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Olive Oil Mill towards Industry 4.0

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Abstract

In recent years many studies have been conducted on olive oil mill and processes for improving Extra Virgin Olive Oil (EVOO) quality. The malaxer is the most studied machine among all, it is responsible for malaxation, which represents a very important and critical step in the EVOO extraction process. The processing conditions allowing a selective control of the enzymes represent a crucial point of the oil mechanical extraction process, strictly related to the sensory and healthy quality of EVOO. The authors designed a malaxer prototype provided with a customized software for the smart management of the malaxation process to obtain high quality EVOO. The SCADA system is equipped with sensors that allow the management of the entire malaxation process: olive paste input and output, exposure to air time and process duration. Different programs of the software can be chosen according both to the variety and quality of the olives and the type of EVOO that is to be obtained in terms of volatile and phenolic components. The innovative machine has been included in a modern olive mill in order to evaluate the quality of Cerasuola and Nocellara del Belice EVOOs. Oil samples were collected after each test, put in 100 mL dark glass bottles, stored at 12 °C and transported to the laboratory where analyses were performed. The results obtained confirm that the quality of EVOO in terms of quantity of volatile and phenolic components can be designed by intervening on some parameters during the malaxation process. This was possible with the use of the malaxer prototype provided with a SCADA system that allowed to manage the biochemical processes that lead to the formation of volatile and phenolic components.

Key words: malaxer, polyphenols, volatile compounds

INTRODUCTION

In recent years many studies have been conducted on olive oil mill and processes for improving Extra Virgin Olive Oil (EVOO) quality (Reboredo-Rodrìguez P. et al., 2014; Inarejos-Garcìa A.M. et al., 2009; Gòmez-Rico et al., 2009). The malaxer is the most studied machine among all, it is responsible for malaxation, which represents a very important and critical step in the EVOO extraction process (Selvaggini et al., 2014). The processing conditions allowing a selective control of the enzymes represent a crucial point of the oil mechanical extraction process, strictly related to the sensory and healthy quality of EVOO (Migliorini et al., 2006). It is well known that during malaxation, the process parameters which EVOO's quality depends on, are temperature, duration of the operation (Angerosa, Mostallino, Basti, & Vito, 2001) and regulation of oxygen concentration as they influence the activity of polyphenoloxydase (PPO) and peroxidase (POD) processes, which lead to enzymatic degradation, reducing the concentrations of phenolic and volatile compounds in EVOO. The automatic control of the

three process parameters, temperature, time and oxygen concentration, is essential for the rationalisation of the EVOO extraction process.

The aim of this study was the realization of a SCADA platform applied to a new malaxer for the control of the main process parameters to obtain EVOO of high quality.

MATERIALS AND METHODS

The study was performed on typical Sicilian olive cultivars "Cerasuola" and "Nocellara del Belice" in 2018 (Catania et al., 2015), manually harvested and processed within 24 hours from harvesting using an industrial oil mill plant. The oil mill plant was equipped with an olive washing machine, a disk crusher, a single-stage malaxation machine, an horizontal decanter, and a vertical centrifuge. It was operated in continuous mode. The drupes were completely healthy and had the same degree of ripeness. The maturity index of the olives was determined by applying the "Jaen index", varying from 0 to 7, according to skin colour (Tombesi, 1996). Harvest time was determined by examining a sample of 100 olives and dividing it into eight classes on the basis of epicarp pigmentation. The processed olives had a maturity index value of 1.96. The same parameters of the extraction process were adopted for all of the tests from beginning to end. The process parameters used for malaxation were chosen to obtain quality EVOO, and precisely temperature of 27 °C (Angerosa et al., 2001; Servili et al., 2009) and time of 45 min (Servili et al., 2003). The variable applied in the different tests was atmospheric composition in the malaxation chamber headspace, which was altered by blowing nitrogen and/or oxygen at different times during the process. In each test 600 kg of olives were processed; the malaxation machine headspace was equal to 15% of the volume of the chamber, and the olive paste-air contact surface was 0.5 m^2. The oil yield was about 20% in all the tests.

