PAPER

THE EFFECT OF AN INCREASE IN PASTE TEMPERATURE BETWEEN MALAXATION AND CENTRIFUGATION ON OLIVE OIL QUALITY AND YIELD: PRELIMINARY RESULTS

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ABSTRACT

Olive oil extraction conditions are usually a compromise between quality and yield. Enhancing yield decreases quality, and vice versa. We aim to understand if a change in temperature between malaxation and centrifugation can result in a better compromise. Thus, malaxation is carried out at 20°C and oil is extracted at 20°C, 27°C, and 35°C.

The results show that a moderate increase in temperature between malaxation and centrifugation (i.e. from 20°C to 27°C) increases both yield and quality of the oil. Conversely, an excessive temperature increase (i.e. from 20°C to 35°C) leads to the production of rancid-related compounds.

Keywords: olive oil, phenols, quality, temperature, yield

1. INTRODUCTION

The extra virgin olive oil extraction involves several subsequent steps. Briefly, olives are washed and crushed to obtain a paste. Then, the olive paste is kneaded (i.e. malaxation phase) and centrifuged to separate the olive oil from water and exhaust solids (i.e. pomace) (GUERRINI *et al.*, 2017a).
Temperature control during extraction is a key issue in extra virgin olive oil (EVOO) production, since it affects both yield and quality (BOSELLI *et al.*, 2009).
The effects of temperature on yield are mainly related to the malaxation and centrifugation steps. During malaxation, temperature influences the physic, chemical and enzymatic activity of olive paste. On the one hand, higher temperatures enhance the coalescence of oil droplets, decrease viscosity, and accelerate the diffusion of substances from the aqueous to the oily phase. Usually, higher temperatures increase yield (TRAPANI *et al.*, 2017a). During malaxation, the slow and continuous kneading of the paste merges oil small droplets into larger ones, creating a continuous liquid phase that can easily be separated mechanically (KALUA *et al.*, 2006). Drops with a diameter >30 μm are considered to be separated more easily with the decanter centrifuge (MARTINEZ MORENO *et al.*, 1957). Furthermore, the viscosity of olive oil and the consistency of the olive paste decrease with an increase in temperature, facilitating EVOO extraction in the decanter (GUERRINI *et al.*, 2017b).
The temperature during the extraction process has a marked effect on some EVOO quality parameters. High temperatures enhance enzymatic reactions involving lipolytic, hydrolytic and oxidative degradation, affecting both phenols and aroma. Furthermore, higher temperatures increase the vapor pressure of volatile substances, and may causes aroma losses (TAMBORRINO, 2014).
Phenols are considered indicators of EVOO quality for their functional, nutritional, and sensory properties (RODIS *et al.*, 2002). Their recovery into the EVOO is strongly affected by temperature. High temperatures enhance phenol solubility in the oily phase (RODIS *et al.*, 2002) and their release from olive tissues on the one hand, while, on the other hand, they improve the rate of enzymatic activity involved in phenol consumption and molecular weight reduction (TRAPANI *et al.*, 2017b).
EVOO flavor is mainly described by fruity and defective attributes. The European directive EC 1019/2002 on marketing standards for olive oil states that the fruity attribute must be perceivable, while no defective attributes should be present. The fruity attribute has been related to lipoxygenase (LOX) pathway compounds (ANGEROSA *et al.*, 2001). LOX activity is significantly affected by temperature. In the same way, temperature affects the appearance in the oil of all enzymatic-related defects (ZHU *et al.*, 2014).
Current practice is to select the malaxation temperature to maximize desired effects (i.e. higher yield, phenolic content and LOX-related compounds) and minimize undesirable ones (i.e. phenol degradation and off-flavor biosynthesis).
Recently, heat exchangers have provided a valuable technological solution to improve the thermal control of olive paste. The first study of heat exchangers in olive mills was conducted by AMIRANTE *et al*. (2006). Destoned olive paste was heated between the crusher and the malaxer to obtain the same yield for stoned and destoned paste (otherwise yield is lower for the latter). On the other hand, in two studies, Veneziani *et al*. (2015, 2017) cooled the olive paste between the crusher and malaxer, and found an increase in EVOO quality without a decrease in yield. These studies highlight that malaxation temperature plays a central role for the EVOO quality. However, we want to test if a fast temperature increase after the malaxation can improve yield without decrease the oil quality. In fact, in a theoretical instantaneous temperature increase, we can reasonable suppose that only the physical effects (change in olive oil/paste viscosity, and change in solubility) occurs. On

the contrary, the chemical and enzymatic reactions occur during the time required for the temperature increase.
Hence, given the improved ability to control temperature during the process, in this work we test, the effect of heating olive paste between the malaxer and the centrifuge. Trials explore the possibility of conducting malaxation at one temperature and extraction at another. The aim was to test if such heating has advantages in terms of both EVOO yield and quality.

