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Pumping Contribution to Dissolved Oxygen in Virgin Olive Oil During Processing

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The overall quality of extra virgin olive oil (EVOO) strictly relates to the evolution of its oxidative state, which in turn depends on the amount of the oxygen availability during the product life, starting with the olive fruit milling. The issue of oil oxygenation during processing has been poorly studied. The few available literature assesses the relative contribution of three main processing steps (paste malaxation, decanter centrifugation, and vertical centrifugation) to the final dissolved oxygen concentration and the consequences on the oil quality decay during storage. Nevertheless, until now information about the contribution of the devices used to moves materials during processing, i.e. screw conveyor and pumps to move olive, olive paste and oil, to the amount of dissolved oxygen and in broader terms on the oil quality, are lacking. It can be reasonably assumed that the intact drupes handling during leaf-removal and washing before crushing, had a negligible effect on the final oil dissolved oxygen content, whereas from crusher to the decanter centrifuge by the malaxer, where olive paste handling occurs, a noticeable effect on the future oil characteristics could occur. The standard and widespread device used to move olive paste during processing, essentially from the crusher to the malaxer and from the malaxer to the decanter centrifuge, is the progressive cavity pump, commonly named mono-pump. Notices of other pumping devices used or proved in EVOO mills are missing. In the present work a peristaltic pump (roller pump) has been tested in comparison to the conventional mono-pump in a continuous centrifugal extraction plant. Specifically, the two pumps were alternatively used to feed the decanter centrifuge by empting the malaxation chambers. The oxygenation effect was assessed in terms of dissolved oxygen amount (DOA) in the produced EVOO, which were also compared for the main qualitative traits such as commercial parameters, phenolic and volatile profiles and phthalates occurrence being the peristaltic pump equipped with a phthalates-free tube. Basically, the qualitative effect of the two pumps significantly differs for the DOA with about 10% saving for the peristaltic pump. The latter also gives significantly ($p<10\%$) higher concentration of trans-2-hexenal and lower concentration of trans-2-hexen-1-ol. Hence, it seems that the lower oxygenation effect reflects in a less advanced oxidative state of volatiles belonging to the LOX pathway. Finally, the peristaltic pump gives a quasi-significant reduction of phthalates, with mean values of about 15-45% lower than the mono-pump at p ranging from 24% to 36%. The lack of significance could rely in the presence of non-phthalates-free tube and piping in the processing devices other than the peristaltic pump.

1. Introduction

The oxidative state of extra virgin olive oil (EVOO) depends on the oxidation degree of the fatty matrix, and the amount and oxidative extent of both the phenolic and volatile compounds (Velasco and Dobarganes, 2002). Its evolution is closely related to the availability of oxygen. Keeping as a reference the timeline of the oil life from extraction to consumption, a tentative classification of the oxygen sources may be as, primary and secondary sources. Accordingly, primary oxygen sources could entail the olive fruit processing until the oil extraction. Secondary oxygen sources could entail the oil handling and management until consumption, through stabilization treatments (sedimentation and filtration), bottling, storage, transportation. Either the primary or the secondary sources, contribute to the addition of oxygen to the oil, thus increasing the dissolved oxygen amount (DOA) available for oxidation reactions. Although mechanisms and models of EVOO stability

