Improving Sustainability of the Vegetable Oils Supply Chains: Innovative Analytical Methods for Quality Control, Valorization of By-products and Reduction of Waste

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This PhD thesis research project is aimed at improving the sustainability of the vegetable oils supply chains, considering the application of innovative analytical methods and the reuse of olive mill by-products and waste vegetable oils. In fact, the research is focusing on the development of innovative, rapid, as well as solvent and reagent efficient analytical approaches for oil quality control (e.g. the use of the microESR to measure oxidative state), on the valorization of mill by-products (such as olive pomace, wastewater, etc.) as raw materials for several industrial applications as well as on the reuse of waste cooking oils (e.g. frying oils) for the biodiesel production.

Miglioramento della sostenibilità delle filiere degli oli vegetali: metodi analitici innovativi per il controllo qualità, la valorizzazione di sottoprodotti e la riduzione degli sprechi

Il progetto di ricerca di tesi di dottorato mira a migliorare la sostenibilità delle filiere degli oli vegetali, considerando l'applicazione di metodi analitici innovativi e il riutilizzo di sottoprodotti oleari e oli vegetali di scarto. Infatti, le ricerche si stanno concentrando sullo sviluppo di approcci analitici innovativi, rapidi ed efficienti in termini di impiego di solventi e reagenti per il controllo della qualità dell'olio (ad es. l'impiego del microESR per misurare lo stato ossidativo), sulla valorizzazione di sottoprodotti del frantoio (come sansa di oliva, acque reflue, ecc.) come materie prime per diverse applicazioni industriali e sul riutilizzo degli oli alimentari esausti (ad es. oli per friggere) per la produzione di biodiesel.

# **1. State-of-the-Art**

The production of olive oil is of great importance for the high economic, sensory and nutritional value of this food and its relevance in the Mediterranean diet. Olive oil is subjected to oxidation, which, in the case of all the oils and fats, affects the shelf-life due to the appearance of rancid (Diaz-Montana et al., 2023). The oxidation determines the formation of primary and secondary products that can be determined by iodometric titration and spectrophotometric measurement of specific ultraviolet extinctions of conjugated dienes and trienes, respectively. These analytical determinations, reported in Reg. (EU) 2022/2105, are among the quality parameters for establishing the commercial category of virgin olive oils. In fact, an olive oil can be classified as extra virgin if the limits, established by the European Union, relating to free acidity, number of peroxides, specific extinctions in the ultraviolet, organoleptic evaluation (by panel test, in relation to the intensity of the fruity attribute and the eventual presence and intensity of defects) and content in ethyl esters of fatty acids are respected. Innovative, more sustainable analytical methods need to be developed in addition to the official ones, in particular with less use of chemicals and solvents (Valli et al., 2016). In fact, for example, the determination of the number of peroxides by titration has many disadvantages such as long lead times, the amount of sample required, the wide use of solvents and the production of waste (Longobardi et al., 2021). The electron spin resonance represents a possible and promising tool for the evaluation of the oxidation state of olive oil, as it is able to detect the presence of free radicals. In the literature there are studies on the application of electron spin resonance to evaluate oxidative stability in different foods and beverages, such as coffee, wheat flour, bread, peanuts, milk powder, chicken meat (Andersen et al., 2018) and hemp oil (Tura et al., 2019). A very important aspect related with the sustainability of the olive oil supply chain, in addition to post-production quality assessments, is certainly the high amounts of by-products and waste that are generated by the mills. In particular, a large amount of vegetation water is produced, which represents an environmental problem, as their polluting power can cause issues also to soil and groundwater (Gómez-Caravaca et al., 2014). In addition, olive leaves represent another rarely valued waste. A possible scenario sees both these by-products combined and valorized for biogas production. However, the high lignin content in the leaves represents a problem for their conversion into biogas (Romero-Garcia et al., 2014). Given the great importance of developing a sustainable olive oil supply chain and a virtuous oil mill, it is necessary to investigate possible pre-treatments to also make olive leaves an efficient substrate that can be used as raw materials in a biodigester together with vegetation water. Finally, at the end of its life cycle, waste vegetable oils, including cooked olive oils, can be used as substrates for biodiesel production. It is important to investigate their physical and chemical characteristics, such as lipidic content and humidity (Sharma et al., 2021), to assess their ability to be exploited for the biodiesel production. In fact, this valorization would help to avoid dispersion of waste oils in the environment, contributing to a circular economy and more sustainable vegetable oils supply chain (Azzena et al., 2023).

