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A System to Control the Atmosphere in the Headspace of the Malaxation Machine to Improve the Fatty Acid Composition of Extra Virgin Olive Oils

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In recent years, oxygen content regulation during malaxation has been noted as a process parameter. As concluded by many studies, the presence of oxygen during malaxation has a key role in for improving the quality of Extra Virgin Olive Oil (EVOO) in terms of volatile and phenolic components. There are, however, very few studies of the influence of oxygen in the malaxation machine headspace on the fatty acid composition of Extra Virgin Olive Oil (EVOO). The aim of this study is to evaluate the influence of oxygen in the malaxation machine headspace on Nocellara del Belice EVOO fatty acids. During of the malaxation process, the atmosphere inside the malaxation machine was modified by blowing pure oxygen from cylinders at specific stages of the process (i.e. 15, 25, and 35 minutes after the start of malaxation), using a system which ensures the automatic and continuous maintenance of a known amount of oxygen into the headspace at a given moment throughout the malaxation process. The results show that the amount of saturated and unsaturated fatty acids present in EVOO depends specifically on the timepoint of the malaxation process when oxygen is blown into the head space of the machine and much less on the amount of oxygen. The study confirms that monitoring and controlling the atmosphere inside the malaxation machine is necessary to obtain high quality EVOO with strong nutraceutical properties.

1. Introduction

Extra Virgin Olive Oil (EVOO) continuous processing can be divided into four steps: crushing the olives to a paste, paste malaxation, decanter centrifugation and vertical centrifugation. The extraction process involves not only simple mechanical separation of oil from olive paste but also some chemical/physical modifications which influence the quality of the final product (Di Giovacchino et al., 2002). During malaxation some important physical phenomena (breaking oil-water emulsion and coalescence of oil drops, migration of the olives components in oil or aqueous phase) and enzymatic transformations (involving phenolic compounds and triacylglicerols) occur (Migliorini et al., 2006). The definition of the processing conditions which allow selective control of the enzymes is a crucial point of the oil mechanical extraction process, strictly related to sensory and healthy quality (Angerosa et al., 2001). The extraction process influences the dissolved oxygen concentration, thus affecting the quality of EVOO (Tamborrino et al., 2014), and specifically the composition of volatiles and phenolic compounds (Leone et al., 2014b). Process monitoring and control are fundamental requirements in the modern EVOO processing industry (Aiello et al., 2012).
In a previous study (Catania et al., 2013a) the authors developed an innovative monitoring system aimed at continuously measuring oxygen concentration during the malaxation process of an important Italian cultivar, Nocellara del Belice (Catania et al., 2014). Malaxation carried out in an oxygen-free atmosphere for the first 25 minutes, followed by the presence of oxygen until the end of the process, enhanced volatile compounds in EVOOs, without compromising the phenolic composition.

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Therefore, it was decided to conduct further research, studying aspects related to the fatty acid composition of the EVOO obtained (Conte et al., 2010). Fatty acids have important anti-cancer and cholesterol-lowering implications from the nutraceutical point of view, and can stimulate the immune system and prevent the onset of diabetes and chronic non-communicable diseases.
EVOO is mainly composed of triacylglicerols (98-99 %), made up of glycerol and three molecules of fatty acids, and from other minor components. The average composition of the most important fatty acids found in EVOO is formed by 9-14 % saturated fatty acids (palmitic acid, stearic acid), 66-80 % monounsaturated fatty acids (palmitoleic acid and oleic acid) and 6-10 % polyunsaturated fatty acids (linoleic acid and linolenic acid). An excess of saturated fatty acids in the blood of the human organism (above 10 %) reduces efficiency, and the number of membrane receptors which are responsible for recognizing the specific proteins of low-density lipoprotein (LDL); LDL have the function of carrying 50 % of blood-cholesterol (Viola and Viola, 2014). An excess of polyunsaturated fatty acids in the human organism start peroxidative processes with the production of free radicals which oxidize LDL via chain reactions. Saturated, monounsaturated and polyunsaturated fatty acids therefore play important structural and functional roles in the human organism.
In literature few studies exist on the composition of EVOO fatty acids concerning the following variables: duration of malaxation process and olives ripening stage (Jimenez et al., 2014).
The aim of this study was to evaluate the influence of oxygen in the malaxation machine headspace on Nocellara del Belice EVOO fatty acids.

