

Designing an olive tree pruning biorefinery for the production of bioethanol, xylitol and antioxidants: A techno-economic assessment

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Running title: **Biorefinery of olive tree pruning**

Designing an olive tree pruning biorefinery for the production of bioethanol, xylitol and antioxidants: A techno-economic assessment

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Abstract: Olive tree crop, extensively cultivated in Southern European countries, yields large amounts of olive tree pruning (OTP) biomass. This could be used within the framework of a bio-based economy that maximizes the utilization of biomass resources in a sustainable way. In the present work, the techno-economic feasibility of an OTP-based integrated biorefinery is evaluated by the process simulation software Aspen Plus, while the process is aiming at the production of ethanol, xylitol, antioxidants, and electricity. Overall, the proposed plant could perform economically, and it is self-sufficient from the energetic point of view. The plant designed yields around 109 L of ethanol, 27 kg of xylitol, and 43 kg of antioxidants per ton of OTP biomass, with estimated production cost of 0.24 € L⁻¹, 1.48 € kg⁻¹ and 5.12 € kg⁻¹, respectively. In a 10-years period, the economic profitability of the biorefinery plant is within a positive investment balance, with a Net Present Value (NPT) of 32.1 M €, and a payback period (PBP) of 5-6 years. These figures point out the opportunities for placing in the market several Based on these data, the construction of small-scale OTP-based lignocellulosic biorefineries seems to be a realistic scenario.

Keywords: Aspen Plus software; Biofuels; Process simulation; Small-scale biorefinery; Value-added compounds.

Introduction

Olive tree cultivation is relevant in Mediterranean countries. In particular, Spain has about 2.3 M ha cultivated, and it is the largest olive oil producer worldwide (Manzanares et al. 2017). This industry generates extensive amounts of lignocellulosic residues such as olive tree pruning (OTP), olive stones, and olive pomace. In the last few years, OTP biomass has attracted great interest from a biorefinery point of view, as it is abundant (about 1.3 t ha⁻¹ y⁻¹ and 3.0 t ha⁻¹ in biennial pruning), cheap, and readily available (Velázquez-Martí et al. 2011). OTP is usually burnt or left on-site (Romero-García et al. 2016). The concept of integrated biorefineries is to apply novel technologies for converting biomass feedstocks into affordable biofuels, biopower, and/or high value bio-based products. OTP biomass is comprised of a mixture of leaves (30%), thin branches (50%) and wood (20%), i.e. it has a complex composition mainly consisting of structural carbohydrates, lignin, and extractives. The carbohydrate content in OTP is around 45-55% (Ballesteros et al. 2011; Negro et al. 2014; Ruiz et al. 2017), thus representing an excellent source to produce fermentation-based products. OTP also contains a significant amount of extractives due to the leaves moiety, which could be converted to mannitol, sugars, polyphenols, and other antioxidant compounds with a potential use in the food and pharmaceutical industries (Conde et al. 2009). On the other hand, the heterogeneity of OTP (i.e. different leaves, branches and wood content) is a challenge in terms of an economical utilization.

Glucose and xylose can be derived from OTP and transformed into ethanol and xylitol, respectively, as the main fermentative products (García Martín et al. 2010; Díaz et al. 2011). Ethanol can be readily integrated into traditional fuel used in the transport sector (Moreno et al. 2017). Xylitol, on the other hand, is a sweetener with low calories, which is suitable for diabetic diet (Mäkinen 1994). Moreover, antioxidants, such as hydroxytyrosol, homovanillyl alcohol, and oleuropein, can be recovered from OTP biomass (Conde et al. 2009). This operation step is performed previously to the conversion of structural carbohydrates into

fermentable sugars. These antioxidants have a high potential as food additives as they prevent lipid oxidation or rancidity processes (Veneziani et al. 2017).

The conversion of lignocellulosic feedstocks into fermentable sugars is not a trivial matter. The process consists of pretreatment, enzymatic saccharification, fermentation, and product recovery. If the recovery of extractives from OTP is intended, a previous water extraction step is necessary. A pretreatment is always indispensable to increase the enzymatic accessibility of cellulose and hemicelluloses. It was demonstrated that phosphoric-acid-catalyzed steam explosion ($SE_{acid-cat}$) is an efficient pretreatment for OTP conversion (Negro et al., 2014). During $SE_{acid-cat}$, biomass is treated with saturated steam in the presence of an acid at 180-240°C and pressures of 1-3.5 MPa. Under these conditions, hemicelluloses are hydrolysed to sugars, while only a small part of lignin is solubilized. After opening the valve, an explosive decompression occurs resulting in the physical disruption of the fibers and the generation of large and porous surfaces. $SE_{acid-cat}$ allows the recovery of a liquid fraction rich in sugars derived from hemicelluloses (mainly xylose), which is the source for xylitol production. Moreover, the obtained cellulose-rich solid fraction has better susceptibility to enzymatic hydrolysis to glucose, which is then fermented to ethanol.

Process economy is crucial in such processes. Small-scale biorefineries have a higher costs saving potential compared to traditional large-scale industries, because of the shorter transportation distances, lower energy requirements, and use less capital-intensive technologies (Kolschoten et al. 2014). Coproducing higher-value-small-market products contributes additionally to the overall process economy. The present work presents a realistic attempt based on experimental results to produce ethanol, xylitol, antioxidants, and electricity from OTP in a small-scale integrated biorefinery system located in Spain. This system will be analysed from a techno-economic point of view concerning its cost-competitiveness. For that, the processing plant was first modeled by the process simulation software Aspen Plus. This simulation is based on the parameters of product concentrations and yields resulted from

previous pilot-scale trials performed in our laboratory. The resulting simulation data served as basis to study the overall energy efficiency and the economic feasibility of an integrated OTP biorefinery system.

