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Molecular distillation of olive pomace oil — Multiobjective optimization for tocopherol and squalene

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ABSTRACT

Olive pomace oil was distilled using a laboratory scale molecular distillation unit aiming a successful separation of squalene. Pressures were 0.02, 0.1 and 0.5 mbar, and temperatures ranged from 160 to 240 °C. Changes in total tocopherol and squalene concentrations of distilled olive pomace oils were monitored. Initial squalene concentration of 10613.1 mg kg^{-1} was succesfully reduced to 54.58 mg kg^{-1} at 0.02 mbar and 240 °C which corresponds to a reduction of 99.49% of initial. However, total tocopherol concentration also reduced to 20.2 mg kg^{-1} from an initial of 204.93 mg kg^{-1} at the same conditions. Similarly, an unfortunate loss of tocopherols with 90.14% at T = 240 °C and P = 0.02 mbar was observed. As being important antioxidants, tocopherols are desired to remain in oil; therefore, a multiobjective optimization (MOO) was performed to keep tocopherols in the oil at maximum, while minimizing squalene concentration. With an interactive MOO method, namely NIMBUS, 20 different alternative conditions could be generated. 9 of 20 paths could be considered as feasible and applicable for executing both objectives. One of the optimized conditions was 160 °C and 0.072 mbar where the highest tocopherol concentration of 204.721 mg kg^{-1} was obtained while squalene concentration was reduced to 3741.586 mg kg^{-1} in oil.

1. Introduction

Olive pomace, the byproduct or solid residue of olive oil production, has been mostly underestimated for years until its significance gained more concerns in recent years. Depending on extraction method from solid waste, olive pomace may contain up to 8% of oil called olive pomace oil (Di Giovacchino, 2013). It was reported that the increasing importance of olive pomace oil (OPO) originates from its composition, which is similar to extra virgin olive oil (EVOO) but differing from EVOO by having some minor compounds at higher concentrations (Perez-Camino & Cert, 1999). The vast majority (> 95%) of OPO is reported as triacylglycerols, then minor compounds such as fatty acids, triterpenic acids and squalene, decreasingly (Sánchez-Gutiérrez, Ruiz-Méndez, Jiménez-Castellanos, & Lucero, 2017). OPO can be obtained with both chemical and physical extraction methods (Moral & Mendez, 2006). After extraction, it is refined and blended with approximately 5% of virgin olive oil (VOO) to be sold in markets (Di Giovacchino, 2013).

It has been previously proved by many studies that high temperature application in refining process negatively affects the quality parameters of the final product (Gotor & Rhazi, 2016; Maza, Ormsbee, & Strecker, 1992). As an important parameter, tocopherols — the important antioxidants in food systems (Kamal-Eldin & Appelqvist, 1996) — are reported to directly affect the oxidative stability of the oily products (Crapiste, Brevedan, & Carelli, 1999). Thus, tocopherols should remain in oil for prevention of oxidation during oil processing. Here, molecular distillation becomes prominent with the advantages of low temperature treatment and vacuum application. There are some research involving molecular distillation and tocopherol recovery/or purification (Gelmez, Ketenoglu, Yavuz, & Tekin, 2017; Martinello, Hecker, & Pramparo, 2007; Martins, Ito, Batistella, & Maciel, 2006; Moraes, Batistella, Alvarez, Filho, & Maciel, 2004; Shimada et al., 2000). Other than tocopherols, squalene is one of the important minor compounds of both olive oil and olive pomace oil. Squalene is a naturally occurring long-chained hydrocarbon (C30), and has usage areas such as moisturizing or emollient in cosmetics (Moreda, Perez-Camino, & Cert, 2001). Olive oil has been reported as a good source of squalene with 800–8000 mg kg^{-1} (Moreda, Rodríguez-Acuña, del Carmen Pérez-Camino, & Cert, 2004). Squalene is a significant constituent (60–75%) of unsaponifiable part of olive oil (Bondioli, Mariani, Lanzani, Fedeli, &

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Muller, 1993) and plays an important role in reduction of cancer risks with olive oil consumption (Newmark, 1997). Apart from chemical production, squalene could also be purified from oil using molecular distillation (Sun, Wiesenborn, Tostenson, Gillespie, & Rayas-Duarte, 1997).

Accordingly, this study aimed to protect tocopherols in oil while removing squalene simultaneously. Different distillation conditions could be optimized in at least one point within reasonable concentrations of both components. With this optimization procedure, we believe that the results will be beneficial for industrial refining of OPO with higher tocopherol concentration while producing squalene as by-product.

2. Materials and methods

2.1. Materials

Neutralized and bleached olive pomace oil was kindly donated by Collective Modern Olive Oil Refinery and Pomace Plant Inc. (Aydın, Turkey) and Güvenal Soap, Pomace and Refined Oil Industry (Gaziantep, Turkey). All chemicals used in analyses were of analytical grade and purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Tocopherol analysis

Official AOCS method (Method #: Ce 8-89) (AOCS., 2003a) was used for tocopherol analysis. A Shimadzu Prominence LC-20A HPLC system (Kyoto, Japan) equipped with a Shimadzu SPD-M20A photodiode array detector (Kyoto, Japan) was used. The column was a Lichrosorb Si60-5 (25 cm × 4.6 mm ID × 5 μm) (Reading, United Kingdom). Oven temperature was set to 25 °C and mobile phase was a mixture of hexane-isopropyl alcohol (99:1) with a flowing rate of 1 mL min^{-1}. Isocratic flow was used and an elution was 20 min. Wavelength of detector was 295 nm.