2. Materials and Methods

2.1 Experimental oil mill plant

The experimental tests were performed in 2013, employing an Alfa Laval oil mill plant on a typical Sicilian olive variety, “Nocellara del Belice”, manually harvested and processed within 24 hours from harvesting. The oil mill plant was operated in continuous mode and was equipped with an olive washing machine, a disk crusher, a single-stage malaxation machine, a horizontal decanter, and a vertical centrifuge. After washing, the olives were processed with a disk crusher; then the malaxation was performed in a closed system for 45 min at a temperature of 27°C. The extraction was performed with a triphasic centrifugal extractor with no water addition. Oil samples were collected after each test, put into 100 mL dark glass bottles, stored at 12 °C and transported to the laboratory where analyses were performed. The malaxation machine used in the tests was the Alfa Laval Atmosphera 650 with a capacity of 650 L, featuring a stainless steel and airtight cylinder. The machine was equipped with a pair of inlet valves for gas in order to achieve a controlled or modified malaxation atmosphere by blowing nitrogen or oxygen into the headspace of the machine, and a probe for olive paste temperature control. The machine has a gap over the entire inner surface of the tank in which hot water is circulated in order to control olive paste temperature. A rotary double bladed reel, with a spiral inside the machine, mixes the olive paste and removes it from the walls avoiding overheating. Paste loading and unloading operations are carried out by means of automatic valves.

2.2 Real time monitoring system

The measurement system has been described in Catania et al. (2013a). The oxygen concentration inside the malaxation machine is sampled by means of a gas extraction system which continuously circulates the gas inside the malaxation machine through a closed loop pipe where the oxygen sensor is located. The oxygen monitoring circuit consists of a pipeline, a gas pump, a filter and an oxygen sensor.

2.3 Experimental tests

The experimental tests consisted of performing the malaxation process in four different configurations. The atmosphere inside the malaxation machine was modified by blowing nitrogen or oxygen (pure gases) using cylinders into the mixing chamber at specific stages of the process. In all the tests except T_C (control), the malaxation machine was filled with nitrogen before the entry of the olive paste. The following test configurations were thus performed (Table 1).
The drupes were completely healthy and had the same degree of ripeness.
The variable applied in the different tests was atmosphere composition in the malaxation chamber headspace, which was altered by blowing nitrogen and/or oxygen at different times during the process.
Test T_C, the control, was conducted without changing the gaseous component in the headspace of the machine. Tests $T_{5\text{-}15}$, $T_{5\text{-}25}$ and $T_{5\text{-}35}$ were carried out by blowing 5 L of oxygen at different timepoints of the process and specifically after 15, 25 and 35 minutes, respectively, from the beginning, and keeping the percentage of oxygen constant until the end. Tests $T_{30\text{-}15}$, $T_{30\text{-}25}$ and $T_{30\text{-}35}$ were carried out by blowing 30 L of oxygen at the same time as in the previous tests.

In these tests, nitrogen for food was introduced immediately after filling and before the start of mixing, eliminating the low amount of oxygen present in the head space of the malaxation chamber. This was done to evaluate the sole effect of oxygen insufflation at different times of malaxation on EVOO fatty acids.

Table 1: Tests used in the experimentation. Pure oxygen was insufflated by cylinders at different stages during malaxation

Test	Description
T_C (control)	Malaxation in un-modified atmosphere
$T_{5\text{-}15}$	5 L of oxygen introduced 15 min after the start of malaxation
$T_{5\text{-}25}$	5 L of oxygen introduced 25 min after the start of malaxation
$T_{5\text{-}35}$	5 L of oxygen introduced 35 min after the start of malaxation
$T_{30\text{-}15}$	30 L of oxygen introduced 15 min after the start of malaxation
$T_{30\text{-}25}$	30 L of oxygen introduced 25 min after the start of malaxation
$T_{30\text{-}35}$	30 L of oxygen introduced 35 min after the start of malaxation

In all of the tests, filling of the malaxation machine lasted for 10 min. The dissolved oxygen measurements in the malaxation machine were performed every 30 s. Each test configuration was replicated three times.
Oil samples were collected immediately after each test and stored in 0.1 L dark glass bottles at 10 °C during transport to the laboratory.

