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New valorization strategies for olive oil production wastes in Spain

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Abstract: Spain is the world largest producer of olive oil. The waste derived from the production processes is usually stored long-term in open dams and burned for energy generation; however, its chemical properties make it an excellent candidate for extraction of high added value compounds and other more efficient recycling strategies.

1. Introduction

Olive oil is the base of the Mediterranean diet. It is a key element of both Spanish culture and economy. In fact, Spain is the world's largest olive oil producer, with an average production of 1,5 million tonnes of oil every year [1]. However, the extraction of oil from the olives generates large amounts of solid residues and wastewater that may be difficult to handle due to their high pollution potential. Traditionally, waste has been stored in open dams and evaporated for months until the solid residue could be burned for energy purposes. This poses several drawbacks such as odour problems, space problems, and spills, along with the lost opportunity of properly recycling olive mill waste and re-introducing it higher in the value chain [2].

The development of a holistic recycling strategy to cover all the steps of the recycling value chain is in line with the circular economy and bioeconomy policies promoted by the European Union institutions during the last decade. Waste coming from olive oil production is an important source of nutritionally valuable compounds including polyphenols, fatty acids, colouring pigments, tocopherols, phytosterol, squalene, volatile and aromatic compounds [3]. Extracting and commercializing these low volume high value compounds is the first step of the recycling value chain. Then, the remaining waste can be treated with less sophisticated recycling techniques to generate compost, biochar, biofuels, and ultimately to burn it as an energy source. The aim of this work is to review some of the new and promising recycling strategies that could enrich the olive oil production value chain.

2. Manufacturing and waste generation

The main olive oil extraction processes are (1) traditional discontinuous press process, (2) three-phase centrifugal process or (3) two-phase extraction process. The difference between methods (2) and (3) is the number of exits in the centrifugation system that separates olive oil from the other substances according to their density. Three-phase centrifugation systems separate the output into olive cake, wastewater, and oil. This requires more water and there is washing of some valuable substances such as polyphenols. Two-phase centrifugation only produces oil and a wet olive cake called “aleporujo”, avoiding polyphenol extraction [4].

During the last decades, more than 90% of the Spanish olive mills adopted the two-phase extraction process. This was incentivized by the government as it consumes less fresh water and generates less volume of residues than other techniques. However, it has its own disadvantages, like the difficulty of treating concentrated and mixed solid-liquid wastes. For every ton of olives, this method produces 200 kg of virgin olive oil along with 900 kg of two-phase olive mill waste (wet olive cake or “alperujo”), while it consumes 0,31 tonnes of water and around 100 kWh (Figure 1) [2].

