Development of an olive mill waste biorefinery

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Abstract This study focuses on giving value to the olive mill wastes (OMW) generated from the production process of olive oil. The developed processes can be applied both on II-phase and III-phase OMW. The treatment and utilisation of such wastes is very challenging mainly due to their high organic loading and the presence of organic compounds which are hard to biodegrade, such as long-chain fatty acids and phenolic compounds. An acidification step is first carried out to extract the residual oil from OMW. The oil is then removed via centrifugation. The aqueous liquid stream passes from an ultrafiltration unit and from an ion-exchange resin unit in order to remove the phenolic compounds. These first two steps not only detoxify the OMW but also produce two high added value products: residual oil and phenolic extract. The remaining liquid contains no inhibitors, and hence, it can be used as substrate in a biological process for the production of biochemicals or bioenergy, together with the retentate stream from ultrafiltration, while the remaining solids enter into a compost production process. The effluent from the anaerobic digestion together with the excess of the sludge can be co-composted with the rest of the solids. The developed biorefinery concept leaves zero wastes and presents an integrated and sustainable approach in treating OMW.

Keywords: OMW Biorefinery, phenolic compounds, residual oil, bioenergy, organohumic fertiliser

1. Introduction

Olive oil is an important part of the Greek economy as it covers 9% of the total agricultural production value in Greece. This sector is characterized as highly dynamic, since Greece is the third largest oil producer in the world, after Spain and Italy, with production of around 0.32 million tons, accounting for 0.4% of its GDP. The last years, new markets have emerged and are currently exhibiting strong demand for olive oil as they gradually become more familiar with olive oil and its beneficial health qualities. Olive oil industry has also a high national socioeconomic importance, since a high number of farmers, treatment-packing facilities and selling points are being part of the supply chain, with high dependence on the quantity and quality of annual production. However, the olive oil production process is accompanied by extensive amounts of wastes which are considered food wastes provoking severe environmental problems.

In 2012, EU Committee published a list of permitted health claims made on foods as per which olive oil polyphenols contribute to the protection of blood lipids from oxidative stress. The wide recognition of olive oil polyphenol’s great importance (e.g. tyrosol, hydroxytyrosol, oleuropein and oleocanthal), which are also contained in significant quantities in OMW, aroused the interest of the scientific community in this area as well as the demand from pharmaceutical and food industries which are exploring new applications of these compounds. Moreover, under the concept of circular bioeconomy, new bioroutes have been explored from academia and industry so as to convert organic wastes to bioenergy and organic fertilizers. The above actions constitute the basis for penetration of innovation into new markets under the concept of circular bioeconomy.

Depending on the applying process, olive oil is extracted by pressing or centrifugation. Pressing is the traditional method of extracting olive oil, which has been gradually replaced by the centrifugation process over the last decades. For the centrifugation process, there are two different systems depending, whether or not, on the use of water during the process: the two-phase and the three-phase olive mills. In three-phase and pressing mills, apart from oil which is the main product, olive pomace (a solid by-product) and wastewater (a liquid waste) are also produced as water is used in large quantities. Olive pomace is used as raw material in pomace oil industries where the pomace oil is extracted using hexane as solvent and the remaining solids are typically used as a solid biofuel.

The last decade in Greece, the three phase mills are gradually replaced by two-phase olive mills due to the lower amount of waste they generate. In Spain, which is the chief producing country in olive oil, more than 85% of the olive oil producers are two-phase olive mills where water is only used during the washing of the olives prior to crushing. Hence, there are only two streams produced, the olive oil and the olive pomace. However, the olive pomace from two-phase olive mills has a higher moisture content (70-80% of water) compared to the one generated from three-phase or pressing mills (45-55% of moisture). Together with the olive pomace, there is also 0.5% of olive leaves that are generated as a by-product. The latter accounts for all types of olive mills. Although, the production cost is lower in two-phase olive mills as the processed volumes are smaller due to the non-addition of water, there is around 1-3% less yield in the production of olive oil compared to the three-phase mills. This loss of olive oil in
the production process remains in the aqueous olive pomace.