2.4 FAME (Fatty Acid Methyl Esters) analytical determinations in EVOO

Fatty acids in olive oil samples (100 mL) were directly methylated with 2 mL of 0.5 M $NaOCH_3$ at 30 °C for 15 minutes, followed by 1 mL of 5 % HCl in methanol at 50 °C for 15 minutes. Fatty acid methyl esters (FAME) were recovered in hexane (1.5 mL). One microliter of each sample was injected by autosampler into an HP 6890 gas chromatography system equipped with a flame-ionization detector (Agilent Technologies Inc., Santa Clara, CA). Fatty acid methyl esters from all samples were separated using a 100-m length, 0.25-mm i.d., 0.25-μm capillary column (CP-Sil 88; Chrompack, Middelburg, the Netherlands). The injector temperature was kept at 255 °C and the detector temperature was kept at 250 °C, with an H_2 flow of 40 mL/min, air flow of 400 mL min^{-1}, and a constant He flow of 45 mL/min. The initial oven temperature was held at 70 °C for 1 min, increased at 5 °C min^{-1} to 100 °C, held for 2 min, increased at 10 °C min^{-1} to 175 °C, held for 40 min, and then finally increased at 5 °C min^{-1} to a final temperature of 225 °C and held for 45 min. Helium, with a head pressure of 158.6 kPa and a flow rate of 0.7 mL min^{-1} (linear velocity of 14 cm/s), was used as the carrier gas. Fatty acid methyl ester hexane mix solution (Nu-Chek Prep Inc., Elysian, MN) was used to identify each FA. The identification of CLA isomers was performed using a commercial mixture of cis- and trans-9,11- and 10,12-ocdecadienoic acid methyl esters (Sigma-Aldrich, Milano, Italy). To quantify total FA, C23:0 (Sigma-Aldrich) was added to each sample (4 mg g^{-1} of lyophilized cheese) as the internal standard (Bonanno et al., 2013). The health-promoting index (HPI) was calculated as the ratio between saturated and unsaturated fatty acid and related to the O_2 application and concentration.

2.5 Statistical analysis

The EVOO analyses were performed on three EVOO samples for each test within one week from the extraction. The data were subjected to the Student “t” test for mean comparison at the 95% confidence level (Statgraphics Centurion, Statpoint Inc., USA, 2005).

3. Results and Discussion

3.1 Evolution of the oxygen concentration during malaxation

In test Tc (control), where malaxation was performed without the addition of any gas, the initial oxygen concentration was 20 %; then it decreased to about 14 % at the 45th minute of the process. Note that in the last 10 minutes, equal to approximately 22 % of the total operation time, malaxation was performed with a constant oxygen concentration of approximately 14 %, without further decreases (Figure 1).
In the tests where 5 L of oxygen were blown ($T_{5\text{-}15}$, $T_{5\text{-}25}$ and $T_{5\text{-}35}$) we note that the oxygen concentration never exceeds 10 %. After that, oxygen concentration never decreases below 5 %. In the tests where 30 L of oxygen were blown ($T_{30\text{-}15}$, $T_{30\text{-}25}$ and $T_{30\text{-}35}$), as a result of oxygen being blown, there was a sudden increase of oxygen up to values of approximately 20 %. After a few minutes the amount of oxygen begins to decrease, always remaining above 15%.

