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Effect of subcritical water and steam explosion pretreatments on the recovery of sterols, phenols and oil from olive pomace

Özge Seçmeler[a,*], Özlem Güçlü Üstündağ[a], Juan Fernández-Bolaños[b], Guillermo Rodríguez-Gutiérrez[b]

[a] Department of Food Engineering, Faculty of Engineering, Yeditepe University, Kayışdağı Cad., 34755 Istanbul, Turkey
[b] Instituto de la Grasa, Consejo Superior de Investigaciones Científicas (CSIC), Avenida Padre García Tejero 4, Sevilla 41012, Spain

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ABSTRACT

Hydrothermal pretreatments including steam explosion and subcritical water (SCW) facilitate hydrolyses of plant cell wall materials and supply environmentally friendly extraction solvents to recover value added compounds. In this study, effect of steam and SCW and temperature (160, 180 and 200 °C, 5 min) on yield and β-sitosterol content of pomace oil and phenolics were compared for value added utilization of olive pomace. Compared to acid hydrolysis, hydrothermal pretreatments yielded similar oil recovery. 54–76% of the bound oil and 18–32% of the bound β-sitosterol of the pomace were recovered by hydrothermal pretreatments. Steam pretreatment was more effective than SCW pretreatment at lower temperatures, however SCW showed increasing trend on oil yield related to steam pretreatment. As further research on process development, use of sequential temperature might be investigated, starting with steam explosion (< 180 °C), followed by SCW pretreatment (> 200 °C) to obtain multiple, aqueous and meal, fractions for total valorization of olive pomace.

1. Introduction

Disposal of olive oil processing waste streams presents a challenging environmental problem due to their high organic content. Recent studies have focused on the use of olive mill waste water (OMW), a liquid waste of three-phase system, for phenols and pectin recovery (Galanakis, 2015, chap. 3), olive stone (Fernández-Bolaños, Felizón, Brenes, Guillén, & Heredia, 1998; Fernández-Bolaños, Felizón, Brenes, Guillén, & Heredia, 2001; Fernández-Bolaños, Felizón, Heredia, Guillén, & Jiménez, 1999; Rodríguez-Gutiérrez et al., 2008; Rodríguez-Gutiérrez, Rubio-Senent, Lama-Muñoz, García, & Fernández-Bolaños, 2014) for the recovery of phenols and sugars for the production of alcohols, biosurfactants, biopolymers, activated carbons and for generation of energy and olive pomace, semi-solid waste of two phase system, for oil and sugar recovery (Fernández-Bolaños et al., 2004; Lama-Muñoz, Rodríguez-Gutiérrez, Rubio-Senent, Gómez-Carretero, & Fernández-Bolaños, 2011; Gameiro, 2016).

In order to achieve industrial olive waste recovery at the desired level a total recovery approach should be used for value added utilization of olive wastes. For recovery of valuable target compounds from food wastes, Galanakis (2015, chap. 3) defined a “5-Stages Universal Recovery Process”, which starts with macroscopic pre-treatment that depends on water content and composition of initial waste, continue with macro- and micromolecules separation, extraction, isolation and purification. For total recovery, an initial “reaction medium” stage is needed to break all bonds between target compounds and the matrix before recovery processes to reach multi valorization.

According to world olive data from 2010 to 2016, 11,778,000 tonnes of two-phase pomace (alperujo, calculated based on 20% oil yield) was generated in the world annually (IOC, 2016). Alperujo is composed of 56–75% moisture, oil (8–20%) containing higher β-sitosterol (339–430 mg/100 g) compared to virgin olive oil (VOO: 181–226 mg/100 g) (Seçmeler, 2017), cell wall constituents such as cellulose (14–25%), lignin (32–56%) and hemicellulose (27–42%), protein (4–12%), water-soluble carbohydrates (1–16%) and phenolic compounds (1–2%) on a dry weight basis (Alburquerque, Gonzálvez, García, & Cegarra, 2004).

The extent of loss of bioactive compounds during olive oil processing and their composition in the waste streams have important implications for the valorization of olive pomace. Significant processing loss was previously shown for β-sitosterol and α-tocopherol (32%, 31%, respectively), while squalene was quantitatively recovered in the oil

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* Corresponding author. Present address. Department of Gastronomy, Faculty of Applied Sciences, Altınbaş University, Büyükdere Caddesi, Yazarlar Sokak, No: 36, Esentepe / İstanbul, Turkey. Tel.: +90 212 373 5900/5003.