Material and methods

Raw materials: OTP was collected from Jaén (Spain) as raw material for bioconversion. The chemical composition was determined through the standard Laboratory Analytical Procedures for biomass analysis provided by the National Renewable Energies Laboratory (Colorado, USA) (NREL, 2018). Table 1 is a compilation of the chemical composition of OTP.

Process description: Due to its high olive tree density, Andalucía (Spain) is the proposed region to locate the designed integrated biorefinery. The projected entrance capacity of the plant is 40,000 t y⁻¹ of OTP. The OTP production capacity is 1.5 t ha⁻¹y⁻¹ (Ruiz et al. 2017), which is collected in an area of about 10 km radius. The final products include antioxidants, xylitol, ethanol, and electricity. Simplified process and simulation diagrams (Figure 1) show the integrated biorefinery concept. The main operation steps: 1) water extraction and pretreatment, 2) antioxidants recovery, 3) xylitol production, 4) ethanol production, 5) wastewater treatment, and 6) power and heat generation.

Water extraction and pretreatment: A water extraction step leads to the recovery of about 90% of extractives in the initial OTP, which is composed of non-structural sugars, antioxidants (defined as total Gallic acid equivalents), and mannitol. The remaining solid (OTP_{extr.}) is composed of cellulose, hemicelluloses and lignins (Ballesteros et al. 2011). The OTP_{extr.} is pretreated by steam explosion (SE_{acid cat.}) at 195°C (1.4 MPa) for 10 min with phosphoric acid (1%) as catalyst (Negro et al. 2014). Pretreated OTP results in a water insoluble solids (WIS) fraction, containing mainly glucose and lignin, and in the liquid prehydrolysate, with xylose and degradation compounds as major constituents. The complete chemical analysis of WIS and prehydrolysate are described by Negro et al. (2014).

Antioxidants recovery: The liquid stream is subjected to a 2nd extraction process with ethyl acetate [3:1 (v/v) liquid-solvent ratio, 35°C], followed by vacuum evaporation and drying processes, to collect the extracted antioxidants (Conde et al. 2009). About 55% antioxidants recovery yield with 36% purity can be achieved. Finally, ethyl acetate is recovered through distillation and can be recirculated into the extraction system. Wastewater obtained at the bottom of this column is sent to the wastewater treatment area (WWT).

Xylitol production: Prior to fermentation, the prehydrolysate fraction is concentrated via evaporation to reach a xylose concentration of ca. 80 g L⁻¹. This fraction is then detoxified by overliming, which mainly removes furans and phenolic compounds (Larsson et al. 1999). Briefly, the pH of prehydrolysate is adjusted with Ca(OH)₂ until a pH 10 is reached, and then neutralized with H₂SO₄ to reach a pH 5.5.

Detoxified prehydrolysate is fermented with *Meyerozyma guilliermondii* (1 g L⁻¹ b.o. dry wt.) for xylitol production. This process is performed under oxygen-limited conditions at 30°C and 300 rpm for 96 h, yielding 0.8 g of xylitol per g of xylose (Abdul-Khalek 2018). The fermentation medium is filtered for yeast removal, and the fermented broth is clarified with 15 g L⁻¹ of activated charcoal to remove major impurities that may influence the colour of the product. Then, the stream is concentrated through vacuum evaporation at 40°C to avoid xylitol decomposition. Finally, to recover the product, a crystallization step at -5°C is performed. Ethanol was added to increase xylitol insolubility (Rivas et al. 2006). Xylitol crystals are ultimately collected by filtration and ethyl acetate and ethanol is recovered through distillation, while the remaining wastewater is sent to the WWT plant. Overall, this process shows a recovery yield of 47% with 99% purity (Rivas et al. 2006).

Ethanol production: WIS fraction collected after pretreatment step is subjected to presaccharification and simultaneous saccharification and fermentation process (PSSF) for bioethanol production. Presaccharification is performed with 240 mg g⁻¹ of glucan Cellic CTec2 (Novozymes, Denmark) at 25% (w/w) solid loading and 50°C. After 48 h of

presaccharification, temperature is reduced to 35°C, and the mixture is inoculated with 1 g L⁻¹ of *Saccharomyces cerevisiae* Ethanol Red (Fermentis, France). After 72 h from inoculation, a PSSF yield of 0.40 g of ethanol g⁻¹ of potential glucose was obtained, which represents 78.4% of the theoretical yield (Sáez et al. 2012).

After PSSF, the fermented broth is sent to the ethanol recovery module, consisting of two distillation columns. In the first column (beer column) ethanol is concentrated to about 50% (w/w) and the stillage stream, mainly composed of lignin and water, is recovered at the bottom of the column. The collected stillage is then filtered for lignin recovery and it is subsequently sent to the power generation area. Ethanol, on the other hand, goes to the second distillation column (rectification column), where is further concentrated to reach the azeotropic point (93% by wt.). The resulting concentrated ethanol is finally purified to about 99.5% by means of molecular sieves. The wastewater generated after rectification column and stillage filtration is processed in the WWT area.

Wastewater treatment (WWT): The wastewater (Fig. 1) is treated in the WWT area. The treatment is based on sequential anaerobic and aerobic processes. The former is carried out under mesophilic conditions (37°C) (Barta et al. 2010), in which 90% of soluble sugars, organic acids, ethanol, enzymes and yeast, and 50% of polysaccharides are degraded, while lignin is left behind. The anaerobic system generates 0.35 Nm³ of biogas per kg of chemical oxygen demand (COD) removed. The resulting biogas, composed of 51% of CH₄ and 49% of CO₂ (on a dry molar basis), is then sent to the power generation area, while the remaining liquid fraction is transferred to aerobic digestion treatment. Here, the organic matter is completely removed, yielding about 0.5 kg of sludge kg⁻¹ of COD (Barta et al. 2010). Finally, the resulting sludge is separated from water by clarification and sent to the power generation area. Treated water is reused as process water.