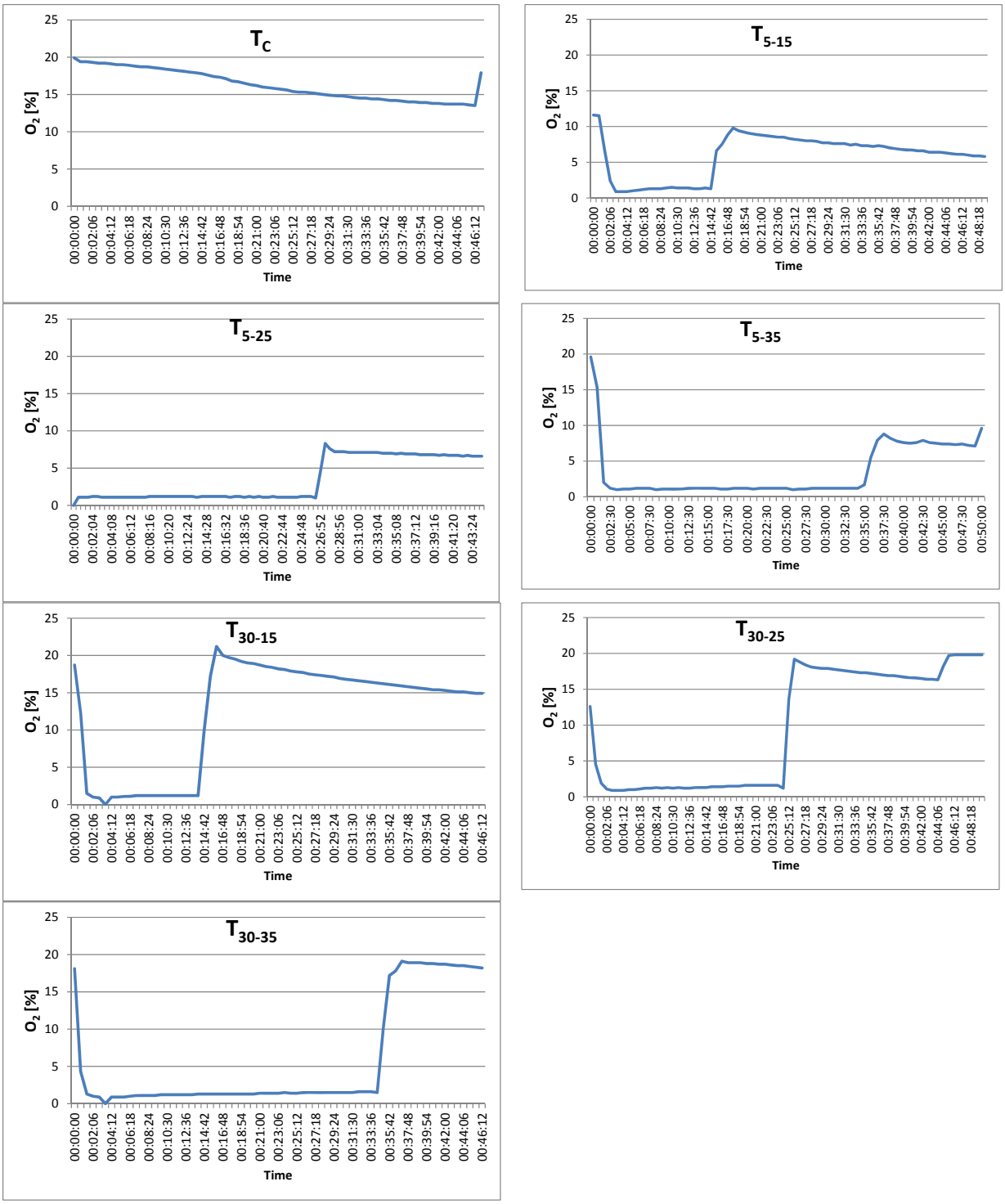

Figure 1: Evolution of the oxygen concentration in the different tests as described in Table 1. Each point on the lines is the mean value of three replicates

3.2 Results of the chemical analyses on EVOOs

The EVOO samples obtained by using different O_2 concentration at different timepoints of the malaxation process were characterized by GC-FID for the individual saturated and unsaturated fatty acids. Proportions of saturated and unsaturated fat characterize different food stuff. It is commonly believed that consumption of

foods containing high amounts of saturated fatty acids is potentially less healthy than consuming fats with a lower proportion of unsaturated fatty acids. The composition of olive and of any vegetable oil is generally defined in terms of the nature and distribution of the fatty acids present in the triacylglycerols and also of the positions at which these fatty acids are attached to the glycerol backbone. Sources of lower saturated fat, but higher proportions of unsaturated fatty acids, include olive oil. There was convincing evidence that partial replacement of saturated fat with unsaturated fat decreases the risk of cardiovascular diseases, especially in men. The HPI index as the ratio of saturated and unsaturated fatty acid showed that the O_2 application clearly modified the ratio between saturated and unsaturated fatty acid. It appears that the lower the HPI index, the healthier the olive oil is. Considering that the control sample showed an HPI index of 33, the application of O_2 promotes a healthier type of olive oil, with the application of a lower concentration (5 L) after 15 minutes, and with the application of a higher concentration (30 L) after 35 minutes (Figure 2).

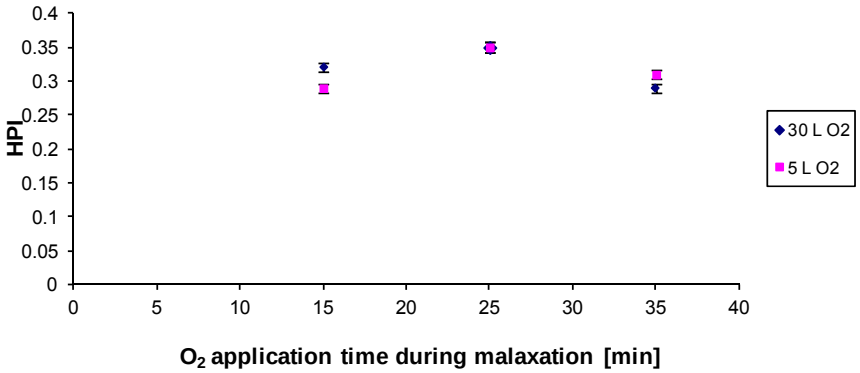

Figure 2: HPI index in EVOOs shown by the tests

The results obtained from this study are in agreement with those obtained by Youssef et al. (2010), which state that the modification in fatty acid composition could affect the oxidative susceptibility, but the latter is also affected by the concentration of natural antioxidants.

4. Conclusions

This study is the first report on the effect of oxygen concentration during malaxation on Nocellara del Belice EVOO saturated and unsaturated fatty acids. It produced interesting results, from both a technical point of view and for the quality of Nocellara del Belice EVOO.
The amount of saturated and unsaturated fatty acids present in EVOO depends, specifically, on the timepoint of the malaxation process when oxygen is blown into the head space of the machine, and much less on its amount.
The results obtained confirm that atmosphere monitoring and control inside the malaxation machine is necessary to obtain high quality EVOO with strong nutraceutical properties.

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