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to oxidation have been well studied (Li and Wang, 2018; Choe and Min, 2006) leading to a wide body of knowledge of the effect of secondary oxygen sources, minor attention has been paid on the issue of oil oxygenation during processing (primary sources) in terms of DOA (Masella et al., 2009; Masella et al., 2010; Masella et al., 2012; Guerrini et al., 2018). The limited available literature evaluates the relative contribution of malaxation, decanter and vertical centrifugation to the final DOA in the produced EVOO (Parenti et al., 2007). Specifically, the highest potential increment of DOA was ascribed to the vertical centrifuge with a rough percentage variation of 50 %, followed by decanter (30 %) and malaxer (20 %). Interestingly, these differences in DOA are also reflected in a worsening of the oxidative state in relation to a slight significant increase in the oil peroxide value. Beside malaxation and centrifugation, the EVOO extraction process consists of olive fruit cleaning (leaf-removal and washing), olive crushing to form an olive paste, olive paste handling from the crusher to the malaxer and from the malaxer to the decanter centrifuge. Information about the contribution of the devices used to moves materials during processing, i.e. screw conveyors and pumps to move olive, olive paste and oil, to the DOA and in broader terms to the oil quality, are still lacking. It can be reasonably assumed that handling of intact drupes during leaf-removal and washing before crushing, have a negligible effect on the final oil DOA, whereas from crusher to the decanter centrifuge through the malaxer, where olive paste handling occurs, a noticeable effect on the future oil characteristics could happen as a consequence of oxygenation. The standard and widespread device used to move the olive paste during processing is the progressive cavity pump, commonly named mono-pump. Notices of other pumping devices used or proved in EVOO mills are missing. In the present work a peristaltic-pump (roller pump) has been tested in comparison to the conventional mono-pump in a continuous centrifugal extraction plant, looking for information about its usability and the potential effects on DOA and parameters related to the oil oxygenation.

2. Materials and Methods

2.1 Experimental procedure

A peristaltic-pump model MS2 by Ragazzini srl, Italy (flow rate from 200 to 17000 L/h, pressure up to 15 bars, tube diameter 55 mm, VFD installed power 4 kW) was tested in an industrial two-phase continuous centrifugal plant for EVOO extraction (Pieralisi Group company, Jesi - AN - Italy). Briefly, the plant consists of a mechanical hammer crusher (for breaking the olives and obtaining a paste), a kneading unit (for mixing the paste), a horizontal centrifugal extractor (for separating the oil from the paste), and a vertical centrifuge (for the oil cleaning). The kneading unit consists of two independent processing lines, each one consisting of a horizontal stainless steel tank, divided into 2 compartments by a central diaphragm equipped with a gate. The single compartment is able to contain about 700 kg of olive paste, for a total capacity (two tanks, four compartments) of about 2800 kg. The transfer of the olive paste from the kneading tanks to the centrifugal extractor (decanter) is carried out by means of conventional mono pumps model P125 (4 kW installed power, Pieralisi Group company, Italy). The decanter has a nominal hourly productivity of 2000 kg/h. Comparative tests between the conventional mono pump and the peristaltic-pump were carried out by inserting the latter on one of the two kneading lines. In this way it was possible to carry out paired tests, alternating the kneading in the two lines and thus feeding the decanter alternatively with the mono-pump or with the peristaltic-pump. A total of 12 extraction tests were carried out, i.e. 6 paired pairs of extractions with mono-pump against peristaltic-pump (6 vs. 6), adopting the same operative conditions (kneading time of 30 min, kneading temperature 27 °C, flow rate to decanter of 1500 kg/h). For each pair of tests, the starting material was previously homogenized (olives of the Moraiolo variety) and then divided into two 700 kg portions. One of these two aliquots was then processed on the kneading line equipped with the mono pump (control), the other one on the kneading line equipped with the peristaltic-pump. This procedure was repeated for each of the 6 pairs of tests. In each trial, the oil was sampled directly downstream from the vertical centrifuge (100ml), for a total of 12 samples which were then subjected to chemical analysis. Main operative parameters of the pumps were recorded during trials, along with the oil extraction yield.

2.2 Chemical Analyses and determinations

Standard commercial quality parameters of EVOO were determined as specified in EEC (1991) (free acidity, peroxide value, UV specific extinction coefficients). Biophenols, pigments, volatiles (by HS-SPME-GC–MS), and DOA (as mg/L by a portable oxygen analyzer model InPro 9500-M701, Mettler-ToledoS.p.A, Italy) were assessed as already described in Masella et al., 2010.

2.3 Statistical Analysis

Statistical significance ($p<0.10$) of the investigated treatment was evaluated through a paired t-test with five degrees of freedom, i.e. six pairs to compare between mono-pump versus peristaltic-pump samples.