Power and heat generation: Lignin collected from the ethanol production area, sludge and biogas from WWT, and yeast biomass obtained from xylitol production are subjected to

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3 combustion at 870°C for the production of high-pressure steam (6 MPa) (Humbird et al.
4 2011), which is fed into a steam turbine at three pressure levels (6/1.4/0.3 MPa) to produce
5 electricity. Steam from the intermediate- and low- pressure levels of the turbine is partially
6 used in the pretreatment unit, and the heat needed for other processes, such as distillation and
7 evaporation.
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12 **Techno-economic evaluation:** The biorefinery system was simulated in Aspen Plus v9.0
13 software (Aspen Technology Inc., USA). To this purpose, the physical-property data of
14 cellulose, hemicelluloses, lignin, enzymes, and yeast were taken from literature (Wooley et al.
15 1996). The non random two liquid (NRTL) thermodynamic model and the Hayden-O'Connell
16 equation-of-state were used to model the liquid and vapour phases, respectively (Quintero et
17 al. 2013). Furthermore, the aforementioned operation conditions and yields described above
18 served as process parameters.
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29 Water extraction block was modelled through a trayed-column with six theoretical
30 stages. Two aspen blocks served to simulate the steam explosion (SE) reactor, a
31 stoichiometric block (RStoic) for the reactor itself and a Flash block to model the explosive
32 decomposition produced in this equipment. PSSF unit was modelled with two RStoic blocks,
33 one for the liquefaction step and the other one for the saccharification and fermentation
34 reactor. The enzymatic hydrolysis (EH) was also modelled based on stoichiometric approach.
35 Finally, the power-generation section was simulated taking into account the isentropic and
36 mechanical efficiencies of the turbine (80% and 95%, respectively).
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46 The capital and operating costs were calculated by means of the software Aspen
47 Economic Analyzer V9.0 (Aspen Technologies, Inc., USA). The analysis was made in euros
48 (€ 2017) for a 10-y life period, and depreciation expenses were calculated using the straight-
49 line method. The interest rate and income tax were fixed in 6% and 25%, respectively,
50 according to the Spanish economy (Bank of Spain, 2017; Ministry of Finance and Public
51 administration, 2015). The operator and supervisor labour costs were assumed to be 17.8 € h⁻¹
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and 26.25 € h⁻¹, respectively (INE, 2017). Market prices of the raw materials, utilities, and products are listed in Table 2. Finally, the economic profitability of the plant was also analysed by estimating the net present value (NPV) and the payback period (PBP). These parameters establish the profits of the process during a project lifetime, and the time required for the investment reimbursement, respectively.

Results and discussion

Process simulation

Table 3 shows production capacities and mass yields for the products generated by the simulated model of the proposed OTP biorefinery. The amount of products expected for a 120 t d⁻¹ of OTP plant (10% moisture content), is 13.1 m³ of ethanol per day as main product, as well as 5.2 and 3.3 t per day of antioxidants and xylitol. These values correspond to a total yield of 108.8 L of ethanol, 42.9 kg of antioxidants and 27.2 kg of xylitol per ton of OTP.

A similar OTP-based biorefinery system was proposed by Romero-García et al. (2016). In that study, higher ethanol yields (about 180 L t⁻¹ of OTP biomass) were obtained because the whole pretreated slurry (including the WIS and prehydrolysate fractions) was utilized for ethanol production, while in the present study, only the WIS fraction was dedicated to this purpose. On the other hand, prehydrolyzate stream was used as feedstock for xylitol production, which has a good commercial value with an estimated annual market of 537 M US \$ (Prakasham et al. 2009). Regarding antioxidants production, Romero-García et al. (2016) assumed antioxidant recovery yields of 22 kg t⁻¹ of OTP, which is ca. 45% lower than that obtained in the present work. This result can be explained that the quoted authors applied an additional non-ionic adsorption chromatography column for purification of antioxidants (not considered in the present study because of costs reduction) resulting in higher product purity (from 36 to 60%).

The energy requirements of the proposed OTP biorefinery were calculated by means of the process simulation software Aspen Plus. The thermal energy is the main contributor to the total energy consumption with 12 GJ t⁻¹ of OTP input. Figure 2 shows the contribution of each biorefinery section to the thermal energy consumption. Such analysis is crucial because of the high thermal energy demand of bioconversion processes (Quintero et al. 2013). As visible in Figure 2, water extraction and pretreatment section (Section 1) presents the highest energy consumption ($\approx 53\%$). This is associated to the steam required for the SE pretreatment. Xylitol production also needs a lot of energy ($\approx 30\%$), basically due to the evaporation of the xylose-rich prehydrolysate and the xylitol-rich liquor. These results are in concordance with previous studies (Quintero et al. 2011; Moncada et al. 2013).

An integration of a power and steam generation module is mandatory for biorefineries. Here, lignin, the sludge from WWT, and the yeast from xylitol production are converted. The steam and electricity generated meets the whole energy demand, i.e. the biorefinery plant is energy self-sufficient. Moreover, even a surplus of electric energy of 1.6 MW is generated, which can be incorporated into the electric grid and improves the overall economic performance.

Economic assessment

Total project cost includes total installed equipment costs and other costs such as field expenses, project contingency, engineering cost, etc. Total installed equipment cost of 25.4 M € and total project cost of 44.1 M € were estimated. Similar total project cost has been previously estimated for other lignocellulose-based biorefineries. For instance, Cardona et al. (2018) obtained a total project cost of around 56 M US \$ (46 M€), considering oil palm rachis as feedstock and ethanol, xylitol, lactic acid and biogas as main products.

