to produce more value-added products that supports the production of this energy vectors at low scale [50].

5. Acknowledgements.

This work has been partially financed by the Spanish Ministerio de Economía y Competitividad (Ref. ENE2014-60090-C2-2-R. including FEDER funds). JCST and CAC thank the support to Departamento Administrativo de Ciencia, Tecnología e Innovación (Colciencias. grant number 761 Jóvenes Investigadores) and the Facultdad de Ingeniería y Arquitectura of the Universidad Nacional de Colombia at Manizales (grant number 206010012730). JMRG gratefully acknowledges the postdoctoral scholarship received from Junta de Andalucía.

6. References.

[1] Shuit, S.H., Tan, K.T., Lee, K.T., Kamaruddin, A.H. (2003) Oil palm biomass as a sustainable energy source: A Malaysian case study. Energy. 34:1225–35.
[2] BP Statistical Review of World Energy. (2017). London, UK.
[3] Olivier, J.G.J., Janssens-Maenhout, G., Muntean. M., Peters J.A.H.W. (2016). Trends in Global CO_2 Emissions: 2016 Report. The Hague: PBL Netherlands Environmental Assessment Agency; Ispra: European Commission, Joint Research Centre.
[4] Gioti-Papadaki, O. (2012). European environmental policy and the strategy “Europe 2020.” Reg Sci Inq J. 4:151–8.
[5] International Energy Agency (IEA) (2017). Key World Energy Statistics 2017.

[6] Renewable Energy Policy Network for the 21st Century (REN21). Renewables 2016 Global Status Report. Paris: 2016.

[7] Eurostat. World Energy Statistics 2017 Edition 2017:179.

[8] Cardona Alzate, C.A., Solarte-Toro, J.C., Peña, Á.G. (2018). Fermentation, thermochemical and catalytic processes in the transformation of biomass through efficient biorefineries. Catal Today 302:61–72.

[9] Cardona, C.A., Solarte, J.C., Tamayo, J.A., Castro, A., García, B.A,. (2017). Palm oil for food or biodiesel: A disjunction in tropical countries. Adv. Chem. Res. Vol. 32:1–36.

[10] Koizumi, T. (2015). Biofuels and food security. Renew Sustain Energy Rev 52:829–41.

[11] Claassen, P. A. M., van Lier, J.B., Lopez Contreras, A. M., van Niel, E.W.J., Sijtsma, L., Stams A.J.M., et al. (1999) Utilisation of biomass for the supply of energy carriers. Appl Microbiol Biotechnol 52:741–55.

[12] Surendra, K.C., Takara, D., Hashimoto, A.G., Khanal, S.K. (2014). Biogas as a sustainable energy source for developing countries: Opportunities and challenges. Renew Sustain Energy Rev 31:846–59.

[13] EPURE. European Renewable Ethanol: State of the Industry Report. Energy 2015.

[14] Del Campo, I., Alegría, I., Zazpe, M., Echeverría, M., Echeverría, I,. (2006). Diluted acid hydrolysis pretreatment of agri-food wastes for bioethanol production. Ind Crops Prod 24:214–21.

[15] Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., et al. (2011). Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. Renew Energy 303:1-147.

[16] Hernández, V., Romero-García, J.M., Dávila, J.A., Castro, E., Cardona, C.A. (2014). Techno-economic and environmental assessment of an olive stone based biorefinery. Resour Conserv Recycl 92:145–50.

[17] Macrelli, S., Mogensen, J., Zacchi, G. (2012). Techno economic evaluation of 2nd generation bioethanol production from sugar cane bagasse and leaves integrated with the sugar based ethanol process. Biotechnol Biofuels 5:22.

[18] Triwahyuni, E., Hariyanti, S., Dahnum, D., Nurdin, M., Abimanyu, H. (2015). Optimization of saccharification and fermentation process in bioethanol production from oil palm fronds. Procedia Chem 16:141–8.

[19] Martínez-Patiño, J.C., Romero, I., Ruiz, E., Cara, C., Romero-García, J.M., Castro, E. (2017). Design and optimization of sulfuric acid pretreatment of extracted olive tree biomass using response surface methodology. BioResources 12:1779–97.

[20] Moncada, J., Aristizábal, V., Cardona, C.A. (2016). Design strategies for sustainable biorefineries. Biochem Eng J 116:122–34.

[21] Flach, B., Lieberz, A.R.A. (2017). EU Annual Biofuels Annual 2017. USDA Foreign Agric Serv 1–44.

[22] Ruiz, E., Romero-García, J.M., Romero, I., Manzanares, P., Negro, M.J., Castro, E. (2017). Olive-derived biomass as a source of energy and chemicals. Biofuels, Bioprod Biorefining 11:1077–94.

[23] Romero-García, J.M., Niño, L., Martínez-Patiño, C., Álvarez, C., Castro, E., Negro, M.J. (2014). Biorefinery based on olive biomass. State of the art and future trends. Bioresour Technol 159:421–32.

[24] Quintero, J.A., Moncada, J., Cardona, C.A. (2013). Techno-economic analysis of bioethanol production from lignocellulosic residues in Colombia: A process simulation approach. Bioresour Technol 139:300–7.

[25] NREL, 2012. National Renewable Energy Laboratory, Washington D.C., EE.UU. Biomass Compositional Analysis Laboratory Procedures, NREL 2017. https://www.nrel.gov/bioenergy/biomass-compositional-analysis.html

[26] Moncada, J., Tamayo, J.A., Cardona, C.A. (2014). Integrating first, second, and third generation biorefineries: Incorporating microalgae into the sugarcane biorefinery. Chem Eng Sci 118:126–140.