2. MATERIAL AND METHODS

2.1. Trials

Olives (cv. *Frantoio*) were manually harvested in Tavarnelle Val di Pesa (Italy) at the beginning of December 2017. The following day they were washed and crushed. Processing was designed to reduce oxidative impact and limit any damage to oil quality due to oxygen. Hence, 1.2 kg of the obtained olive paste was weighed and malaxed in sealed conditions for 30 min at 20°C. The result was divided into three portions of 400 g each. Each portion was put in a sealed jar and the temperature was bring at 20°C, 27°C, or 35°C in one of three thermostatic baths. The time required for the temperature increase was 7 min. Preliminary trials established the water temperature needed in each of the thermostatic baths to obtain these three temperatures in 7 min. Then the paste was centrifuged for 2 min at 2000 rpm (TRAPANI *et al.*, 2017a) to separate olive oil from other phases. Three replicates were conducted.

2.2. Yield, water and oil content

The oil extraction yields were calculated both as the actual yield (OY) and as an Extractability Index (EI):

$$OY = \frac{OE_x}{Ol_m} \cdot 100 \quad (1)$$

$$EI = \frac{OE_x}{OC_{om}} \cdot 100 \quad (2)$$

where:
OE_x was the measured extracted olive oil (g);
Ol_m was the measured olive paste (g);
OC_{om} was the oil content of the olive paste (g), which was determined from the oil content of the olive fruits (%).
Water content was measured using the gravimetric method. Total oil content was determined in olive paste and pomace with hexane in an automatic Randall extractor (mod. 148, Velp Scientifica, Milan, Italy), following the analytical technique described in Cherubini *et al*. (2009). Results were expressed as the percentage of total weight.

2.3. Chemical analysis

Olive oils were tested for free fatty acid content, peroxide value, K232, K270 and ΔK based on methods set out in European Commission Regulation EEC/2568/91. Total and individual biophenol content were recorded according to the method described in

IOOC/T.20 Doc. N 29. Volatile compounds were measured with the HS-SPME-GC-MS technique (FORTINI *et al*. 2017).

2.4. Statistical analysis

Data were processed with a one-way ANOVA to assess differences among the three extraction temperatures. Where a significant difference ($p<0.05$) was found, a Tukey Honest Significant Difference post-hoc test was carried out.

3. RESULTS AND DISCUSSION

3.1. The effect of paste temperature increase after a malaxation at low temperature for 30 min

The EVOO samples were analyzed after their extraction by centrifugation of the olive paste, which were malaxed at 20°C for 30 min and then, kept at 20°C for 7 min or heated to 27°C and 35°C in 7 min (Tables 1 and 2).
In the above EVOO samples the oil extraction yields and the EU legal chemical parameters (i.e. able to measure the triglycerides degradation level due the lipase hydrolytic activity and the auto-oxidation and photo-oxidation phenomena) were measured (Table 1).

Table 1. Parameters of EVOO extracted by centrifugation of the olive paste, which had no malaxation (i.e. at time $t = 0$) and were malaxed at 20°C for 30 min and then, kept at 20°C for 7 min or heated to 27 and 35°C in 7 min; a and b represent a statistically significant difference ($p<0.05$) based on the Tukey HSD post-hoc test.

		Final temperature after olive paste heating (°C)			
Parameter	**At time $t = 0$**	**20 °C**	**27 °C**	**35 °C**	**p**
OY (%)	n.d.	20.7±0.8 b	23.3±0.3 a	23.7±0.9 a	0.01
EY (%)*	n.d.	79±4 b	89±2 a	91±6 a	0.01
Free fatty acids content (%)	n.d.	0.43±0.01	0.47±0.04	0.47±0.06	ns
Peroxide number (m_{eq}/kg)	n.d.	11.4±0.7	11±3	11±1	ns
K_{232}	n.d.	1.73±0.03	1.67±0.04	1.74±0.03	ns
K_{270}	n.d.	0.08±0.02	0.08±0.01	0.09±0.01	ns
$\triangle K$	n.d.	0.002±0.001 a	0.003±0.001 ab	0.003±0.001 b	0.03
Total phenolic content (mg/kg)	230±31 b	238±23 b	290±10 a	298±37 a	0.04
3,4-DHPEA-EDA (mg/kg)	21±1 a	23±1 a	29±2 b	46±2 c	0.03
Total LOX compounds (mg/kg)	n.d.	45.36±5.50	46.00±13.45	44.90±6.01	ns
E-2-Hexenal (mg/kg)	n.d.	41.88±4.95	42.20±12.69	41.13±5.15	ns
1-penten-3-ol (mg/kg)	n.d.	0.26±0.03 a	0.31±0.01 b	0.33±0.03 b	0.05
E-2-Heptenal (μg/kg)	n.d.	25±3 a	27±3 a	39±3 b	0.04

*From the oil content of olive paste (%) = 26.2±0.7; n.d. = not determined.