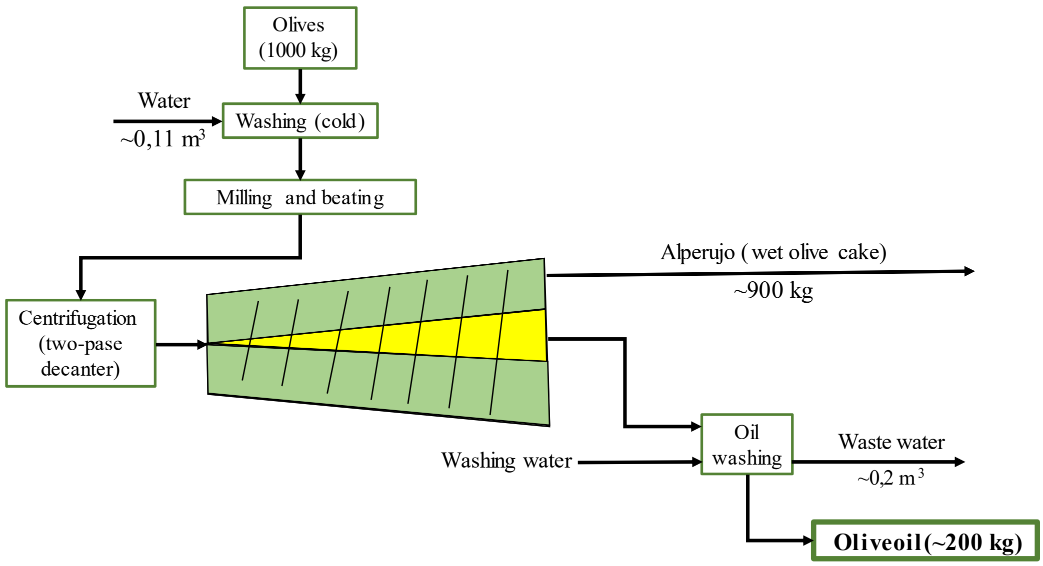

Figure 1. Two-phase olive oil production. 1 ton of olives as functional unit. Adapted from [5].

Considering that Spain produces 1,5 million tonnes of olive oil annually, and that 90% of it is produced through the two-phase method, it is possible to estimate the production of wet olive cake or alperujo in 6 million tonnes every year. Most of the olive stones are separated and used for energy generation (75%) and the rest undergoes industrial transformations to produce animal feed or high quality biofuels (25%). Around 80% of alperujo is destined to secondary extraction plants, where low quality olive oil (orujo olive oil) is produced using hexane as a solvent, with poor yields. Small percentages of alperujo are also used for compost and energy generation. The secondary extraction process generates exhausted olive pomace or orujillo, which is the last waste and used almost entirely for energy purposes [6]. A scheme of the described cascade route is shown in Figure 2.

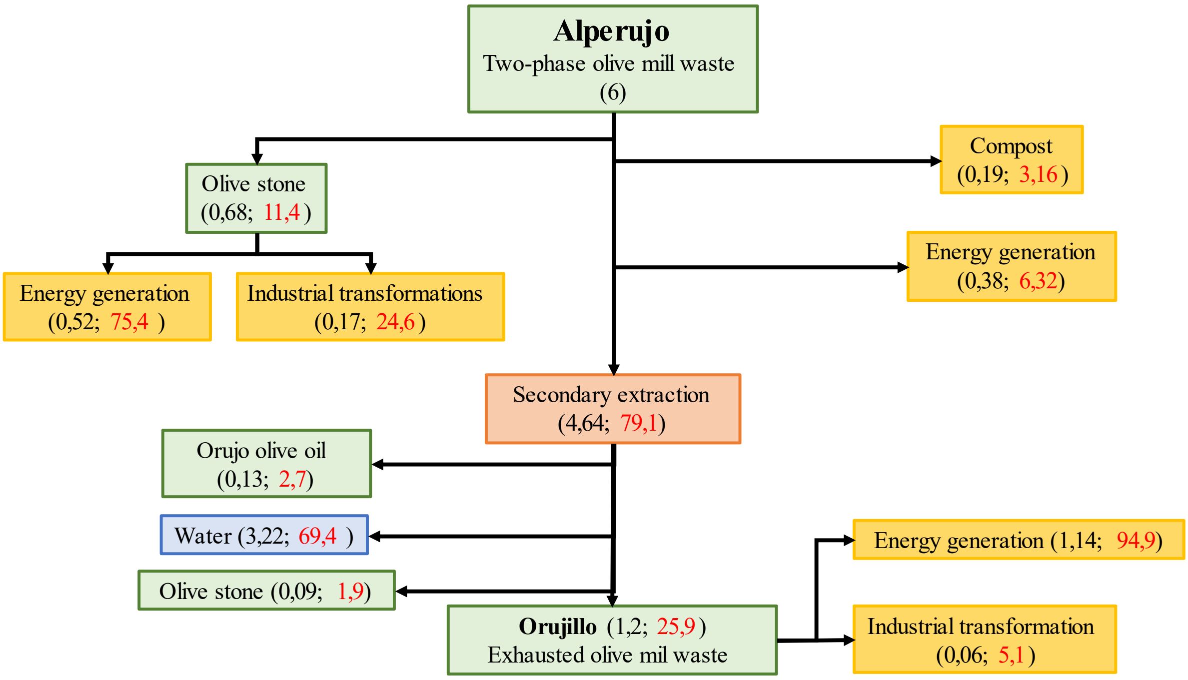

Figure 2. Destinations of alperujo. Between parenthesis, quantity in million tonnes per year and percentage in red. Adapted from [6].