Operating cost includes inputs (OTP, chemical compounds, enzymes, and water), utilities, depreciation expense, labour cost, maintenance, and administrative cost and

insurance as well as credits by electricity production. Table 4 shows the annualized operating cost for the plant and the contribution of each element to the total operating cost. With an annual cost of 4.41 M €, depreciation expense was identified as the largest contributor to the total operating cost (35%), followed by 3.14 M € of inputs cost (25%). Additionally, labour cost, utilities and maintenance costs show significant contributions around 10%.

Techno-economic studies described in the literature usually highlight the inputs as the main contributors to the operating cost ($\approx 50\%$) (Mussatto et al. 2013; Dávila et al. 2017). However, these studies assumed an enzyme price of about 2.0-9.0 € kg⁻¹, which is about 5-25 times higher than the one considered in the present evaluation. A great progress was made in the last years to reduce enzyme costs, which is one of the major steps towards the commercialization of lignocellulosic biorefineries (Johnson 2016). The contribution of each input category to the total inputs cost is illustrated in Figure 3. As visible, OTP cost is dominating, being 60% of the total input. Enzyme and phosphoric acid also contribute significantly (22 and 11%, respectively). The other costs are altogether around 6%.

The economic profitability of the OTP-based biorefinery was evaluated by estimating the net present value (NPV) and pay back period values (PBP) (Table 3). To this purpose, current market prices of ethanol, xylitol, and antioxidants (Table 2), and the corresponding interest rate (6%) and income tax (25%) were used. Considering a 10-years life period, NPV presents a positive value of 32.1 M € at the end of the lifetime (Figure 4). PBP reaches a value of 5-6 years to recover the initial investment, which is an indicator for a good profitability.

The production costs of ethanol, xylitol and antioxidants were also calculated by using an economic allocation approach to distribute the operating cost, being 0.09 (ethanol), 0.14 (xylitol) and 0.77 (antioxidants) (see Tables 2 and 3), and this leads to estimated production costs of 0.24, 1.48, and 5.12 € kg⁻¹, respectively. These values are lower than the market prices in all cases, thus positive profit margins can be expected.

The presented plant shows an overall good economic performance, but the final profitability depends on the market price of the value-added compounds. This was also pointed out by Gnansounou and Dauriat (2010), who analysed the economy of lignocellulosics' conversion into ethanol. In this context, the price fluctuation of antioxidants is critical. To evaluate this point, the antioxidants selling price, the NPV, and the production cost of each product are presented in Figure 5. Ethanol and xylitol show negative profit margins, when the antioxidants market price is lower than 3 € kg⁻¹ and 4 € kg⁻¹, respectively. Nevertheless, to reach a NPV equal to zero, a minimum antioxidants selling price of 7.8 € kg⁻¹ is needed.

The enzymes prices are also variable (Chovau et al. 2013). Dávila et al. (2017) simulated a biorefinery based on a spent pulp of Colombian Andes Berry and considered enzymes costs 8-times higher (2.6 € kg⁻¹) than the one assumed in the present study. Figure 6 shows the influence of prices on the production cost of each product and the NPV. Accordingly, ethanol, xylitol, and antioxidants have positive profit margins within an enzymes cost range of 0.1-4 € kg⁻¹. However, according to the NPV, the plant would be non-economically viable with enzyme costs higher than 3 € kg⁻¹. However, the variation in the antioxidants' market prices are more influential on the process economy than the enzymes' costs. In fact, an enzymes price of 2 € kg⁻¹ reduces the NPV by 60%.

Conclusions

In this work, the software Aspen Plus has been successfully applied as an useful modelling tool for the subsequent techno-economic evaluation of a biorefinery plant based on OTP as feedstock. The bioethanol production together with the integrated byproducts production and marketing (xylitol and antioxidants) is technically and economically feasible. A prerequisite is the steam explosion pretreatment and the optimized concentration of xylose-rich prehydrolysate and xylitol-rich liquor, which have been also identified as the main energy

demanding steps. Power and steam co-generation from combustion of residual solid material and methane produced by anaerobic digestion of wastewater are also necessary for improving the overall economic performance of the system.

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References

- Abdul-Khalek, N. (2018) Evaluación de la producción de etanol y xilitol mediante procesos fermentativos a partir de paja de cebada pretratada por explosión por vapor. Master Thesis – Universidad Complutense de Madrid, Madrid, Spain.
- Bank of Spain (2017) Interest rate. <https://cliente.bancario.bde.es/pcb/es/menu-horizontal/productoservici/relacionados/tiposinteres/>. Last accessed date: April 23, 2018.
- Ballesteros, I., Ballesteros, M., Cara, C., Sáez, F., Castro, E., Manzanares, P., Negro M.J., Oliva, J.M. (2011) Effect of water extraction on sugars recovery from steam exploded olive tree pruning. *Bioresour. Technol.* 102:6611–6616.
- Barta, Z., Reczey, K., Zacchi, G. (2010) Techno-economic evaluation of stillage treatment with anaerobic digestion in a softwood-to-ethanol process. *Biotechnol. Biofuels* 3:21.
- Cardona, C.A., Solarte-Toro, J.C., Peña, A.G. (2018) Fermentation, thermochemical and catalytic processes in the transformation of biomass through efficient biorefineries. *Catal. Today* 302:61–72.
- Chovau, S., Degrauwe, D., Van der Bruggen, B. (2013) Critical analysis of techno-economic estimates for the production cost of lignocellulosic bio-ethanol. *Renew. Sust. Energ Rev* 26:307 – 321.
- Conde, E., Cara, C., Moure, A., Ruiz, E., Castro, E., Dominguez, H. (2009) Antioxidant activity of the phenolic compounds released by hydrothermal treatment of olive tree pruning. *Food Chem.* 114:806-812.
- Consorcio de aguas (2018) Tarifas de agua y saneamiento. <https://oficinavirtual.consorciodedaguas.com/FacturaElectronica/AtencionCliente/tarifas.aspx>. Last accessed date: April 23, 2018.
- Dávila, J.A., Rosenberg, M., Cardona, C.A. (2017) A biorefinery for efficient processing and utilization of spent pulp of Colombia Andes Berry (*Rubus glaucus* Benth.): Experimental, techno-economic and environmental assessment. *Bioresour. Technol.* 223:227–236.
- Díaz, M., Huijgen, W., van der Laan, R., Reith, J.H., Cara, C., Castro, E. (2011) Organosolv pretreatment of olive tree biomass for fermentable sugars. *Holzforschung* 65(2):177-183.
- European Commission (2015) From the sugar platform to biofuels and biochemicals. Final report for the European Commission Directorate-General Energy. N°ENER/C2/423-2012/s12.673791.
- García Martín, J., Sánchez, S., Bravo, V., Cuevas, M., Rigal, L., Gaset, A. (2010) Xylitol production from olive-pruning debris by sulphuric acid hydrolysis and fermentation with *Candida tropicalis*. *Holzforschung*, 65(1):59-65.
- Gnansounou, E., Dauriat, A. (2010) Techno-economic analysis of lignocellulosic ethanol: A review. *Bioresour. Technol.* 101(13):4980–4991.

- Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., Sexton, D., Dudgeon, D. (2011) Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. NREL/TP-5100-47764.
- ICIS (2018) Indicatives Chemical Prices A-Z. <https://www.icis.com/chemicals/channel-info-chemicals-a-z/>. Last accessed date: April 24, 2018.
- INE (2017) Salarios y costes laborales. http://www.ine.es/dyngs/INEbase/es/categoria.htm?c=Estadistica_P&cid=1254735976596. Last accessed date: April 24, 2018.
- Johnson, E. (2016) Modeling and analysis integrated enzyme production lowers the cost of cellulosic ethanol. *Biofuels*. Bioprod. Bioref. 10:1064–1074.
- Kolfschoten, R.C., Bruins, M.E., Sanders, J.P. (2014) Opportunities for small-scale biorefinery for production of sugar and ethanol in the Netherlands. *Biofuels*, Bioprod. Bioref. 8:475-486.
- Larsson, S., Reimann, A., Nilvebrant, N.O., Jönsson, L.J. (1999). Comparison of different methods for the detoxification of lignocellulose hydrolyzates of spruce. *Appl. Biochem. Biotechnol.* 77(1-3):91-103.
- Lopez, F.J., Pinzi, S., Ruiz, J.J., Lopez, A., Dorado, M.P. (2010) Economic viability of the use of olive tree pruning as fuel for heating system in public institutions in South Spain. *Fuel* 89:1386–1391.
- Mäkinen, K.K. (1994) Sugar Alcohols. In: *Functional Foods: Designer foods, pharmafoods, nutraceuticals*. Ed. Goldberg, I. Springer, Boston, USA. pp. 219-241.
- Manzanares, P., Ruiz, E., Ballesteros, M., Negro, M.J., Gallego, F.J., López-Linares, J.C., Castro, E. (2017) Residual biomass potential in olive tree cultivation and olive oil industry in Spain: valorization proposal in a biorefinery context. *Span. J. Agric. Res.* 15(3):e0206.
- Ministry of Finance and Public Administration (2015) Government approves fiscal reform to reduce taxes to 20 million tax payers. <http://www.minhfp.gob.es/Documentacion/Publico/GabineteMinistro/Notas%20Prensa/2014/S.E.%20HACIENDA/01-08-14%20Nota%20aprobaci%C3%B3n%20reforma%20fiscal.pdf>. Last accessed date: April 23, 2018.
- Moncada, J., El-Halwagi, M.M., Cardona, C.A. (2013) Techno-economic analysis for a sugarcane biorefinery: Colombian case. *Bioresour. Technol.* 135:533–543.
- Moreno, A.D., Alvira, P., Ibarra, D., Tomás-Pejó, E. (2017) Production of ethanol from lignocellulosic biomass. In: *Production of platform chemicals from sustainable resources. Biofuels and biorefineries*. Eds. Fang, Z., Smith, Jr. R., Qi, X. pp. Springer, Singapore. pp. 375-410.
- Mussatto, S.I., Moncada, J., Roberto, I.C., Cardona, C.A. (2013) Techno-economic analysis for brewer's spent grains use on a biorefinery concept: The Brazilian case. *Bioresour. Technol.* 148: 302–310.
- Negro, M.J., Alvarez, C., Ballesteros, I., Romero, I., Ballesteros, M., Castro, E., Manzanares, P., Moya, M., Oliva, J.M. (2014) Ethanol production from glucose and xylose obtained from steam exploded water-extracted olive tree pruning using phosphoric acid as catalyst. *Bioresour. Technol.* 153:101–107.
- NREL. Biomass compositional analysis laboratory procedures. <https://www.nrel.gov/bioenergy/biomass-compositional-analysis.html>. Last accessed date: April 24, 2018.
- Prakasham, R.S., Rao, R.S., Hobbs, P.J. (2009) Current trends in biotechnological production of xylitol and future prospects. *Curr. Trends. Biotechnol. Pharm.* 3(1): 8-36.
- 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.

