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# Indirect indices of oxidative damage to phenolic compounds for the implementation of olive paste malaxation optimization charts

S. Trapani [a], C. Breschi [a], L. Cecchi [b], L. Guerrini [c], N. Mulinacci [b], A. Parenti [c], V. Canuti [a], M. Picchi [a], G. Caruso [d], R. Gucci [d], B. Zanoni [a, *]

[a] Department of Agricultural, Food and Forestry Systems Management (GESAAF) – Food Science and Technology and Microbiology Section, Università degli Studi di Firenze, Via Donizetti 6, 50144 Florence, Italy
[b] Department of Neurosciences, Psychology, Drug Research and Child Health (NEUROFARBA), Università degli Studi di Firenze, Via Schiff 6, 50019 Sesto Fiorentino, Italy
[c] Department of Agricultural, Food and Forestry Systems Management (GESAAF) – Agricultural, Forest and Biosystem Engineering Section, Università degli Studi di Firenze, Piazzale delle Cascine 15, 50144 Florence, Italy
[d] Department of Agriculture, Food and Environment, Università degli Studi di Pisa, Via del Borghetto 80, 56124 Pisa, Italy

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ABSTRACT

An original kinetic study of the transformation phenomena of phenolic compounds in olive paste was carried out at different malaxation time-temperature conditions under exposure to air, using Abencor lab equipment to process olives (Frantoio cv) of a known degree of ripeness.

Empirical kinetic models and the relevant apparent kinetic constants were determined for the following significant indices: total phenolic compound content in waste water samples using the Folin-Ciocalteu method; verbascoside and β-OH-verbascoside contents in olive paste samples using HPLC; and 3,4-DHPEA-EDA contents in olive oil samples using HPLC. Two opposite phenolic compound transformation phenomena were proposed to explain the kinetic models: (i) enzymatic oxidative damage of phenolic compounds; (ii) physical and enzymatic release of phenolic compounds from cellular tissues. It was possible to propose a reference optimization chart to predict "selective" time-temperature conditions to maximize the apparent EVOO extraction yield while minimizing the degradation phenomena of phenolic compounds during malaxation.



## 1. Introduction

Oxidation is the most frequent degradation behaviour of food after microbial spoilage phenomena. Oxidative damage to food consists of oxidation reactions in lipids, proteins and minor compounds, causing a negative effect on food, particularly in terms of sensory and nutritional qualities. Oxidative reactions involve enzymatic or non-enzymatic phenomena and they are proportionally related to food temperature (Diplock et al., 1998; Parkin and Damodoran, 2003).

One of food technology's missions is to minimize oxidative damage in food processing where exposure to oxygen and, in general, operating conditions with high potentials of redox can occur. Therefore, it is necessary to select effective indices to both monitor and optimize operating conditions to control oxidative damage in food.

Extra virgin olive oil (EVOO) extraction processing can be an interesting example of how this approach can be applied in consideration of effects on the phenolic compounds in olive fruits. The phenolic profile has a critical role in the quality of EVOO. The amount of the different phenolic compounds is positively related to the preservation of oil quality from oxidation during shelf life, and it is responsible for EVOO's "bitter" and "pungent" sensory descriptors. Moreover, these compounds prevent ageing phenomena and several chronic diseases in humans (Clodoveo et al., 2014). Biochemical, chemical and physical phenomena that affect EVOO's phenolic profile, including enzymatic oxidative reactions, occur during the ripening of the olive fruits and the oil extraction process (Zanoni, 2014).

An impressive number of phenolic compounds (i.e. particularly oleoside compounds) are present in *Olea europaea* fruits. Secoiridoids, such as oleuropein, demethyloleuropein and ligstroside

* Corresponding author.
*E-mail address:* bruno.zanoni@unifi.it (B. Zanoni).

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represent the predominant phenolic oleosides, whereas verbascoside is the main hydroxycinnamic derivative of olive oil fruits. Simpler phenolic compounds such as hydroxytyrosol and tyrosol are also present. The olive cultivar, geographical area of production, climatic conditions during the crop season, crop load and olive health conditions affect the phenolic profile of olive oil fruits (El Riachy et al., 2011).

However, the phenolic profile of olive oil fruits is not the same as the phenolic profile of extractable EVOO, since numerous transformation phenomena occur during the oil extraction process. Phenolic compounds are distributed greatly between the water and oil phases of olive paste, obtained by crushing the olive fruits. The greater affinity of phenolic compounds towards the water phase means that only 0.3%–2% of the phenols available in the olive fruits are transferred to the oil (Rodis et al., 2002). Secoiridoids are the compounds with the highest transfer rate from fruits to oil, followed by simple phenols; due to its structure, no verbascoside is found in EVOO (Klen and Vodopivec, 2012; Talhaoui et al., 2016). Moreover, rupturing of the olive cell tissues activates a series of enzymatic and non-enzymatic phenomena in the phenolic compounds. New phenolic compounds, which are hydrolytic forms of oleoeuropein and ligstroside, appear in the olive paste, whereas some fruit phenols disappear after crushing; therefore, the dialdehydic form of decarboxymethyl oleuropein aglycone (3,4-DHPEA-EDA) is often EVOO's most abundant phenolic compound (Zanoni, 2014; Klen et al., 2015a).