3. Biochemical characterization of production wastes

The chemical composition of the different wastes can vary significantly according to olive species, origin, culture conditions and extraction processes. Alperujo or wet olive cake is a mixed liquid-solid waste with about 60% water content, 3% oil content and biomass comprising olive stone and pomace. It is acidic (pH 5,3-5,8) and without further treatment it is phytotoxic, so it can not be used directly for agricultural purposes [2].

Olive stone is a lignocellulosic material, consequently hemicellulose, cellulose and lignin are its main components. In addition, olive stones are also rich in fats, proteins, phenols, free sugars, and polyols. The water content is usually around 10%. Despite their content in high value compounds, their main use is energy generation by combustion due to their high combustion heat (17,16 kJ/kg) [7].

Exhausted olive pomace or orujillo is another lignocellulosic residue with high combustion heat. Humidity values are usually around 15% and it is comparatively easy to work with and transport due to its density and granulometry. Its content in extractives, mainly aqueous extractives, is interesting, and it is high (~40%) compared to other lignocellulosic wastes. The presence of bioactive and antioxidants compounds in the extractive fraction of orujillo has been widely reported. This includes phenolic compounds and polyols such as mannitol. Its ashes are also valued for the high content in potassium, calcium, and magnesium [8].

4. Current recovery strategies

Wastes derived from the production of olive oil in Spain are almost entirely used for something else. For instance, Andalucía region (more than 70% of Spanish production) estimates that only 0,7% of the waste is burn in open field or managed as a residue. In the same region, 80% of the waste is dedicated to production of electricity or thermal energy. This can be extrapolated to the rest of the country. With this strategy, it is possible to produce 809 GWh/year only from olive oil production waste in Andalucía. This is enough to match the electric energy consumption of half a million inhabitants, accounting for 2,1% of the total electrical energy production of the region [6].

Although this is clearly a success, it shows some concerning disadvantages. For example, the use of biomass as renewable fuel is losing support due to particle emissions. Some of the most worrying emissions related to biomass are aromatic compounds, sulphur, chlorinated compounds, dioxins, or furans, which are considered dangerous for the humans and the environment [8].

Furthermore, finding new uses for olive oil production wastes would diversify its applications, thus making its economical network stronger. It would also help to generate more value from them. For this reason, companies are institutions are now investing in finding alternative valorization strategies based on the extraction of high value compounds and the elaboration of high quality biofuels.

5. Promising valorization strategies

Olive stones are the most versatile component of the waste. They are mainly used for direct energy generation, but one quarter of the production is destined to industrial transformations to elaborate some products such as activated carbon, furfural, plastic filler, abrasives, and skin exfoliating compound in cosmetics. It is even possible to perform pyrolysis to generate bio-oils with similar properties to petroleum, or torrefaction to obtains solids with high heating values. These uses should be further incentivised along with other promising applications still in development like extraction of medical compounds or the use of olive stones as dietary animal supplementation [7].

The wet olive pomace (alperujo) does not find that variety of applications outside direct energy generation, although torrefaction can also generate high heating value solids. Olive oil coming from secondary extraction has been studies as a candidate for biodiesel elaboration, including a steam pre-treatment. The quality was comparable to other biodiesels, but the small raw material supply and high costs stopped the expansion. Promising applications for the future include treatment with microorganisms to generate soil amendment and animal feed, or to generate bioethanol or hydrogen [9].

Exhausted olive pomace or orujillo has been investigated as a candidate for gasification with promising results. Also, because orujillo does not contain water or oil, it is possible to perform solid state fermentation to obtain enzymes. It is also considered a raw material in biorefinery processes for ethanol production, but also proteins, sugars, and lignin [9].