The final temperature after the olive paste heating influenced significantly the extraction yields. The OY values increased approximately from 21% at 20°C to 24% at 35°C and the EY values increased approximately from 79% at 20°C to 91% at 35°C; the OY and EI values had no significant differences between 27°C and 35°C final temperatures. These results

were consistent with the literature data, which showed a positive relationship between temperature and extraction yield (TRAPANI *et al.*, 2017a). However, in all of these works the temperature was kept constant throughout the process, while our data show that a yield increase can be obtained with a temperature increase that is limited to the centrifugation process.

No significant effect of the final temperatures occurred for the free fatty acids content, the peroxide number, the K232 and the K270 UV spectroscopic indexes. Although the ΔK spectroscopic index showed a slight increase between 20°C and 35°C, EVOO samples were in compliance with the EU legal chemical parameters.

The total phenolic content increased significantly with the final temperature (Table 1). The EVOO samples which were extracted at the 20°C final temperature contained a significant lower content (about 25%) of phenols than those extracted at 27°C and 35°C reached temperatures.

The dialdehydic form of decarboxymethyl oleuropein aglycone - 3,4 DHPEA-EDA content (i.e the EVOO's most abundant phenolic compound – ZANONI, 2014) was also found to significantly increase with the final temperature (Table 1); it increased from 23 mg/kg at 20 °C to 46 mg/kg at 35°C. The positive effect of temperature on the phenolic compounds content was already described in the literature. Veneziani *et al*. (2015; 2017) described an increase in both the total phenolic content and the 3,4 DHPEA-EDA content in relation with the malaxation temperature, due to the combined activities of endogenous enzymes. Rodis *et al*. (2002) found that the partition coefficients (oil/water) of phenolic compounds increased with temperature from 25°C to 45°C; hence, high temperatures were associated with high phenolic compounds content in the oily phase.

No significant variation of the total phenolic and 3,4 DHPEA-EDA contents occurred between EVOO samples that were not malaxed (i.e. at time t = 0) and those processed at 20°C.

Volatile composition of EVOO samples was measured to verify the behavior of both the lipoxygenase (LOX) pathway compounds, related to positive sensory attributes, and the compounds related to sensory defects (Table 1). The experimental data of LOX compounds content were similar at all the final temperatures. No significant differences were found for aldehydes and esters and only one alcohol (1-penten-3-ol) was found to increase with the highest temperatures. The olive paste heating after malaxation did not affect the LOX pathway, but the C5 and C6 compounds contents in EVOO samples seemed only related to the malaxation at 20°C for 30 min; Angerosa *et al*. (2002) reported that malaxation conditions with temperature lower than 25°C for 30-45 min are optimal for the LOX pathway.

Only one volatile compound related to sensory defects (i.e. the used method measured 48 defective compounds; FORTINI *et al.*, 2017) was significant in the EVOO samples (Table 1). The (E)-2-Heptenal, which is related to the rancid defect (KALUA *et al.*, 2006; ZHU *et al.*, 2016), occurred in all EVOO samples and it increased with the final temperatures after the heating of malaxed olive paste. No significant differences were found between 20°C and 27 °C, but a significant difference was found at 35°C. The content of the (E)-2-Heptenal varied approximately from 25 to 40 μg/kg, which are values above the relevant literature odor threshold of 0.005 mg/kg (KOTTI *et al.*, 2011); values around 40 μg/kg of the (E)-2-Heptenal content were significantly correlated with olive oil samples with sensory defects (ZANONI *et al.*, 2015).

3.2. A predicted comparison of EVOO yield and quality between the paste temperature increase after a malaxation treatment and the time-temperature malaxation treatment under stationary conditions