SCADA System

The oxygen concentration inside the malaxation machine is sampled by means of a gas extraction system which continuously circulates the gas inside the machine through a closed loop pipe where the oxygen sensor is located. SCADA system thus consists of a pipeline, a gas pump, a filter and an oxygen sensor. The gas pump employed is the NMP 830 KNE from knf, which is a micro-diaphragm gas pump based on an elastic diaphragm, fixed on its edge, moved up and down its central point by means of an eccentric. In this way the gas is transferred using automatic special valves which ensure the minimum resistance to flow.

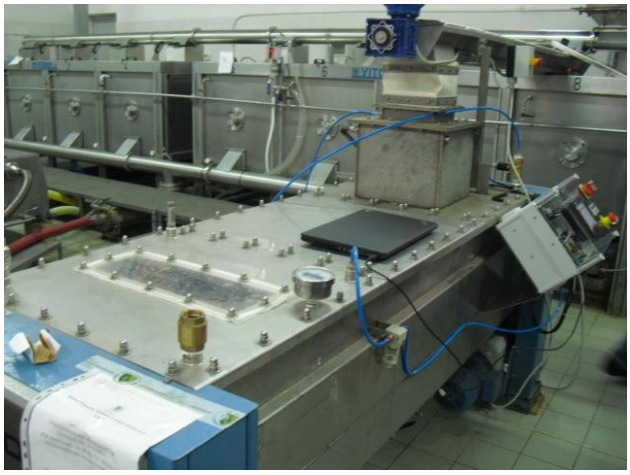

Figure 1. Malaxer prototype equipped with the SCADA system used during the tests.

The micro pump employed can be operated in a temperature range between 5 and 40 °C ensuring a flow of approx. 1.5 l/min at STP at the atmospheric pressure. As the atmosphere extracted from the malaxation machine circulates through the closed loop pipe, the oxygen sensor periodically samples the oxygen concentration. The sensor employed is the GS YUASA SK-25 which is a galvanic cell type sensor, generating a current fairly proportional to the

oxygen concentration. The galvanic cell in fact is a diffusion-limited metal/air battery, where the oxygen in the sample, diffusing through a barrier, is reduced to hydroxyl ions at the cathode and oxidizes a metal anode passing through the electrolyte. A current, proportional to the rate of consumption of oxygen, is generated when the cathode/anode circuit is completed, the cell operating in what is virtually a short-circuit condition. Since the rate at which oxygen reaches the cathode is limited by the diffusion barrier, the cell current is a direct function of this rate, this in turn being a direct function of the concentration of oxygen in the sample. Test T0, the control, was conducted without changing the gaseous component in the headspace of the machine, test T20 was carried out by blowing 12 l of oxygen after 20 min of malaxation from the beginning of the process and keeping constant the percentage of oxygen until the end. Moreover, in this test, nitrogen for food was introduced immediately after filling and before the start of mixing, thus 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 time of malaxation on both the enzyme complex responsible for the volatile compounds and on the oxidation of the phenolic component. In all the tests, the malaxation machine filling took 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.