# **2. PhD Thesis Objectives and Milestones**

Within the overall objective mentioned above this PhD thesis project can be subdivided into the following future activities (second and third PhD years) according to the Gantt diagram given in Table 1:

A1) **Bibliographical research.**

A2) **Use of microESR to measure olive oil oxidation state**: in A2.1) the first step is to develop a model system to assess microESR values with respect to peroxides, ultraviolet spectrophotometric extinction coefficients, OSI time, fatty acids profile, total phenols, and sensory analysis results. To this aim, an olive oil sample was oxidised with the Rancimat instrument for 3, 6, 12, 15, 18, 21 and 24 h. These amounts of time were chosen because the olive oil that was selected shows an OSI time of 21.7 h and the goal was having 8 points representing the kinetic of the olive oil oxidation. Subsequently, it is planned to construct a statistical model for the estimation of the oxidative state. Afterwards, a study of the oxidative state (A2.2) will be carried out by correlating the microESR values and the results of the abovementioned instrumental and sensory analysis, as well as volatile compounds profiles, on a set of around 100 virgin olive oil samples.

A3) **Valorization of olive mill by-products**: characterization of olive wastewaters, pomace, stones, leaves, and experimental trials on biogas production by using olive wastewaters and leaves as raw materials.

A4) **Characterization of waste vegetable oils for biogas production**: chemical and physical characterisation of waste vegetable oils through the analysis of fatty acids profile, oxidation stability, free acidity, sterols profile, pigments contents, waxes content, and humidity.

A5) **Writing the PhD thesis, scientific papers as well as oral and/or poster presentations.**

***Table 2***Gantt diagram for this PhD thesis project.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Activity Months | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** | **23** | **24** |
| A1) | ***Bibliographic research*** |   |   |   |  |  |  |  |   |   |  |  |  |  |   |  |  |  |  |   |   |  |  |  |  |
| A2) | ***Use of microESR to measure olive oil oxidation state*** |   |   |   |  |  |  |  |   |   |  |  |  |  |   |   |   |  |   |   |   |  |  |  |  |
|  | 1) Set up of the model system: analysis of the olive oil samples |   |   |   |  |  |  |  |   |   |  |  |  |  |   |   |  |  |  |   |   |  |  |  |  |
|  | 2) Oxidative state study on around 100 olive oils |   |  |   |  |  |  |  |   |   |  |  |  |  |   |  |   |  |   |   |   |  |  |  |  |
|  | 3) Data analysis |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A3) | ***Valorization of olive mill by-products*** |   |  |   |   |   |   |  |   |   |   |   |   |  |   |  |  |  |  |   |   |   |   |   |  |
|  | 1) Characterization of olive mill by-products |   |  |   |   |   |  |  |   |   |   |   |  |  |   |  |  |  |  |   |   |   |   |  |  |
|  | 2) Experimental trials on biogas production using wastewaters and olive leaves as raw materials |   |  |   |  |  |   |  |   |   |  |  |   |  |   |  |  |  |  |   |   |  |  |   |  |
| A4) | ***Characterization of waste vegetable oils for biogas production*** |   |  |   |  |  |   |   |   |   |  |  |   |   |   |  |  |  |  |   |   |  |  |   |   |
| A5) | ***Thesis and Paper Preparation*** |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |  |   |   |   |   |   |   |   |

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