3. Results and discussion

Overall, the chemical parameters considered made it possible to obtain an exhaustive picture of the qualitative characteristics of the oils produced during the experimental tests. In general, all the samples can be considered EVOO as shown by the values of the standard quality indices of Table 1, which are well below the limits set by the regulation. However, it is not possible to highlight statistically significant differences between the oil samples produced with the mono-pump and the peristaltic-pump, respectively. This result appears to be consistent with relations already known between the chemical parameters in question and the variables of the extraction process. In particular, free acidity is generally unrelated to the process conditions, while peroxides and UV coefficients may be partially affected by operative conditions such as the reduced concentration of oxygen in contact with the olive paste due to interactions with the activity of the paste enzymes.

Table 1: Qualitative effects of olive paste feeding to the decanter centrifuge by the peristaltic-pump against the mono-pump, commercial EVOO quality indices

Parameter	Mono-pump (±SD)	Peristaltic-pump(±SD)	Mean difference# (±SD)
Free acidity (%)	0.30 (0.04)	0.32 (0.04)	0.03 (0.03) ns
Peroxide value ($meqO_2/kg_{oil}$)	6.41 (0.38)	6.64 (0.42)	0.22 (0.54) ns
K_{232}	1.17 (0.04)	1.18 (0.01)	0.01 (0.04) ns
K_{270}	0.10 (0.01)	0.09 (0.01)	0.01 (0.01) ns

#Mean difference values signed with asterisk are significantly different from 0 (paired t-test *p <0.10; ns= non-significant); SD=standard deviation

Conditions of this type occur, for example, in processing plants that provide for inertization of kneading, with oxygen concentrations that generally drop below 5 %. The use of the peristaltic-pump during the transfer of the olive paste from the kneader to the decanter (i.e. for feeding the centrifugal extraction) is probably not able to determine processing conditions such as to affect the aforementioned chemical parameters. Nevertheless, the peristaltic-pump allows a significant reduction of DOA in the oil (Figure 1, mean difference significantly different from 0 at p < 0.1 according to paired t-test).

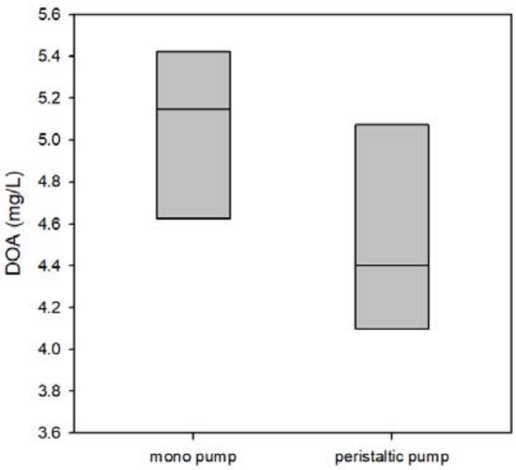

Figure 1: Dissolved oxygen amount (DOA) in the oil samples produced with mono-pump or peristaltic-pump during decanter feeding (boxes horizontal lines stay for 25th, 50th and 75th percentiles)

If compared with the results reported by Masella et al. (2012), the oxygenation saving allowed by using the peristaltic-pump it might seem of minor importance (about 10% saving against the mono pump, corresponding to a mean difference of about 0.5 mg/L). However it should be considered that the observed DOA variation does not indicate the absolute contribution of pumping to the oil oxygenation, but only that a significant oxygenation occurs during olive paste handling from the kneader to the decanter, and that this oxygenation depends on the specific device used to move the olive paste (i.e. the pump type). This implies that a proper management of the paste handling has the potential to reduce the oil oxygenation. As cited previously in the introduction section, the oil oxidative state depends on the extent of oxidation at three interrelated levels: the fatty matrix, the antioxidant compounds (amount, type and profile), and the volatile compounds. According to Table 1, the fatty matrix was not affected by the DOA variations induced by the substitution of the mono-pump with the peristaltic-pump, as proved by non-significant variation of peroxides and UV coefficients. In the same way, at the antioxidant level (biophenols and pigments) any significant effect can be highlighted (Table 2).