Chemical Analytical Determinations in EVOO

Total phenolic content

The olive oil phenolic composition was analyzed by HPLC-DAD. Namely, a chromatograph equipped with a Shimadzu LC-10ADVP pump, a DAD Shimadzu a SCL-10AVP system controller, a 8125 Rheodyne manual injector with a 20 µL loop and a 5-µm particle size C18 Luna column, 15 cm, 2 mm i.d., (Phenomenex, UK) was used. Phenolic standard compounds were purchased from Sigma Aldrich (Milano, Italy). All solvents (methanol, acetonitrile, and n-hexane) were of HPLC grade and purchased from Fluka. Formic acid was purchased from Sigma Chemical Co. (St. Louis, MO). The ultrapure water generated by the MilliQ system (Millipore, Bedford, MA), and MilliQ water/methanol (90/10 v:v) as the most suitable solvent for the standards were used. The samples were stored in dark-brown glass bottles at 4 °C until analysis. The oil was extracted from high-quality olives and met the standards set by the European Commission (Commission Regulation (EEC) n 2568/91 of July 1991 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis, 1991) for extra-virgin quality. To clean and concentrate the sample, the polar fraction was obtained from 3 g of oil sample using an SPE diol cartridge (Vac RC 500 mg, Waters, Milford, MA). 6 mL of n-hexane, 6 mL of methanol: water (80:20), and 3 mL of acetonitrile was used to achieve the activation of stationary phase. The oil was washed with 10 mL of n-hexane under vacuum to remove the nonpolar fraction. Afterward, phenolic compounds were eluted with 8 mL of methanol: water and 4 mL of acetonitrile. The vacuum was maintained at less than 30 kPa. The eluent was evaporated to 2 mL under a gentle N_2 flow. A 13-mm PTFE 0.45 um membrane filter, purchase from Waters, were used to filter the sample. 20 µL was injected into the liquid chromatography. The entire process was performed in darkness conditions with brown glass material. The HPLC-DAD column was kept at ambient temperature. The mobile phase consisted of a binary solvent system using water acidified with 0.1% formic acid (solvent A) and 100% acetonitrile (solvent B), kept at a flow rate of 0.5 mL min^{-1}. The gradient program started with 90 % eluent A and 10 % eluent B, which ramped linearly to 25 % in 12 min. This percentage was maintained for 7 min, and eluent B was ramped again linearly to 40 % at 30 min and to 60 % at 40 min. Each phenolic compound was expressed with its standard and the linearity of the calibration method was fortificated by triplicate analyses.

Volatile Organic Compounds (TA)

The volatile fraction was isolated and identified by using HS-SPME and GC-MS. An HP 5890 GC-MS equipped with the mass selective detector HP 5973 was used in order to identify the target compounds. An HP5-MS, 5% diphenyl-95% dimethylpolysiloxane, capillary column (30 m 0.2 mm, 0.25 mm film thickness) was used as stationary phase. Chromatographic conditions were splitless injection, using He as carrier gas at 10^{-3} L min^{-1}. The injector temperature was 250 °C. Oven temperature program: 8 min of 60 °C isotherm followed by a linear temperature increase of 4 °C min^{-1} up to 180 °C held for 2 min. MS scan conditions: source temperature 230 °C, interface temperature 280 °C, E energy 70 eV, mass scan range 39–350 amu.

Linear retention indices were calculated with references to n-alkanes (C6–C22), obtained from FLUKA, and run under the chromatographic condition described above. Standard mixtures of selected essential oils were also injected in the GC inlet and retention indices determined. Response factors of reference compounds from different classes of monoterpenes, sequiterpenes, monoterpene alcohols and aldehydes, ester were determined and found to range from 0.85 to 1.2 versus n hexanol, averaging 1.0. Response factors were therefore taken as 1.0 for all compounds.

Experiments of singular components standard addition have been carried out in order to evaluate matrix interference. Identification of the oil components was done using a commercial library (NIST 2005) and an FFC (flavor and fragrance components) bank provided with linear retention indices determined on the same column, to be used interactively with MS data for compound identification. All analyses were carried out in triplicate and the total content of the single compounds was calculated as percent of total chromatographic area (Mondello et al., 1995).

Statistical analysis

Chemical analyses of EVOO were performed on three EVOO samples for each case of studies within one week from extraction. The data were subjected to ANOVA and t-test to evaluate the statistical significance of the tests for each variety at the 95% confidence level (Statgraphics Centurion, Statpoint Inc., USA, 2005). All the statistical analyses were carried out using Statistica 6.0 for Windows (Stat Soft Italia).

RESULTS AND DISCUSSION

The percentage of oxygen values inside the malaxation head space are shown in real time after they have been acquired by the SCADA system.

Composition of the biophenol extracts of Nocellara del Belice and Cerasuola olive oil samples obtained from the two extraction systems are reported in table 1.

The presence of oxygen in "precision dose" modality has not modified the biophenols composition of the EVOO of the two varieties. The results confirm those previously obtained by the authors (Catania et al 2015; Catania et al 2016; Catania et al. 2017).

Table 2 shows the amount of volatile compounds of Nocellara del Belice and Cerasuola EVOOs. C6 volatile compounds (aldehydes and alcohols) originated in the lipoxygenase pathway, are connected to positive sensory characteristics of olive oil and contribute to the green olive oil aroma (Gòmez-Rico et al., 2009). C5 volatile compounds which originate in the additional branch of the lipoxygenase pathway contribute to the pleasant aroma and positively correlate with bitterness and pungency of EVOO (Gòmez-Rico et al., 2009).