E-mail addresses: osecmeler@gmail.com, ozge.secmeler@altinbas.edu.tr (Ö. Seçmeler), ozlemg.ustundag@yeditepe.edu.tr (Ö. Güçlü Üstündağ), jfbg@cica.es (J. Fernández-Bolaños), guirogu@cica.es (G. Rodríguez-Gutiérrez).

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stream (Seçmeler & Güçlü Üstündağ, 2017b). Comparison of these values with the loss value for oil (6%), and the relative distribution of these compounds in the olive matrix point to differences in the extraction and degradation behavior of these compounds. Recovery of sterols from plant matrices might be increased by minimizing their interactions with matrix components such as phospholipids, proteins and cellulose (Seçmeler & Güçlü Üstündağ, 2017b).

Hydrothermal processes/pretreatments involving hydrolysis, liquefaction, and/or extraction using steam, subcritical water (SCW) and supercritical water offer an innovative green approach for olive waste processing. Hydrothermal pretreatments have been used for the hydrolysis of hemicellulose, cellulose and lignin in olive pomace, olive stone and OMW for biofuel production (Möller, Nilges, Harnisch, & Schröder, 2011; Garrote, Domínguez, & Parajo, 1999; Fernández-Bolaños et al., 1999, 2001; Abu Tayeh, Levy-Shalev, Azaizeh, & Dosoretz, 2016; Kumar, Barrett, Delwiche, & Stroeve, 2009) and for the recovery/extraction of phenolics (Fernández-Bolaños et al., 1999).

Steam pretreatment or steam explosion (at 160–260 °C, 0.69–4.83 MPa) of olive pomace is used to breakdown the lignocellulosic matrix. While steam treatment affects the lignocellulosic materials via autohydrolysis reactions (i.e. hydrolysis of acetyl groups present in hemicellulose), mechanical forces also contribute during steam explosion (Manorach, 2014). Steam explosion of olive stones and alperujo was used for the recovery of the major phenols (hydroxytyrosol and tyrosol), to increase digestibility and to recover dietary fiber by converting hemicelluloses into soluble carbohydrates (monosaccharides xylose, arabinose, and glucose; mannitol and oligosaccharides) and to enhance enzymatic hydrolysis of cellulose (Fernández-Bolaños et al., 1999, 2004; Rodríguez-Gutiérrez et al., 2008; Rodríguez-Gutiérrez et al., 2014; Fernández-Bolaños et al., 1998; Fernández-Bolaños, Rodríguez, Rodríguez, Guillén, & Jiménez, 2002). Alperujo were pretreated with steam explosion in a 2 L reactor at 160–240 °C for 2–10 min with acid (Fernández-Bolaños et al., 2004; Fernández-Bolaños et al., 2002) where treatment at 200 °C for 5 min resulted in reduced hemicellulose (75–88%), lignin and protein content (50%), and a separate liquid fraction containing hydroxytyrosol, oligosaccharides, glucose, mannitol (Rodríguez-Gutiérrez, Rodríguez, Jiménez, Guillén, & Fernández-Bolaños, 2007). Solubilization of lignin fragments resulted from de-polymerization of polysaccharides (mainly hemicellulose) and breaking of the lignin-carbohydrate bonds (Rodríguez-Gutiérrez et al., 2008). Further degradation of monosaccharides lead to hydroxymethylfurfural (HMF) and furfural formation at higher temperatures.

In another reactor (100 L reactor), steam pretreatment of alperujo without explosion (150–170 °C; 15–90 min) resulted in a reduction in solids (up to 35.6–47.6%) and an increase in oil yield and sterols (up to 97% and 33%, respectively) due to solubilization of cell wall material and release of bound oil and sterols (Lama-Muñoz et al., 2011). Even at 160 °C after 15 min, a significant increase in the level of β-sitosterol was observed (Lama-Muñoz et al., 2011).

From ambient boiling point (> 100 °C and 0.1 MPa) to supercritical conditions (374 °C at 22.1 MPa), solvent power of water is modified, its polarity and pH value decrease while its reactivity increases (Möller et al., 2011). SCW can be used as a solvent for extraction of compounds having a wide range of polarity because dielectric constant of water can be decreased. SCW extraction of olive pulp (160 °C, 30 min) was found to be more efficient than methanol extraction (2 h) for the recovery of phenolics (Yu, Zhu, Zhong, Li, & Ma, 2014).

