

Optimization of Countercurrent Supercritical Fluid Extraction of Minor Components from Olive Oil

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Abstract: A process based on the use of a semi-continuous countercurrent supercritical fluid extraction (CC-SFE) has been optimized to concentrate minor components, with functional properties, from olive oil. The optimization of the main variables involved in the supercritical extraction process (extraction pressure, temperature and sample flow rate) was performed using a surface response methodology (RSM). A central composite circumscribed design (CCCD) was employed to study the responses selected to describe the process, such as the extraction yield, the concentration of the different minor compounds (squalene, sterols and tocopherols) in the CO₂-rich upper current stream, and the recovery of these compounds from the olive oil. Parameters of the model, for each response variable, were simultaneously estimated by Partial Least Squares (PLS) regression. The statistical analysis of the results allowed obtaining mathematical models able to predict the behavior of the different responses selected as a function of the main variables involved in the process. The optimum conditions obtained, that maximized all the responses as a whole, were: extraction pressure, 234 bar; extraction temperature, 35°C and sample flow rate, 82 mL/h, working with a solvent flow rate equal to 2000 mL/h (S/F equal to 28.4 kg CO₂/kg oil). The optimum of the model was experimentally confirmed allowing around 90% recovery of squalene without significant changes on the nutritional and physicochemical properties of the oil.

Keywords: CC-SFE, olive oil, optimization, squalene, sterols, tocopherols.

1. INTRODUCTION

The economic impact of the vegetable oil industry is extremely important all over the world. Spain is one of the main olive and sunflower oil producers of the world; olive oil has an extremely important socioeconomic impact being one of the most important vegetable oils consumed in the countries of the Mediterranean Basin.

In the vegetable oil industry, minor compounds (such as sterols, squalene and tocopherols) are of great interest as high added-value products because of their potential bioactivities that can help to increase the value of other food products, for example, low quality olive oil [1-3]. Squalene can be found in relatively large amounts in olive oil, representing more than 50% of its unsaponifiable fraction, and has important applications in the pharmaceutical and food industry. Its greater interest can be related to the production of functional food ingredients due to its positive impact in human health [4, 5]. Tocopherols are well known as components of vitamin E, their presence has been extensively described in the olive oil [6], their interest is related to their antioxidant activity and other nutraceutical effects [7]. Also important are the

effects associated to the human consumption of phytosterols, being the most important those related with cardiovascular diseases [8]. These sterols are relatively abundant in vegetable oils.

Fats and oil fractionation using supercritical carbon dioxide has been used to obtain products with improved functionality for specific applications or with better nutritional value. Among the different processes developed for vegetable oils, only deacidification has been studied in depth for olive oil [9-12]. As for minor compounds extraction from olive oil, using supercritical fluids, few studies have been conducted for example, to selectively isolate tocopherols from natural products [13-15] and squalene from deodorized distillates and olive pomace [16-18].

Previous work done in our laboratory [19-20] using a countercurrent supercritical fluid extraction column at pilot scale allowed the experimental determination of the efficiency (measured as number of transfer units (NTU) and height of a transfer unit (HTU)) and the selectivity of different random packings towards the isolation of sterols and tocopherols from olive oil. These studies were conducted to optimize, in a first step, the mass transfer of the process. Nevertheless, in order to be able to extract minor components, the concentration of these compounds in the supercritical carbon dioxide stream has to be also maximized

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Table 5. Experimental values at the optimum conditions, obtained for the different responses studied.

Response Variable	Experimental Values	Relative Standard Deviation
Extraction yield (Y_1)	7.26	0.45
g extract/kg CO ₂ (Y_2)	2.56	0.16
g squalene/kg CO ₂ (Y_3)	0.14	0.02
mg tocopherols/kg CO ₂ (Y_4)	0.15	0.03
g sterols/kg CO ₂ (Y_5)	0.017	0.002
% Recovery of squalene (Y_6)	89.19	11.73
% Recovery of tocopherols (Y_7)	3.25	0.58
% Recovery of sterols (Y_8)	8.73	0.97

conditions that oxidized the olive oil sample, and therefore, decreased the tocopherol content in the olive oil to be processed (from 0.0205% w/w to 0.013% w/w).

Therefore, results presented demonstrate the ability of a RSM to optimize the extraction of valuable minor compounds from low quality olive oil by using a CC-SFE process. Mathematical models provided were able to properly predict the behavior of the system considering the factors that mostly influence the countercurrent supercritical extraction process.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

This work has been financed under a R +D program of the Spanish Ministry of Education and Science, project Consolider Ingenio 2010 FUN-C-FOOD (CSD2007-0063) and of the Comunidad Autónoma de Madrid (S-0505/AGR/000153).

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