Tests T20 show C6 and C5 compounds values higher than those obtained in tests T0 for both varieties. A 55% and 41% increase is to be noted for Nocellara del Belice variety respectively for the compounds 2,4 Hexadienal, (E,E) and 1-Penten 3-ol. For Cerasuola variety there was an increase in 2,4 Hexadienal, (E,E) (+40%), 9, Hexanal (+21%), 1-Penten 3-ol (+38%), 2 esen 1 olo (+45%) and 1-Hexanol (+13%). SCADA platform applied to the malaxer prototype allowed to increase C5 and C6 volatile compounds (aldehydes and alcohols) for both varieties. The C5 and C6 volatile compounds higher values greatly improve the quality of EVOOs in

terms of sensory notes (cut grass, artichoke, tomato, rosemary, etc.). For the Sicilian EVOOs varieties that generally have a low quantity of such compounds, the SCADA system application plays an important role to make the EVOO more balanced in terms of polyphenols and volatile compounds.

Table 1. Composition of the biophenol extracts (mean ± SD) of Nocellara del Belice and Cerasuola olive oils at two times point (T0 and T20).

	Nocellara del Belice		Cerasuola	
	T0	T20	T0	T20
HT	4.65 ±1.5 a	9.78 ±3.2 a	2.16 ±0.4 a	1.56 ±0.7 a
TY	6.2 ±3.5 a	7.18 ±4.1 a	1.11 ±0.8 a	1.13 ±0.5 a
pCA	0.0 ±0.0 b	5.29 ±1.2 a	0.0 ±0.0 a	0.0 ±0.0 a
FA	0.0 ±0.0 b	6.18 ±2.5 a	0.0 ±0.0 a	0.0 ±0.0 a
TY ac	2.26 ±0.5 a	0.0 ±0.0 b	13.39 ±1.9 a	3.94 ±0.4 b
PN	23.89 ±5.5 a	26.22 ±4.7 a	42.78 ±5.3 b	58.69 ±6.2 a
LU	0.0 ±0.0 b	6.35 ±1.2 a	8.5 ±1.3 a	9.43 ±1.1 a
AP	0.0 ±0.0 a	0.0 ±0.0 a	13.52 ±1.9 a	5.16 ±0.8 b
mLU	0.0 ±0.0 a	0.0 ±0.0 a	13.83 ±3.1 a	12.19 ±1.8 a
Ligst. der	47.48 ±2.5 b	73.25 ±3.5 a	73.56 ±5.2 b	93.61 ±5.4 b
Oleur der.	22.37 ±1.1 a	17.52 ±1.5 b	92.94 ±2.5 a	73.83 ±3.5 a
TPC	106.8 ±15.0 b	152.0 ±16.0 a	260.0 ±17.0 a	259.0 ±15.0 a

HT: Hydroxytyrosol, TY: Tyrosol, pCA: *p*-Coumaric acid, FA: Ferulic acid, TY: Tyrosol acetate, PN: Pinoresinol, LU: Luteolin, AP: Apigenin, mLU: Methyl luteolin, Ligst. der: Total concentration of the ligostride derivatives, Oleur der: Total concentration of the oleuropein derivatives, TPC: Total phenol content.

Table 2. Volatile composition (mean ± SD) of Nocellara del Belice and Cerasuola olive oils at two times point (T0 and T20).

	Nocellara del Belice		Cerasuola	
	T0	T20	T0	T20
2,4 Hexadienal, (E,E)	258 ±19.5 b	569 ±55.7 a	415 ±32.7 b	696 ±61.9 a
2-pentenale (E)	48 ±2.1 b	58 ±2.7 a	40 ±1.5 b	55 ±3.1 a
Hexanal	124 ±8.8 a	144 ±10.1 a	158 ±10.1 b	200 ±12.4 a
Pentenal 2-(E)	32 ±1.7 b	41 ±2.2 a	91 ±5.5 a	95 ±4.5 a
1-Penten 3-ol	48 ±1.3 b	81 ±1.7 a	38 ±1.02 b	61 ±1.0 a
2 esen 1 olo	4585 ±339.2 b	6145 ±380.9 a	5214 ±430.1 b	9541 ±776.6 a
1-Hexanol	381 ±13.7 b	414 ±12.4 a	535 ±12.8 b	614 ±13.5 a
3-Hexen 1-ol (Z)	1758 ±96.6 a	1351 ±63.4 b	2841 ±68.1 a	2910 ±72.7 a

