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New Strategies for the Valorisation of Deodorizer Distillates of Vegetable Oils Refining in a Sustainable Circular Economy Development

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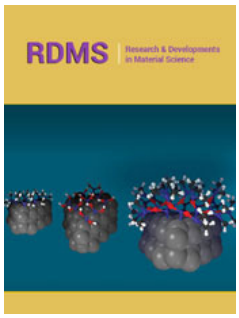

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Abstract

A new opportunity has arisen to produce new biomaterials from agro-industrial organic waste, within a circular economy and bio-based strategy. IRODDI is an ambitious initiative that proposes the development of new, greener processes to obtain bio-based products with specific properties/functionalities derived from the Free Fatty Acids (FFA) contained in deodorization distillates, by-products obtained in the refining processes of vegetable oils/fats. It consists in the development of new sustainable processes to produce new bio-based products with specific properties/functionalities using innovative technologies based on supercritical CO_2 ($scCO_2$) and to isolate valuable minor compounds in gentler and environmentally friendly operating conditions, preserving their original quality and developing gentler extraction technologies.

Introduction

Oilseed's processing and refining to obtain edible oils and further modifications to convert them into oleochemicals produce a variety of waste products. Distillates of deodorizer (DODs) are obtained in the last step in the refining process of oils and fats, where compounds that are responsible for the odour and unacceptable flavour in oil are removed by vacuum distillation [1]. Due to the conditions of the distillation process, some fractions of minor components are also separated and become an important part of the product. Thus, valuable unsaponifiable compounds such as tocopherols, tocotrienols, phytosterols, and hydrocarbons such as squalene, plus mono-glycerides, Free Fatty Acids (FFAs) can be found in the deodorizer distillate, as well as di and triglycerides by entrainment [2]. The principal commercial value of the DODs is mainly dependent on their tocopherol and squalene content. Due to the operational conditions employed in the distillation, the quality of these compounds can be affected. On the other hand, FFAs are components present in the DODs which can be converted into fuels/oleochemical products to maintain the profitability of the DODs valorisation process.

Products from deodorizer distillates waste streams

FFAs valorisation to biodiesel: FFAs can be an important income source for DOD valorization, however, they are usually devoted to energetic purposes (biodiesel production). These FFAs streams are cheaper than vegetable oils, but usually, they are formed by complex mixtures, and their efficient conversion to biodiesel, necessarily involves the combination of different reactions such as esterification of FFAs, saponification of glycerides and phospholipids, and final esterification of the remaining salts of fatty acids to ensure the total hydrolysis of the

mixture. Sequential purification washes are also needed to obtain fatty methyl esters of adequate quality, and high amounts of sodium sulfate are generated to neutralize the acid and alkaline solutions used for biodiesel purification [3] FFAs present characteristics and properties for considering applications in diverse chemical sectors with a higher added value than biodiesel, and there is an increasing demand of FFA in various end-use industries such as metalworking fluids, lubricants, polyols, solvents, fuels, detergents & surfactants, and coating & food among others.

FFAs valorisation to biodegradable surfactants: Surfactants are molecules that posse both hydrophilic and hydrophobic moieties and can adsorb onto the interface between different phases [4]. Most of the surfactants used at the industrial level are chemically synthesized from petroleum-based resources which are not biodegradable and possess toxicity to the environment. IRODDI proposes the combination of bio-based ILs with the FFAs present in DDOs to obtain biodegradable surfactants for different detergency applications. The ionic fatty salts obtained present higher solubility properties, even in cold water, and very good degreasing power.

FFAs valorisation to biodegradable lubricants: Bio-based commercial lubricant base fluids mainly consist of organic esters (derived from vegetable oils) and un-modified vegetable oils. An important result of IRODDI is the tailor-made mixture of mono-, di- and triglycerides showing high performance in tribology and emulsifying properties to be applied as lubricant base-fluid. With this new base fluid, the number of chemical additives can be reduced.

Isolation of minor valuable compounds present in the DODs. Classical methods: Classical techniques for isolating tocopherols, squalene, and sterols include solvent extraction, chemical treatment, crystallization, or complexation. In general, most processes have two main parts. In the initial step, they are designed to remove either fatty acids or sterols, followed by tocopherol and squalene concentration by other methods. Moreover, in order to separate the squalene from DODs, the main challenge is the separation between itself and the other components, especially in the case of a couple of components: tocopherol-squalene, tocopherol-fatty acids, tocopherol–sterol and sterol-squalene [5]. Molecular distillation or short-path distillation is the principal isolation process industrially employed, characterized by a high vacuum inside the column, during short contact time. An important economic factor is the equipment cost, a high-quality vacuum pump is needed for ensuring enough vacuum condition for each distillatory, so equipment investment and operation costs are very large. As a result of this, the operation temperature has to be increased to compensate when vacuum pressure decreases for stabilizing the concentration of the fractions.

New isolation greener technologies: IRODDI proposes the reduction of organic solvents consumed in conventional extraction processes. These are undesirable due to the high proportions of solvent needed for the extracted material, and low selectivity to obtain a suitable separation between the unsaponifiable components.

It is intended to eliminate the use of high temperatures during distillation that affects the quality of the products at temperature levels in the order of 433K (where the formation of tocopherols dimmers and other degradation products is evidenced). The extraction of valuable compounds is accomplished by the development of economical, green, and secure technologies that will preserve the quality of the different minor components present in the DODs. For selective valuable components isolation, supercritical carbon dioxide (scCO2) is proposed as a promising alternative that uses mild operational temperatures, and non-toxic solvents, and has a moderate cost since the impact of the energy for high-pressure operations.

Conclusion

IRODDI fosters a circular economy approach that does not exhaust the available resources and is focused on the valorisation of a residual organic side stream to offer more environmentally friendly products following sustainable development.

Conflict of Interest

The authors declare that there is not any conflict of interest.

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