In Spain, there is a technology that removes this residual oil by 50-60% from the olive pomace called “repasso”, however this technology has not been applied to Greece due to its significant high investment with respect to the small or middle size olive mills that usually operate in Greece. Therefore, the aqueous state of this by-product creates two essential problems regarding its transportation and handling. It needs to be transported in liquid carts, and hence, the transportation cost is increased considerably. Moreover, in the pomace oil industries the operational cost is substantial higher than processing olive pomace from three phase olive mills due to the increased amount of water that needs to be removed prior to the oil extraction process. Due to the above reasons, the olive pomace industries usually do not process olive pomace from two-phase olive mills.

This study presents an innovative integrated solution for managing and utilizing the olive mill wastes (OMW) and creates opportunities for developing multiple commercial activities around the olive oil by-products. It also proposes economically viable and realistic feasible processes even for small and medium olive oil producers.

2. Materials and methods

a. Olive Mill Waste (OMW)

The OMW that was used in this study was taken from a II-phase olive mill plant operated in the northern part of Greece and specifically from the island of Thasos.

b. Acidification/Hydrolysis process and Oil separation

Initially, the pretreatment of OMW aims on recovering marketable products such as pomace oil and high value added products like antioxidants. At the same time, its pretreatment will facilitate the biological processes that follow. Both the pomace oil and the phenolic compounds act as inhibitors in almost all bioprocesses. The separation and recovery of the pomace oil which is physically bonded in the OMW is carried out using a novel acidification/hydrolysis process involving a strong acid (hydrochloric or sulphuric acid by 1%), dilution sample to water 1:2, controlled temperature and controlled agitation. Each hydrolysis experiment lasted for 1 hour. The initial quantity of OMW was 100 g. At the end of the reaction, the residual oil was separated via centrifugation at 10,000 rpm. Experiments conducted using different reaction temperatures. All runs were implemented in triplicates.

2.2 Determination of Total Phenolic Content

Total Phenolic Content (TPC) was measured using Folin Ciocalteu reagents, using gallic acid as a standard phenolic compound. Briefly, 0.2 N Folin-Ciocalteu reagent solution (2.50 mL) was added to the aqueous solution (0.5mL) and the mixture was shaken for 5 min. After this procedure, Na₂CO₃ (75 g L⁻¹, 2 mL) was added and the mixture was shaken once again for 1.5 h at 30 °C. Finally, the absorbance at 765 nm (25 °C) was measured using a spectrophotometer.

3. Results

Table 1 shows the results from the conducted experiments using different hydrolysis temperatures. It is observed that higher temperatures results in higher recovery of residual oil from 23.7 mg-oil/g dry OMW to 27.5 mg-oil/g dry OMW. The initial oil content of OMW (db) was found to be 10% while the moisture content of this waste was 70%. As there is a large room for improvement (i.e. the oil is only recovered by 25%) optimization experiments are currently carried out (results not shown) to improve the oil yield. Moreover, the COD of the obtained liquid after the centrifugation and the oil removal is 1.5-2.2 mg-O₂/g of dry OMW in all experimental runs while the TPC ranges between 36.7-37.0 mg-gallic acid/g of dry base OMW.

3. Conclusions

Higher temperatures seems to favor the removal of oil from olive mill waste, while COD and TPC do not seem to be affected. This study presents the first step of an integrated biorefinery from olive mill wastes for the recovery of high added value compounds like residual oil as illustrated in Figure 1. Future steps will focus on the extraction of phenolic compounds using ion-exchange resins, biological processes for the production of biochemical like succinic acid, the production of bioenergy and the compost production.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature</th>
<th>Residual oil (mg/g of dry base OMW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50°C</td>
<td>23.7</td>
</tr>
<tr>
<td>2</td>
<td>60°C</td>
<td>24.2</td>
</tr>
<tr>
<td>3</td>
<td>70°C</td>
<td>27.5</td>
</tr>
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</table>
Figure 1. The biorefinery concept from olive mill wastes

References