CONCLUSIONS

The study aimed at evaluating the quality of Cerasuola and Nocellara del Belice EVOOs through the application of a SCADA platform at industrial scale. The SCADA system equipped with sensors allowed the management of the entire malaxation process: olive paste input and output, exposure to air time and process duration. The results indicate that the application of digitalis in olive oil extraction plants has a fundamental role for improving the quality of EVOOs. This study suggests new research scenarios concerning EVOO extraction in order to launch the Olive Oil Mill sector towards Industry 4.0.

Literature cited

Angerosa, F., Mostallino, R., Basti, C., and Vito, R., (2001). Influence of malaxation temperature and time on the quality of virgin olive oils. Food Chem. *72*, 19–28.

Catania, P., Febo, P., De Pasquale, C., Aboud, F., and Vallone, M. (2015). A system to control the atmosphere in the headspace of the malaxation machine to improve the fatty acid composition of extra virgin olive oils. Chem. Eng. Trans. *44*, 73-78.

Catania, P., Vallone, M., Farid, A., and De Pasquale, C. (2016). Effect of O_2 control and monitoring on the nutraceutical properties of Extra Virgin Olive Oils, J. Food Eng. *169*, 179-188.

Catania, P., Febo, P., Vallone, M., and De Pasquale, C. (2017). Influence of O_2 on extra virgin olive oil fatty acids composition during malaxation. Chem. Eng. Trans. *58*, 439-444.

Gòmez-Rico, A., Inarejos-Garcìa, A.M., Salvador, M.D., and Fregapane, G. (2009). Effect of malaxation conditions on phenol and volatile profiles in olive paste and the corresponding virgin olive oils (Olea europea L. Cv. Cornicabra). J. Agric. Food Chem. *57*, 3587-3595.

Inarejos-Garcìa, A.M., Gòmez-Rico, A., Desamparados Salvador, M., and Fregapane, G. (2009). Influence of malaxation conditions on virgin olive oil yield, overall quality and composition. Eur. Food Res. Technol., *228*, 671-677.

Migliorini, M., Mugelli, M., Cherubini ,C., Viti, P., and Zanoni, B. (2006). Influence of O_2 on the quality of virgin olive oil during malaxation. J. Sci. Food Agr. *86*, 2140-2146.

Mondello, L., Dugo, P.,Basile, A., Dugo,G., and Bartle, K.D. (1995). Interactive use of linear retention indices, on polar and apolar columns, with a MS-library for reliable identification of complex mixtures. J. Microcol. Sep. *7*, 581–591.

Reboredo-Rodríguez, P., González-Barreiro, C., Cancho-Grande, B., and Simal-Gándara, J. (2014). Improvements in the malaxation process to enhance the aroma quality of extra virgin olive oils. Food Chem. *158*, 534-545.

Selvaggini, R., Esposito, S., Taticchi, A., Urbani, S., Veneziani, G., Di Maio, I., Sordini, B., and Servili, M. (2014). Optimization of the temperature and oxygen concentration conditions in the malaxation during the oil mechanical extraction process of four Italian olive cultivars. J. Agric. Food Chem. *62*, 3813−3822.

Servili, M., Selvaggini, R., Taticchi, A., Esposto, S., and Montedoro, G. (2003). Volatile compounds and phenolic composition of virgin olive oil: optimization of temperature and time of exposure of olive pastes to air contact during the mechanical extraction process. J. Agric.Food Chem., *51*, 7980-7988.

Servili, M., Esposto, S., Fabiani, R., Urbani, S., Taticchi, A., Mariucci, F., et al. (2009). Phenolic compounds in olive oil: antioxidant, health and organoleptic activities according to their chemical structure. Inflammopharmacology, *17*, 1-9.

Tombesi, A. (1996). La raccolta meccanica delle olive. Rivista di Frutticoltura, *2*, 31e35.