All of the three main types of residues (olive stones, alperujo and orujillo) share what might be the most important valorization strategy: extraction of polyphenols. These substances (mainly hydroxytyrosol and tyrosol) are present in high quantities in olive oil production wastes, specifically around 5,5% dry weight, depending on the kind of waste. They present high antioxidant, antibacterial and antitumoral activity, finding applications in food, cosmetics, and nutraceutical industries. The extraction of phenolic compounds improves the economic viability of the recovery, and reduces the toxicity of the pre-hydrolized waste, thus improving the yield of the enzymatic hydrolysis that can be performed in the remaining waste to obtain bio-ethanol and other chemical compounds [10].

In conclusion, the valorization potential of the different olive oil production wastes has been proven. Although all the mentioned processes are feasible on their own, trends in the industry advance through integration of all the steps in the same installation, following the concept of biorefinery. This consists in leveraging the different components of the waste through steps, extracting the low volume high value compounds first and then moving along to the elaboration of biofuels and, in a last stage, burning the remaining waste for energy purposes [9].

6. References

[1] Statista, “Producción aceite de oliva en España.” https://es.statista.com/estadisticas/516683/produccion-de-aceite-de-oliva-en-espana/ (accessed Jul. 02, 2022).

[2] N. Azbar, A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul, and A. Ozer, “A review of waste management options in olive oil production,” *Critical Reviews in Environmental Science and Technology*, vol. 34, no. 3. pp. 209–247, 2004, doi: 10.1080/10643380490279932.

[3] V. J. Inglezakis, J. L. Moreno, and M. K. Doula, “Olive oil waste management EU legislation: Current situation and policy recommendations.” [Online]. Available: www.journal-ijcees.com.

[4] S. Dermeche, M. Nadour, C. Larroche, F. Moulti-Mati, and P. Michaud, “Olive mill wastes: Biochemical characterizations and valorization strategies,” *Process Biochemistry*, vol. 48, no. 10. pp. 1532–1552, Oct. 2013, doi: 10.1016/j.procbio.2013.07.010.

[5] A. Hamid, Z. Bibi, I. Ghafoor, Z. Anwar, and J. Z. K. Khattak, “Approach of bioremediation in olive oil and dairy industry: A review,” *Research Journal of Applied Sciences, Engineering and Technology*, vol. 5, no. 6. Maxwell Science Publications, pp. 2255–2263, 2013, doi: 10.19026/rjaset.5.4780.

[6] J. Antonio, C. López, T. Parra Heras, and T. M. Gordillo, “Evaluación de la producción y usos de los subproductos de las agroindustrias del olivar en Andalucía.”

[7] G. Rodríguez, A. Lama, R. Rodríguez, A. Jiménez, R. Guillén, and J. Fernández-Bolaños, “Olive stone an attractive source of bioactive and valuable compounds,” *Bioresource Technology*, vol. 99, no. 13. pp. 5261–5269, Sep. 2008, doi: 10.1016/j.biortech.2007.11.027.

[8] “Valorisation of Exhausted Olive Pomace by an Eco-Friendly Solvent Extraction Process of Natural Antioxidants _ Enhanced Reader.”

[9] E. Ruiz, J. M. Romero-García, I. Romero, P. Manzanares, M. J. Negro, and E. Castro, “Olive-derived biomass as a source of energy and chemicals,” *Biofuels, Bioproducts and Biorefining*, vol. 11, no. 6. John Wiley and Sons Ltd, pp. 1077–1094, Nov. 01, 2017, doi: 10.1002/bbb.1812.

[10] M. Araújo, F. B. Pimentel, R. C. Alves, and M. B. P. P. Oliveira, “Phenolic compounds from olive mill wastes: Health effects, analytical approach and application as food antioxidants,” *Trends in Food Science and Technology*, vol. 45, no. 2. Elsevier Ltd, pp. 200–211, Oct. 01, 2015, doi: 10.1016/j.tifs.2015.06.010.