- 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.* 139:300–307.
- Rivas, B., Torre, P., Domínguez, J.M., Converti, A., Parajó, J.C. (2006) Purification of xylitol obtained by fermentation of corncob hydrolysates. *J. Agric. Food Chem.* 54:4430–4435.
- Romero-García, J.M., Sanchez, A., Rendón-Acosta, G., Martínez-Patiño, J.C., Ruiz, E., Magaña, G., Castro, E. (2016) An olive tree pruning biorefinery for co-producing high value-added bioproducts and biofuels: Economic and energy efficiency analysis. *Bioenerg. Res.* 9(4):1070-1086.
- 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. Bioref.* 11:1077–1094.
- Sáez, F., Álvarez, C., Ballesteros, I., Ballesteros, M., Manzanares, P., Negro, M.J., Oliva, J.M. (2012) Second-generation ethanol production from olive tree pruning. In: *Advanced biofuels in a biorefinery approach* (February 28 - March 1, 2012, Copenhagen, Denmark). Ed. Jørgensen, H. *Forest & Landscape Working Papers* No. 70-2012. Frederiksberg, Denmark. p. 68.
- Ulrich, G.D., Vasudevan, P.T. (2006) How to estimate utility cost. *Chem. Eng.* 2006:66–69.
- Velázquez-Martí, B., Fernández-González, E., López-Cortés, I., Salazar-Hernández, D.M. (2011) Quantification of the residual biomass obtained from pruning of trees in Mediterranean olive groves. *Biomass Bioenerg.* 35:3208–3217.
- Veneziani, G., Novelli, E., Esposto, S., Taticchi, A., Servili, M. (2017) Applications of recovered bioactive compounds in food products. In: *Olive Mill Waste*. Ed. Galanakis, C.M. Academic Press, London (UK), San Diego (USA), Cambridge (USA), Oxford (UK). pp. 231-253.
- Wooley, R., Putsche, V. (1996) Development of an ASPEN PLUS physical property database for biofuels components. NREL/TP-425-20685.

Table captions

Table 1. Chemical composition of the Olive Tree Pruning (OTP) biomass.

Table 2. Market prices of the raw material, utilities, and products

Table 3. Production capacities and mass yields for the different products generated in the simulated model

Table 4. Annualized operating cost of OTP-based biorefinery

Figure captions

Figure 1a. Simplified diagram of the integrated biorefinery system based on olive tree pruning (OTP) biomass. SSF, simultaneous saccharification and fermentation; WIS, water insoluble solids. **Figure 1b.** Simplified simulation diagram of the OTP-based biorefinery.

Figure 2. Contribution of the operation modules to the total thermal energy consumption of the OTP-based biorefinery

Figure 3. Share of each input category to the total inputs cost

Figure 4. Net present value (NPV) of the OTP-based biorefinery in a 10-years lifetime

Figure 5. Influence of antioxidants market price on (a) ethanol and (b) xylitol production costs, and (c) NPV. The red lines represent the market prices for ethanol and xylitol, respectively.

Figure 6. Influence of enzymes price on (a) ethanol, (b) antioxidants, and (c) xylitol production costs, and (d) NPV. The red lines represent the market prices for ethanol, antioxidants, and xylitol, respectively.

Table 1. Chemical composition of olive tree pruning (OTP)

Component	(%)*
Extracts	24.5 ± 1.1
Glucose	6.4 ± 0.6
Xylose	0.2 ± 0.1
Galactose	0.8 ± 0.2
Arabinose	0.1 ± 0.0
Mannose	0.1 ± 0.0
Mannitol	3.4 ± 0.4
Antioxidants	3.1 ± 0.5
Glucan	23.1 ± 0.8
Hemicelluloses	18.4 ± 0.5
Xylan	10.6 ± 0.3
Galactan	2.1 ± 0.1
Arabinan	2.7 ± 0.2
Mannan	1.3 ± 0.2
Acetyl groups	1.7 ± 0.5
Lignin	20.4 ± 0.3
Ash	4.8 ± 0.2

*b.o. dry weight

Table 2. Market prices of the raw material, utilities, and products

Compound	Value
OTP	44.70 ^a € t ⁻¹
Enzyme	370.00 ^b € t ⁻¹
Process water	1.30 ^c € m ⁻³
Calcium hydroxide	7.10 ^d € t ⁻¹
Phosphoric acid	370.00 ^d € t ⁻¹
Ethyl acetate	1,210.00 ^d € t ⁻¹
Cooling Water	0.10 ^e € m ⁻³
Refrigerant	0.02 ^e € MJ ⁻¹
Ethanol	580.06 ^f € m ⁻³
Antioxidants	11,000.00 ^g € t ⁻¹
Xylitol	3,170.00 ^f € t ⁻¹

^a Price based on literature report (Lopez et al. 2010) and including transportation cost

^b Price based on Johnson (2016).

^c Price taken from Consorcio de aguas (2018).

^d Price taken from ICIS Pricing (2018).

^e Price estimated based on literature reports (Ulrich et al. 2006).

^f Price based on literature report (European Commission, 2015).

^g Price estimated based on Romero-García et al. (2016). The price represents 15% of the value reported by these authors based on purity differences.