In addition to being an environmentally friendly extraction solvent, SCW is a unique and sustainable reaction/pretreatment medium (Möller et al., 2011). The decreased dielectric constant and the increased ionic strength of SCW ($K_w > 10^{-14}$) lead to generation of hydronium ions, which are involved in ionic reactions, such as hydrolyses of cell wall materials (hemicellulose, lignin and cellulose) into sugar-monomers and polar lipids (phospholipids and glycolipids), and further degradation of HMF to carboxylic acids, as a reactant (Garrote et al., 1999). In the subcritical region the density of water remains constant between 100 °C and 374 °C so the pressure effect on physical properties of SCW is minimal (Möller et al., 2011).

Using SCW pretreatment, cellulose degradation above 210–220 °C and optimum conditions (200 °C, 30 min with 2 mL/min flow at 220 bar) in recovery of protein, sugar and lignin from deoiled olive pomace were reported, respectively (Garrote et al., 1999; Kazan, Çeliktaş, Sargın, & Yeşil-Çeliktaş, 2015). Maillard and caramelization reactions, which occur at temperatures higher than 180 °C, and biofuel production are limited if the samples are rich in phenolic compounds (Plaza, Amigo-Benavent, del Castillo, Ibáñez, & Herrero, 2010) and sterol glucosides (Songtawee, Ratanawilai, & Tongurai, 2014), respectively. Therefore temperature and time of SCW treatment need to be optimized based on the target compound(s) and the end use of the pretreated pomace. SCW can thus be an effective reaction medium/solvent for the total valorization of olive pomace, which offers the advantage of semi-continuous processing and the recovery of multiple fractions.

While previous studies have shown the effects of steam and SCW on the components of biomass and their potential for the recovery of oil, phenols and sterols from olive pomace, process development studies for the recovery of multiple value added products aiming at total valorization are lacking. Olive oils enriched with bioactive compounds emerge as an important value added product in this respect based on research on "positive effects of enriched olive oil on human health and on quality of olive oil" (Reboredo-Rodríguez et al., 2017; Figueiredo-Gonzáleza et al., 2018; Mora-Ruiz et al., 2017).

Therefore, the main objective of this study was to use hydrothermal pretreatments for value added utilization of olive pomace to obtain sterol enriched oil and phenols. The pretreated biomass, which would be free of sterol glucosides and phenols, could further be utilized for biofuel production. Specific objectives of this study were to investigate the effect of pretreatment method (steam and SCW), and temperature on oil, β-sitosterol (BS) and phenol recovery from olive pomace.

2. Materials and methods

2.1. Samples

Olive pomace (alperujo) samples of picual type olives were obtained from the pilot VOO production plant (including a hammer crusher, two serial malaxers (25.2 °C and 26.3 °C), a decanter (2-phase, 3000 rpm), and separator) at the Instituto de la Grasa in Sevilla, Spain (November 2015). Fresh pomace samples were stored in cooling cabinets for short period (4 °C) and long period (−20 °C), protected from light.

Fresh pomace samples were homogenized, freeze dried and stored in a desiccator. Moisture and oil content (by Soxhlet) of pomace samples were determined in triplicate.

After hydrothermal treatment processed samples, which included pomace and process water, were centrifuged (13,180*g*, 20 min) to separate aqueous and meal fractions. Aqueous fraction was concentrated by vacuum evaporator at 50 °C. Aqueous and meal fractions were also freeze dried and then homogenized and stored in a desiccator until further analysis (Fig. 1). Dried meal fraction and pomace were milled and sieved (1 mm) to separate pit (& cuticle).

2.2. Chemicals and reagents

β-sitosterol (100 μg/mL in chloroform, analytical standard) and triolein (Glyceryl trioleate, 61%) were obtained from Supelco (PA and WI, US). Chlorotrimethylsilane (TMCS) (GC Grade) was obtained from Sigma-Aldrich (Damstadt, Germany). Chloroform (GPR Rectapur) and *n*-hexane (HPLC Grade) were obtained from VWR (Fotenay-sous-Bois, France). 5α-cholestane (99.57%, GC Grade) and pyrogallol (HPLC) were obtained from Sigma-Aldrich (Jerusalem, Israel and Dorset, UK). *n*-hexane (99%, GC grade) was obtained from Sigma-Aldrich (Israel).