Three main steps in the oil extraction process affect the EVOO's phenolic profile: the crushing of the olive fruits, malaxation of the olive paste, and mechanical separation of the oil. The crushing step causes the initial physical partition of the phenolic compounds into the oil and water phases of the olive paste and activates the enzymatic (i.e. β-glucosidase activity) and non-enzymatic hydrolytic phenomena that transform oleoeuropein and ligstroside into their respective aglycones and decarboxymethylated forms (Clodoveo et al., 2014; Leone et al., 2015). The malaxation step consists of slow and continuous kneading of the olive paste to induce physical phenomena (i.e. oil droplet coalescence, rising of oil to the surface) that improve the oil process yield (Trapani et al., 2017); in general, malaxation is expected to continue the above hydrolytic phenomena without any enzymatic oxidative degradation (i.e. polyphenol oxidase and peroxidase activities) of the phenolic compounds (Clodoveo, 2012). Finally, the processing parameters during separation of the oil by centrifugation (i.e. use of a horizontal centrifuge with screw conveyor, namely “decanter”) from the solid and water phases of olive paste have to be planned and controlled to maximize phenolic compound dissolution in the extractable EVOO (Altieri et al., 2013; Caponio et al., 2014).

In view of the various possible combinations of operating conditions, such as time, temperature, oxygen exposure and kneading tools, several studies on the effect of malaxation on the phenolic profile of EVOO can be reported (Angerosa et al., 2001; Ranalli et al., 2001, 2003; Parenti and Spugnoli, 2002; Kalua et al., 2006; Migliorini et al., 2006; Artajo et al., 2007; Parenti et al., 2008; Servili et al., 2008; Boselli et al., 2009; Gomez-Rico et al., 2009; Migliorini et al., 2009, 2012; Espinola et al., 2011; Catania et al., 2013; Taticchi et al., 2013; Tamborrino et al., 2014a; Klen et al., 2015a). The literature data shows that the malaxation behaves in a more complex way than the one described above. The secoiridoid profile depends on a combination of the following three kinds of opposite phenomena: (i) enzymatic oxidative degradation catalyzed by polyphenol oxidases (PPOs) and peroxidases (PODs), which cause a decrease in the phenolic compound content; (ii) enzymatic (i.e. β-glucosidase activity) and non-enzymatic hydrolytic phenomena that transform oleoeuropein and ligstroside into their respective aglycones and decarboxymethylated forms, especially the 3,4-DHPEA-EDA compound; (iii) physical and enzymatic (i.e. pectinase and cellulase activities) phenomena which promote the release of phenolic compounds from cellular tissues and then cause an increase in the phenolic compound content. Among the cinnamic acids, verbascoside content decreases, whereas its derivatives, such as the β-OH-verbascoside diastereoisomers, increase during malaxation.

The literature data shows an incomplete and not uniform overview of the overall effect of the above phenomena on the phenolic profile of EVOO (relevant remarkable data are presented as supplementary material in Table S1). However, two common behaviours seemed to be observed: the phenolic compound content tends to decrease with malaxation time at a constant temperature, while it tends to increase with malaxation temperature at a constant time. These effects inversely depend on the oxygen exposure of the olive paste during malaxation: the higher the partial oxygen pressure, the greater the above decrease in phenolic compound content with time and the smaller the above increase in phenolic compound content with temperature.

No modelling based on pseudo *n*-order kinetics has been carried out on either the phenomena involved or the relationships of relevant rate constants with temperature under exposure to air. Therefore, the lack of quantitative time-temperature relationships makes it more difficult to apply the literature data to control olive paste malaxation. A kinetic approach to phenolic compound transformation phenomena under exposure to air may also link up to our previous time-temperature kinetic study to predict the potential effect of malaxation on extraction yield (Trapani et al., 2017), in order to strike a balance between oil yield and oil quality characteristics.

The aim of this work is to apply a time-temperature kinetic approach to phenolic compound transformation phenomena under exposure to air in order to select technological indices for the implementation of olive paste malaxation optimization charts.

## 2. Material and methods

### 2.1. Malaxation trials

The kinetic study was performed using Abencor lab equipment (Abencor analyser, MC2 Ingegneria Y Sistemas S.L., Seville, Spain) following Trapani et al. (2017). With respect to its usual use, the equipment was utilized both for the olive crushing and olive paste malaxation, but not for the olive paste centrifugation. The equipment consisted of an “MM-100” hammer mill (with 5.5 mm-diameter crusher holes) and a thermostated water bath (Thermomixer TB-100), with eight work sites; the work sites consisted of eight stainless steel mixing jars (speed of mixing blades: 50 rpm) under exposure to air, so that several olive paste malaxation treatments could be simulated in parallel. It was deliberately decided to perform the malaxation in this manner to make the oxidative degradation phenomena more evident.

The malaxation trials were carried out in triplicate at 22, 27, 32 and 37 °C for 0, 20, 40, 60, 80 and 100 min; the water and paste temperatures were monitored using a type T thermocouple thermometer (Testo 926, Milan, Italy). Approximately 2.1 kg of olive paste, separated into six mixing jars each containing 350 g of olive paste, were used for each malaxation trial.

The olive paste samples were partly used to measure the phenolic compound content and partly to measure the apparent oil extraction yield, as reported below in the description of the analysis methods.