Table 2: Qualitative effects of olive paste feeding to the decanter centrifuge by the peristaltic-pump against the mono-pump, antioxidant EVOO compounds

Parameter	Mono-pump (±SD)	Peristaltic-pump(±SD)	Mean difference[#] (±SD)
Biophenols (mg/kg)	238.59 (71.46)	236.18 (58.93)	2.41 (27.60) [ns]
Pigments (mg/kg)	14.69 (3.10)	22.63 (12.65)	7.94 (14.40) [ns]

[#]Mean difference values signed with asterisk are significantly different from 0 (paired t-test *p <0.10; ns= non-significant); SD=standard deviation

The concentration of biophenolic compounds, regardless of the type of pump used was relatively low (about 240 mg/kg) if compared to the concentrations that generally characterize Tuscan productions (typically greater than 400 mg/kg). This result is probably linked to the advanced state of ripeness of the olives. As reported in Table 2, it is not possible to highlight significant differences between the oil samples produced with the two types of pump, with average biophenolic concentrations very close to each other. Similarly, it is not possible to highlight significant effects of the use of one or the other pump on the concentration in total pigments compounds, which stand at similar total concentrations. The same applies for the total amount of volatile compounds reported in Table 3. Nevertheless, in this case significant differences have been found in two important specific compounds.

Table 3: Qualitative effects of olive paste feeding to the decanter centrifuge by the peristaltic-pump against the mono-pump, volatile EVOO compounds

Parameter	Mono-pump (±SD)	Peristaltic-pump(±SD)	Mean difference[#] (±SD)
total volatiles (mg/kg)	62.64 (12.49)	61.08 (8.60)	1.56 (4.78)[ns]
trans-2-hexenal (mg/kg)	25.07 (6.61)	28.82 (2.68)	3.76 (4.61)*
trans-2-hexen-1-ol	3.41 (2.54)	1.76 (1.12)	1.65 (1.58)*

[#]Mean difference values signed with asterisk are significantly different from 0 (paired t-test *p <0.10; ns= non-significant); SD=standard deviation

The peristaltic-pump provides significantly (p<10%) higher concentration of trans-2-hexenal and lower concentration of trans-2-hexen-1-ol. Hence, it seems that the lower oxygenation effect, as proved by the significant lower concentration of DOA, reflects in a less advanced oxidative state of volatiles belonging to the LOX pathway. Thus, the sensory notes of EVOO describing freshness and fresh-green, leafy, fruity with rich vegetative nuances, should be more pronounced in the oils produced with the peristaltic pump.

A further interesting feature of the peristaltic-pump under investigation is the absence of phthalates in the working tube. These chemical compounds, diesters of phthalic acid, are used as plasticizers in various polymeric materials, such as PVC, in order to increase their flexibility, transparency, and durability (Benson, 2015). Since phthalates only bind through weak secondary molecular interactions, their migration from the polymer matrix to the contact materials can occur through simple extraction and/or evaporation processes. Furthermore, the considerable worldwide production of phthalates and their use in many products of daily use has led to a wide diffusion of these compounds in the environment with the consequence that the most widely used phthalate (bis(2-ethylhexyl) phthalate, DEHP), can be considered an ubiquitous pollutant in the environment and in particular in food matrices. The possible negative effects of phthalates on human health are still the subject of heated debate today. In any way, since 2004 the European Union has banned the use of some phthalates as ingredients for cosmetics and for the construction of toys for babies. Therefore, the problem of phthalates contamination potentially affects also the food industry, in all those stages of production processes where the food matrix comes into contact with plastic materials containing phthalates. In the case of the EVOO extraction process, critical points appear essentially the contact of the product (olive paste and/or oil) with the PVC pipes and/or with the inner stators of the mono-pumps used to move the paste under processing. In the plant used for the experiment, there were three mono-pumps:

1. between crusher and kneading tanks, for filling the kneaders;
2. between kneading tanks and decanter, for feeding the decanter centrifuge;

3. between decanter and vertical centrifugal separator, to feed the separator.
With the exception of the connection of the first mono-pump feeding the kneading tanks by steel pipes, in the other cases the connection was made with PVC pipes. These three points therefore represent as many critical points for a possible phthalates contamination of the oil. During the experimental tests, the peristaltic-pump was tested as an alternative to the mono-pump used to feed the decanter. In this way, one of the possible points of contamination has therefore been eliminated since, in accordance with the manufacturer's statements, the internal tubular element of the peristaltic is made of phthalate-free material. At the same time, the other points of potential phthalates contamination still remained, thus adding uncontrolled variability to the occurrence of phthalates in the oils. This happening is well evidenced in Figure 2, where the total phthalates concentration has been reported.