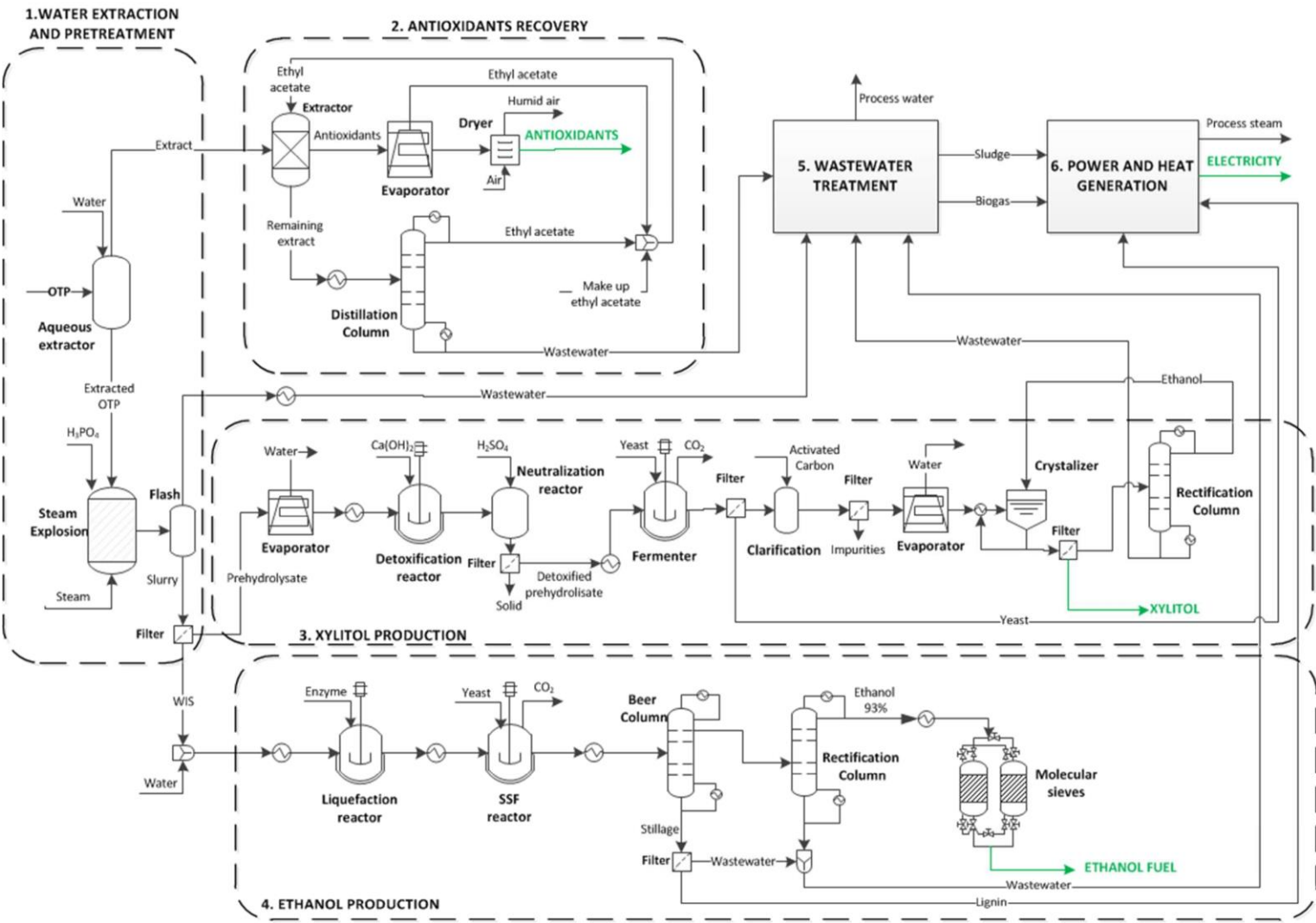
Table 3. Production capacities and mass yields for the different products generated in the simulated model

Product	Production	Yield
Ethanol	13.1 m ³ day ⁻¹	108.8 L t ⁻¹ OTP
Xylitol	3.3 t day ⁻¹	27.2 kg t ⁻¹ OTP
Antioxidants	5.2 t day ⁻¹	42.9 kg t ⁻¹ OTP

Table 4. Annualized operating cost of OTP-based biorefinery.

Parameters	Cost (M€ year⁻¹)	Contrib. (%)
Inputs	3.14	25
Utilities	1.54	12
Depreciation expense	4.41	35
Labour cost	1.84	15
Maintenance	1.32	11
Admin. and insurance	0.31	2
Credit by electricity	-1.08	
Total (incl. electricity)	11.42	

