

## Olive leaves as a source of lignin, antioxidants and bioethanol. A technical evaluation

J. M. Romero-García<sup>1\*</sup>, J.C. Solarte-Toro<sup>2</sup>, E. Ruiz-Ramos<sup>1</sup>, I. Romero-Pulido<sup>1</sup>, C.A. Cardona-Alzate<sup>2</sup>, E. Castro-Galiano<sup>1</sup>

<sup>1</sup>Department of Chemical, Environmental and Materials Engineering; Centre for Advanced Studies in Earth Sciences, Energy and Environment (CEACTEMA). Universidad de Jaén. Campus Las Lagunillas s/n | 23071 - Jaén (España).

<sup>2</sup>Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia, Manizales campus. Manizales - Colombia. Km 07 via al Magdalena.

Keywords: Organosolv pretreatment, Olive biomass, Process simulation, Simultaneous saccharification and fermentation.

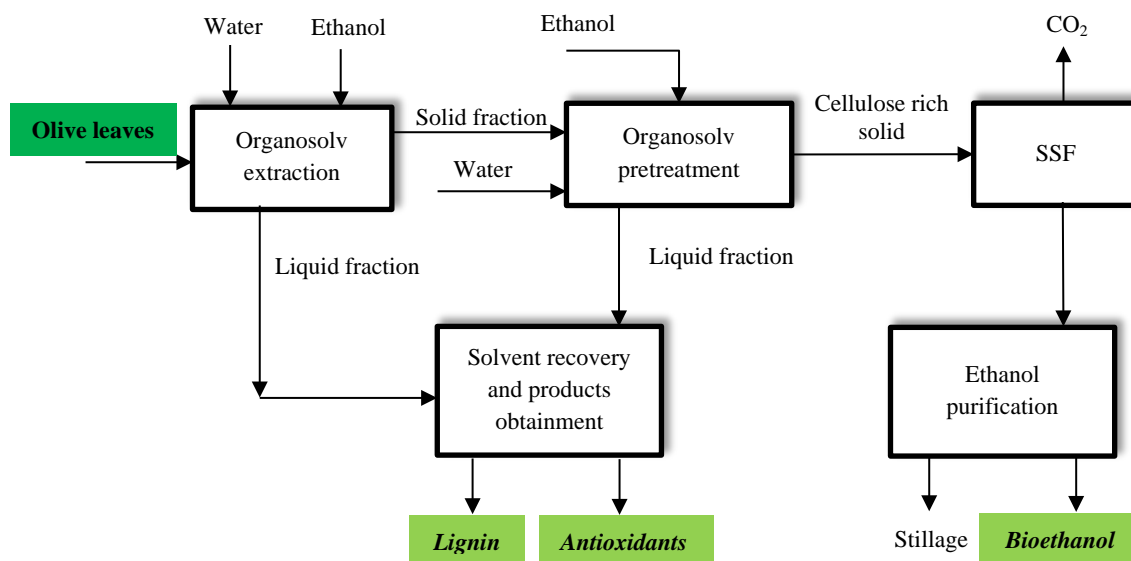
\*Presenting author email: [jrgarcia@ujaen.es](mailto:jrgarcia@ujaen.es)

Olive leaves are a lignocellulosic material derived from the olive crop, which is produced during the olive harvesting and olive fruit cleaning which can be considered as centralized and controlled (Romero-García et al., 2014). According to Lama-Muñoz et al (2020), olive leaves have a high extractives and lignin content. As consequence, this lignocellulosic residue has a great potential to be used in a biorefinery to produce value-added products such as lignin and antioxidants as well as energy vectors like bioethanol. However, the use of conventional technologies such as acid pretreatment or alkali pretreatment could not be suitable for obtaining these products. On the other hand, organosolv process has been proposed by other authors as pretreatment method that can be used to recover the main three fractions of the lignocellulosic biomass (i.e. cellulose, hemicellulose and lignin) (Kautto, Realf, & Ragauskas, 2013; Viell, Harwardt, Seiler, & Marquardt, 2013). Thus, a two-stage organosolv pretreatment and a simultaneous saccharification and fermentation process have been proposed for the antioxidants extraction, lignin recovery and bioethanol production from olive leaves. Good extraction yields have been found for this proposed process scheme, but its feasibility at industrial level must be evaluated. Therefore, the aim of this work is to evaluate from the techno-economic point of view, the production of lignin, antioxidants and bioethanol using olive leaves as raw material through a two-stage organosolv pretreatment and a simultaneous saccharification and fermentation process taking into account experimental yields obtained at laboratory scale.