2.3. Squalene analysis

Squalene analysis was performed according to official AOCS method (Method #: Ch 8-02) (AOCS, 2003b). As described in official method, the first step is fractionation of olive pomace oil by elution with *n*-hexane through silica gel column. Glass column was 35 cm long with an internal diameter of 15 mm. Lauryl arachidate was used as internal standard. Eluent was collected in a flask, and then rotary evaporator was used to remove excess solvent. After all steps of official method were completed, squalene was determined with addition of squalene standard. For this purpose, squalene peak was obtained using a Shimadzu GC-2010 gas chromatography system (Kyoto, Japan) equipped with a non-polar fused silica HP-5 column (12 m × 0.32 mm ID × 0.25 μm) (Agilent, Santa Clara, CA) with flame ionization detector. Helium was used as carrier gas with a flow rate of 1.8 mL min^{-1}. Temperatures were 300 and 350 °C for injection port and detector, respectively. Oven temperature program was as following: 1) hold at 80 °C for 1 min, 2) ramp to 240 °C with 20 °C.min^{-1} rate, 3) ramp to 325 °C with 5 °C.min^{-1} rate and hold for 6 min, 4) ramp to 340 °C with 20 °C.min^{-1} rate and hold for 10 min. Injection mode was set to splitless.

2.4. Molecular distillation

A laboratory scale KDL-5 short path distillation unit (UiC GmbH, Alzenau-Hoerstein, Germany) was used for molecular distillations with the following parameters:

- Evaporation temperatures: 160–240 °C (increment: 10 °C)
- Pressure: 0.02, 0.1 and 0.5 mbar
- Feed flow rate: 3 mL min^{-1}

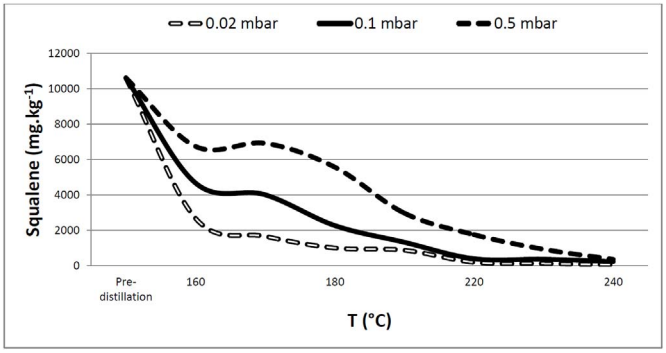

Fig. 1. Squalene concentrations of distilled OPO.

- Condenser temperature: 20 °C
- Rotational wiping speed: 240 rpm
- Evaporation surface area: 0.048 m^2

All results were averaged from duplicates of molecular distillations and chemical analyses. Residual streams of distillation trials and pre-distilled oil materials were bottled under nitrogen and stored in dark at 4 °C until analyzed.

2.5. Multiobjective optimization

Multiobjective optimization (MOO) is a simultaneous process aiming to optimize objective functions within their constrains. This procedure relies on Pareto optimality, which expresses the impossibility of enhancing only one of the functions without relinquishment in the others. If this is the case, then objective functions are in "Pareto optimal" state. For optimization process, experimental data were fitted on quadratic equations using Statistica v10 (Statsoft, Tulsa, OK). Then, MOO process was performed with these equations using an interactive method called NIMBUS (Miettinen & Mäkelä, 2006). Objective functions, variables, boundaries were given in Eqs. (1)–(4):

$$0 < \text{Maximum (Tocopherol)} = f_{Toc.}(P,T) < 205 \quad (1)$$

$$0 < \text{Minimum (Squalene)} = f_{Squ.}(P,T) < 10600 \quad (2)$$

$$160 \le T \le 240;\ T \text{ in } °C \quad (3)$$

$$0.02 \le P \le 0.5;\ P \text{ in mbar} \quad (4)$$

The optimum alternatives which were chosen among all feasible Pareto fronts were expressed as a combined objective function as given in Eq. (5). MOO method was run with 500 number of generations at 1.0E-6 termination accuracy.

$$\text{Maximum } f_{Toc.}(P,T) + \text{Minimum } f_{Squ.}(P,T) \quad (5)$$

3. Results

Olive pomace oil (OPO) is generally considered as a low-quality oil compared to virgin olive oil (VOO) and extra virgin olive oil (EVOO). However, minor compounds profile of OPO might consist of such compounds as tocopherols, sterols and squalene, most of which are extracted with chemical methods due to their commercial value. As an efficient way for extraction, molecular distillation technique is considered as an easier way for physical separation of these valuable compounds due to high vacuum levels. Also, higher purities could be achieved resulted from low evaporating temperatures.

OPO was subjected to molecular distillation under 160–240 °C temperatures with 0.02, 0.1 and 0.5 mbar pressures. The lowest temperature was set to 160 °C, because results of preliminary studies guided us that no or very low evaporation rates could be achieved below