Figure 1a



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Figure 2

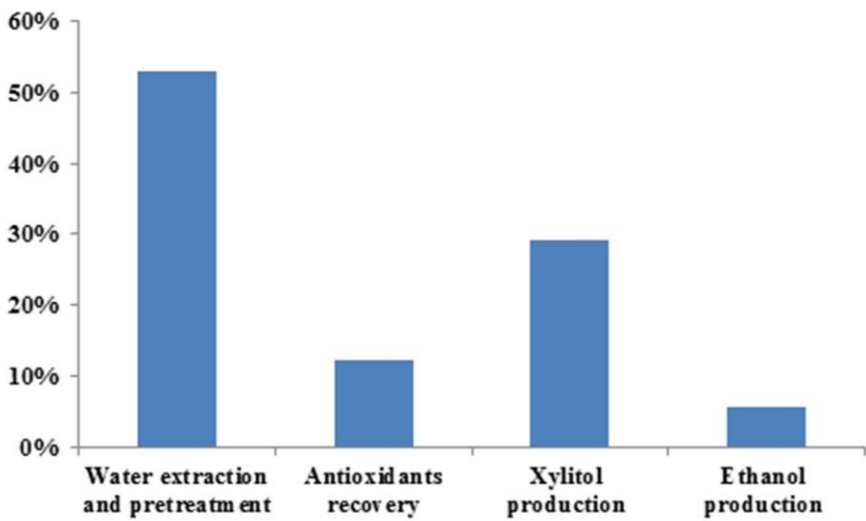


Figure 3

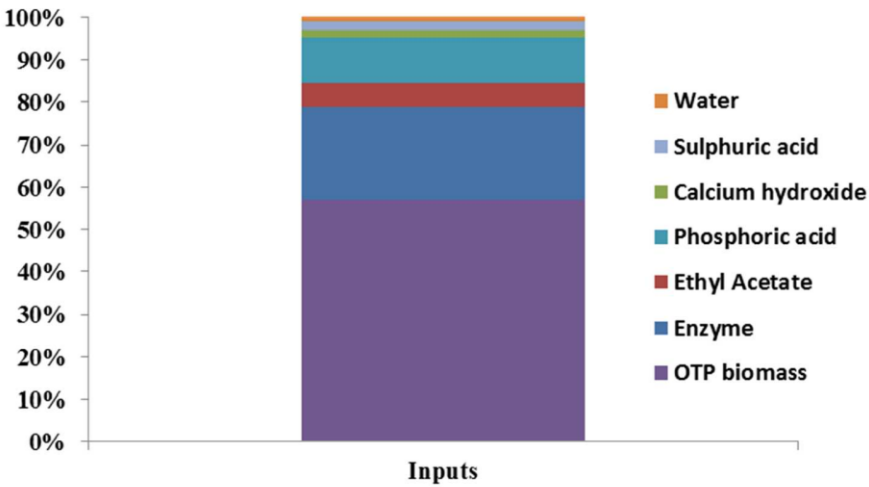


Figure 4

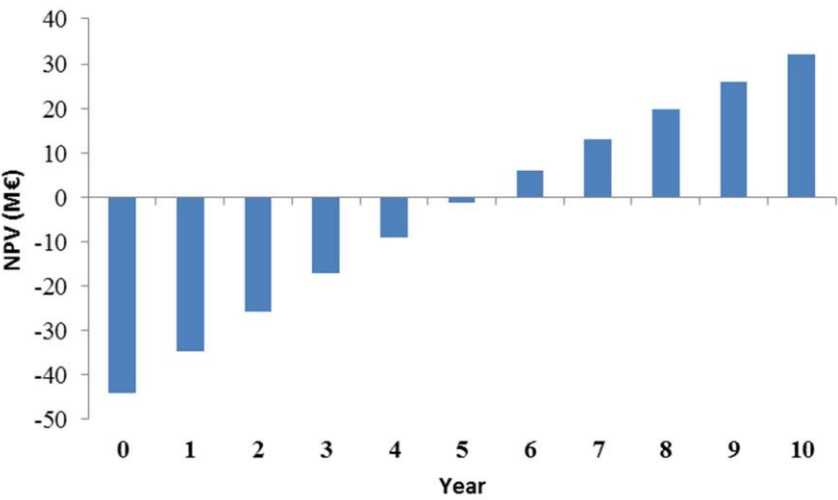


Figure 5

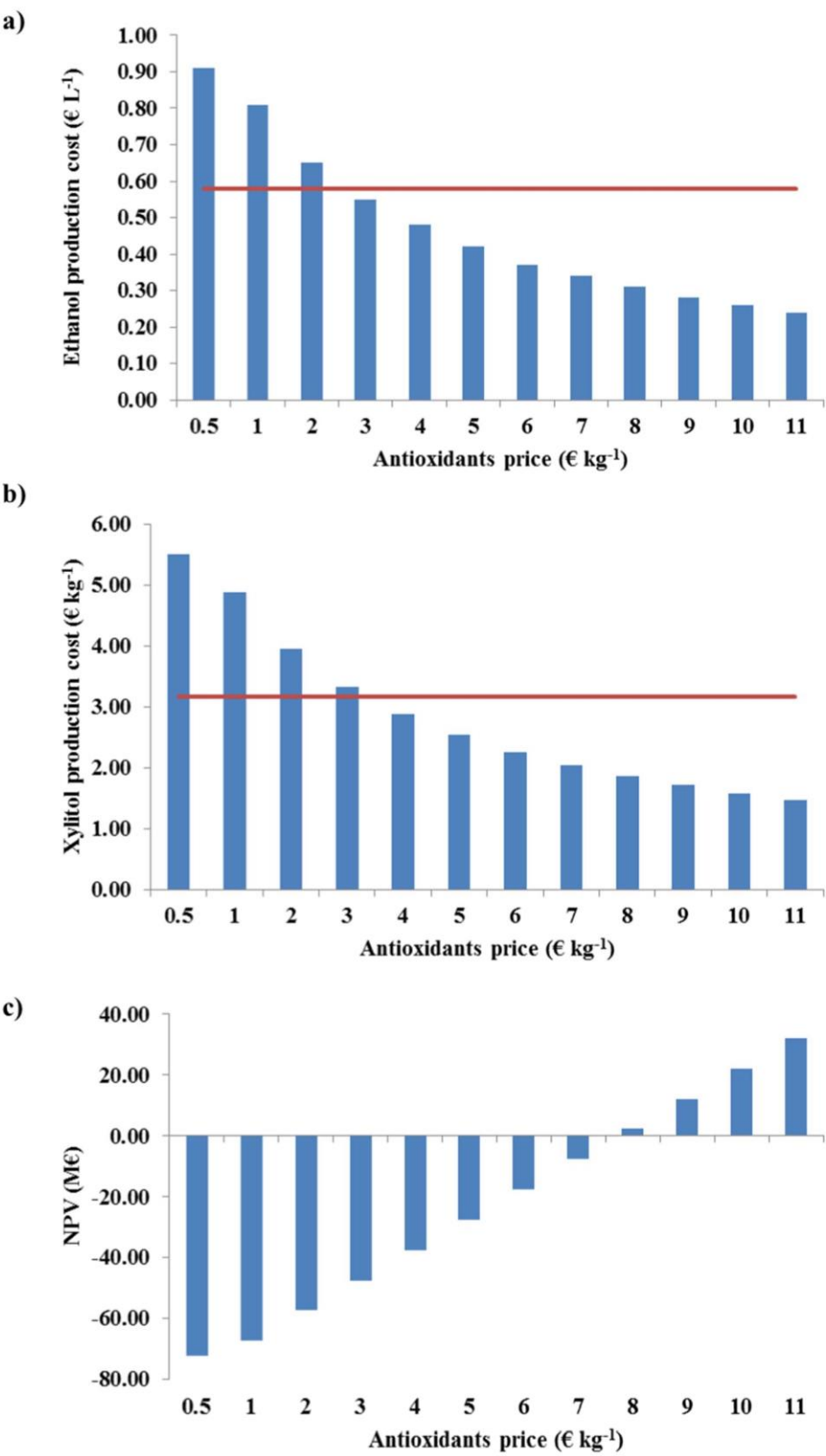


Figure 6