To carry out the prefeasibility assessment, the software Aspen Plus v9.0 and the Aspen Process Economic Analyzer v9.0 were used. The employed simulation procedure is similar to that reported by Cardona *et al* (2017) As mentioned above, the proposed process consists of three main blocks. The first one is an organosolv extraction at low temperature and high residence time with a solids loading of 15%. This process was carried out to remove a large amount of phenolic compounds, which have high antioxidant capacity. The second block is an organosolv process performed at high temperature and low residence time, with the goal to remove the lignin content using an ethanol – water mixture (50% v/v) and sulfuric acid (1% w/v) as catalyst. The solid liquid ratio employed in this pretreatment was 10% w/v. Finally, the third stage is a simultaneous saccharification and fermentation (SSF) process, which was performed to accomplish the ethanol production consuming the C<sub>5</sub> and C<sub>6</sub> fraction derived from the cellulose and hemicellulose content. In addition, a solvent recovery stage and purification stage were included into the simulation. These stages were designed and simulated applying process engineering tools and distillation concepts. The block diagram of the proposed process is shown in Figure 1.

Results show that the ethanol production in the proposed scheme is cheaper than its production in standalone using other olive derived feedstocks (i.e. olive tree biomass). In addition, the lignin and antioxidants production improve the use of olive leaves. From the technical perspective, in the first organosolv extraction the cellulose and hemicellulose content as well as the lignin content were not affected in high proportions. However, the second organosolv stage removed high quantities of lignin from the lignocellulosic matrix. Therefore, the two-stage organosolv process improve the mass yields for the antioxidants and lignin recovery. Finally, the amount of produced bioethanol in comparison with the ethanol employed as a solvent in the organosolv process, is low.

Moreover, the techno-economic assessment shows that the raw materials and utilities costs are the highest costs in the proposed scheme. In addition, the implementation of the simultaneous saccharification and fermentation process improved the ethanol production in terms of equipment and utilities cost.



**Figure 1.** Two-stage organosolv process and simultaneous saccharification and fermentation of olive leaves.

As a conclusion from this work, the organosolv process has great advantages from the technical point of view, because it allows to recover the main three fractions of the lignocellulosic matrix of the olive leaves. In addition, at low operating conditions, the antioxidants obtainment is possible. However, the economics of this process must be analyzed more deeply with the end to elucidate if the organosolv technology is economically feasible. This work also shows that the production of high value-added products such as antioxidants can slightly support the production of bulk chemicals such as bioethanol. Finally, it was possible to determine that the olive leaves are a high potential feedstock that can be used to increase the value of the olive production chain using different conversion technologies that not necessarily include those evaluated in this work.

#### Acknowledgements

Financial support from Agencia Estatal de Investigación and Fondo Europeo de Desarrollo Regional (Reference projects PID2020-112594RB-C31). J.M. Romero-García expresses his gratitude to the Junta de Andalucía for financial support (Postdoctoral researcher R-29/12/2020).

#### References

- Cardona Alzate, C. A., Solarte Toro, J. C., & Peña, Á. G. (2017). Fermentation, thermochemical and catalytic processes in the transformation of biomass through efficient biorefineries. *Catalysis Today*, 302(September 2017), 61–72. <https://doi.org/10.1016/j.cattod.2017.09.034>
- Kautto, J., Realf, M. J., & Ragauskas, A. J. (2013). Design and simulation of an organosolv process for bioethanol production. *Biomass Conversion and Biorefinery*, 3(3), 199–212. <https://doi.org/10.1007/s13399-013-0074-6>
- Lama-Muñoz, A., Contreras, M.M., Espínola, F., Moya, M., Romero, I., Castro, E. (2020). Characterization of the lignocellulosic and sugars composition of different olive leaves cultivars. *Food Chemistry*, 329, art. no. 127153. <https://doi.org/10.1016/j.foodchem.2020.127153>
- 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. *Bioresource Technology*, 159, 421–432. <https://doi.org/10.1016/j.biortech.2014.03.062>
- Viell, J., Harwardt, A., Seiler, J., & Marquardt, W. (2013). Is biomass fractionation by Organosolv-like processes economically viable? A conceptual design study. *Bioresource Technology*, 150, 89–97. <https://doi.org/10.1016/j.biortech.2013.09.078>