[27] Rodrigues, F., Pimentel, F.B., Oliveira, M.B.P.P. (2015). Olive by-products: Challenge application in cosmetic industry. Ind Crops Prod 70:116–124.

[28] Roselló-Soto, E., Koubaa, M., Moubarik, A., Lopes, R.P., Saraiva, J.A., Boussetta, N., et al. (2015). Emerging opportunities for the effective valorization of wastes and by-products generated during olive oil production process: Non-conventional methods for the recovery of high-added value compounds. Trends Food Sci Technol 45:296–310.

[29] Talhaoui, N., Taamalli, A., Gómez-Caravaca, A.M., Fernández-Gutiérrez, A., Segura-Carretero, A. (2015). Phenolic compounds in olive leaves: Analytical determination, biotic and abiotic influence, and health benefits. Food Res Int 77:92–108.

[30] Paz-Astudillo, I.C. (2010). Diseño integral de biorreactores continuos de tanque agitado aplicados a procesos de fermentación. Universidad Nacional de Colombia - Sede Manizales.

[31] Da Silva, E.A.B., Zabkova, M., Araújo, J.D., Cateto, C.A., Barreiro, M.F., Belgacem, M.N., et al. (2009). An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. Chem Eng Res Des 87:1276–1292.

[32] Yoshikawa, T., Yagi, T., Shinohara, S., Fukunaga, T., Nakasaka, Y., Tago, T., et al. (2012). Production

of phenols from lignin via depolymerization and catalytic cracking. Fuel Process Technol. 108:69–75.

[33] Carvajal, J.C., Gómez, Á., Cardona, C.A. (2016). Comparison of lignin extraction processes: Economic and environmental assessment. Bioresour Technol 214:468–476.

[34] Quintero, J.A., Cardona, C.A. (2011). Process simulation of fuel ethanol production from lignocellulosics using aspen plus. Ind Eng Chem Res 50:6205–6212.

[35] Daza-Serna, L. V., Solarte-Toro, J.C., Serna-Loaiza, S., Chacón-Perez, Y., Cardona, C.A. (2016). Agricultural waste management through energy producing biorefineries: The Colombian case. Waste and Biomass Valorization 1–10.

[36] Al-Malah, K. (2017) Aspen Plus: Chemical engineering applications. 1 ed. Wiley.

[37] NIS, National Institute of Statistics. (2017) Encuesta Trimestral de Coste Laboral (ETCL) : Segundo Trimestre de 2017. Spain.

[38] Indicative Chemical Prices A-Z. http://www.icis.com/chemicals/channel-info-chemicals-a-z/ (accessed November 20, 2017).

[39] Hernández, V., Romero-García, J.M., Dávila, J.A., Castro, E., Cardona, C.A. (2014). Techno-economic and environmental assessment of an olive stone based biorefinery. Resour Conserv Recycl 92:145–150.

[40] Frankó, B., Galbe, M., Wallberg, O. (2016). Bioethanol production from forestry residues: A comparative techno-economic analysis Applied Energy 184: 727–736.

[41] Fasahati, P., Woo, H.C., Liu, J.J. (2015). Industrial-scale bioethanol production from brown algae: Effects of pretreatment processes on plant economics. Applied Energy 139:175–187.

[42] Meyer, P.A., Tews, I.J., Magnuson, J.K., Karagiosis, S.A., Jones, S.B. (2013). Techno-economic analysis of corn stover fungal fermentation to ethanol. Applied Energy 111:657–668

[43] Cara, C., Moya, M., Ballesteros, I., Negro, M.J., González, A., Ruiz, E. (2007) Influence of solid loading on enzymatic hydrolysis of steam exploded or liquid hot water pretreated olive tree biomass. Process Biochem 42: 1003-1009.

[44] Rodrigues Gurgel da Silva, A., Torres Ortega, C.E., Rong B.G. (2016). Techno-economic analysis of different pretreatment processes for lignocellulosic-based bioethanol production. Bioresource Technology 218:561–570.

[45] Larnaudie, V., Rochón, E., Ferrari, M.D., Lareo, C. (2016). Energy evaluation of fuel bioethanol production from sweet sorghum using very high gravity (VHG) conditions. Renewable Energy 88:280-287

[46] Van Rijn, R., Nieves, I.U., Shanmugam, K.T., Ingram, L.O., Vermerris, W. (2018). Techno-Economic Evaluation of Cellulosic Ethanol Production Based on Pilot Biorefinery Data: a Case Study of Sweet Sorghum Bagasse Processed via L+SScF. BioEnergy Research https://doi.org/10.1007/s12155-018-9906-3.

[47] ICIS (2018). Bioethanol Rotterdam price. https://www.icis.com/resources/news/2018/03/29/10207802/eu-fuel-ethanol-prices-plummet-on-market-length-eu-policy-worries/

[48] Ekman, A., Wallberg, O., Joelsson, E., Börjesson, P. (2013). Possibilities for sustainable biorefineries based on agricultural residues – A case study of potential straw-based ethanol production in Sweden. Applied Energy 102:299–308.

[49] Chovau, S., Degrauwe, D., Van der Bruggen, B. (2013). Critical analysis of techno-economic estimates for the production cost of lignocellulosic bio-ethanol. Renewable and Sustainable Energy Reviews 26:307–321

[50] Kefeng Huang, Wangyun Won, Kevin J. Barnett, Zachary J. Brentzel, David M. Alonso, George W. Huber, James A. Dumesic, Christos T. Maravelias (2018). Improving economics of lignocellulosic biofuels: An integrated strategy for coproducing 1,5-pentanediol and ethanol. Applied Energy 213:585-594.