In this paragraph we compare the effects of a malaxation at 20° C for 30 min, followed by 7 min of olive paste heating to 20, 27 and 35°C (i.e. the tested theses), with the effects of a malaxation carried out under stationary temperature conditions (i.e. at 20, 27 and 35°C) for the same time (i.e. 37 min).
For this aim we use the mathematical predictions obtained with the computer program (MalaxAction 1.0). The software is the only tool available today in literature (ZANONI *et al.*, 2018) for the comparisons of the effects of different olive paste malaxation conditions at laboratory scale. The computer program is based on the kinetic studies of Trapani *et al.* (2017a; 2017b), which were carried out with the reference Abencor lab equipment under exposure to air. The computer program is able to predict (i) the oil extraction yield as function of the olive paste oil content, expressed as EI%; (ii) the relative variation of the 3,4 DHPEA-EDA in the olive oil as the quality index that best represents the effect on the phenolic compounds in the extractable oil.
Table 2 reports the comparison between our results and the predictive model. To evaluate the EI% during the experimental trials we used the total oil content of the olive paste (i.e. roughly the 26% - Table 1); to evaluate the change in 3,4 DHPEA-EDA content in the olive oil samples we used the concentration in non-malaxed olive paste (i.e at time t = 0) of 22 mg/kg. Finally we report a semi-quantitative evaluation of the rancid defect obtained using the odor threshold of (E)-2-Heptenal in olive oil samples (Table 1).
The comparison between the EI% values and the relative variation of 3.4 DHPEA-EDA content showed similar results between the experimental values and the predicted values at 20 °C. It is important to point out that this is the only case among those studied without olive paste heating (i.e. malaxation at 20°C for 37 min). The results predicted by the computer program are consistent with the measured value (Table 2), and the MalaxAction 1.0 software has been considered suitable for the comparisons.

Table 2. The predicted comparison of EVOO yield and quality between the paste temperature increase after a malaxation treatment and the time-temperature malaxation treatment under stationary conditions.

Parameter	Predictive comparison at 20°C		Predictive comparison at 27°C		Predictive comparison at 35°C	
	Experimental data (final temperature of 20°C)	Predicted data (malaxation at 20°C for 37 min)	Experimental data (final temperature of 27°C)	Predicted data (malaxation at 27°C for 37 min)	Experimental data (final temperature of 35°C)	Predicted data (malaxation at 35°C for 37 min)
Oil Extractability Index - EI (%)	79	80	89	89	91	92
Decrease (-) or increase (+) of 3,4 DHPEA-EDA content in oi (%)	0	0	+30	-61	+110	-4

The values of EI% obtained during our trials were similar those predicted by *MalaxAction 1.0* (Table 2). This result remarks that the paste heating between malaxation and centrifugation allow to obtain the same yield results than the whole process at higher temperature.
The model for EI% described by Trapani and co-workers (2017a) tends to asymptotically reach the maximum value of 100%; low increases in temperature and short increases in

malaxation time have a high impact on EI% when temperature and time values are low. On the other hand, for long times and high temperatures the increase in EI% due to a further increase of such parameters is lower. Consistently with the predictive model, a short heating of the olive paste was sufficient to increase the yield between 20°C and 27°C, while no further yield increase was obtained between 27 and 35°C.
The model was not able to predict the changes in 3,4-DHPEA-EDA content (Table 2). Moreover, the model was built for olive paste under exposure to air, while this test was conducted in a sealed malaxer (i.e. only the oxygen in the malaxer headspace was available). However, the 3,4-DHPEA-EDA contents can be considered consistent with the general kinetic theory of Trapani *et al*. (2017b). It suggested that the phenolic compound transformation phenomenon during a time-temperature treatment of olive paste is caused by two opposing phenomena during olive paste malaxation: (i) a decreasing phenomenon probably due to enzymatic oxidative damage of the phenolic compounds; (ii) an increasing phenomenon probably due to a physical and enzymatic release of phenolic compounds from the cellular tissues. Obviously, the change in the oxygen availability reduces the extent of the decreasing phenomenon. Thus, discrepancies between 3,4-DHPEA-EDA measured and predicted values were found. At 27 °C the model predicted a 3,4-DHPEA-EDA decrease of 61%, while at 35°C of 4%. In the trial data we measured an increase of 30% and 110% of 3,4-DHPEA-EDA at 27°C and 35°C, respectively. In our trial, the above decreasing phenomenon was inhibited by the reduced oxidative conditions, resulting in a 3,4-DHPEA-EDA increase.

4. CONCLUSIONS

The current trend in high-quality EVOO production is to reduce the malaxation time and temperature. Although this enhances quality, it reduces yield. Recent works have aimed to improve control of the temperature of the process by introducing a heat exchanger between the crusher and the malaxer. This is designed to improve the control of the process, allowing to maintain quality and increase yield for shorter malaxation times, or improve quality without decreasing yield.
A further improvement can be obtained by placing a heat exchanger between the malaxer and the centrifuge and increasing the temperature. This approach obtains a remarkable increase in yield and increases phenols in the olive oil. However, an excessive temperature increase appears to be self-defeating, since at higher temperature off-flavour compounds appeared and no further yield increases were measured.
The placement of a heat exchanger between the malaxer and the "decanter" further improves the control of the extraction process and seems to be complementary to the current trend to place a heat exchanger between the crusher and the malaxer.

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