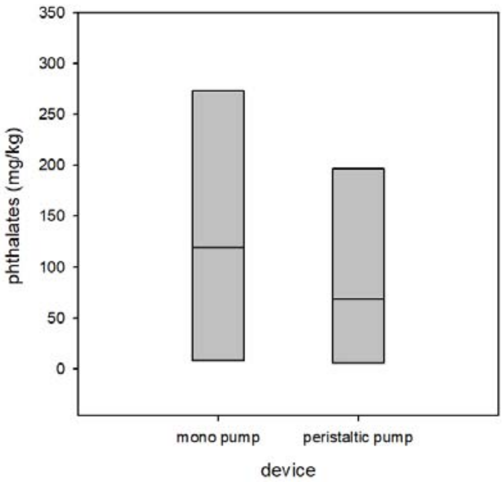

Figure 2: Total phthalates in the oil samples produced with the two pumps (boxes horizontal lines stay for 25th, 50th and 75th percentiles)

According to the paired t-test results, in this case the peristaltic pump gives a quasi-significant reduction of phthalates, with mean values of about 15-45% (for Bis(2-ethylhexyl) phthalate, Diisobutyl phthalate, and total Phthalates) lower than the mono-pump at p ranging from 24% to 36%. Once again, the lack of significance could rely in the presence of non-phthalates-free tube and piping in the processing devices other than the peristaltic-pump.
Some final operative remarks can be drawn about testing the peristaltic-pump. The extraction trials did not highlight any operational problems of the centrifugal extractor, as proved by the paired comparison of extraction yields reported in Table 4. This indicates the effective possibility of using this type of pump in the EVOO extraction process (Table 3).

Table 4: Extraction yields obtained with the peristaltic-pump against the mono-pump

Parameter	Mono-pump (±SD)	Peristaltic-pump(±SD)	Mean difference# (±SD)
Oil extraction yield (%)	17.77 (0.71)	17.93 (0.84)	0.15 (1.19)^{ns}

#Mean difference values signed with asterisk are significantly different from 0 (paired t-test *p <0.10; ns= non-significant); SD=standard deviation

The tests provide this result either in correspondence of different feeding rate of the decanter centrifuge, or during processing olive pastes with different physical characteristics (moisture content, consistency, viscosity) (data not showed). Another element to note is the simplicity with which it is possible to clean the pump at the end of use. After applying the same washing procedures (flow of pressurized hot water for 5 min) to the two types of pumps, the mono-pump still showed significant quantities of paste and pits residues inside the pump body, which were instead absent in the peristaltic-pump.

4. Conclusions

The peristaltic-pump seems to be a valid alternative to be implemented in the continuous EVOO extraction plants for olive paste handling. Basically, the pump does not interfere with the extraction efficiency of the decanter centrifuge. At the same time, it has also emerged the possibility of obtaining useful information about the physical state of the pastes linked to their extractability and on the basis of which it seems likely the possibility of modifying some process variables in real time (times and temperatures of kneading, feed rate to the decanter) in order to optimize the work of the extractor. As regards the qualitative aspects, the peristaltic-pump allows a significant lower oxygenation of the oil as stated by a reduced DOA. This provides EVOOs with a volatile profile with potential more pronounced fresh green notes. A further positive element relies on the ease-of-clean of the pump. Although it was not possible to evaluate the weight of this factor on the quality of the oil in this experiment, it still appears to be a positive element for the hygienic control of the EVOO extraction process. Finally, the possibility of limiting phthalates contamination of the oil during processing clearly emerged by replacing traditional mono pumps with peristaltic pumps. For a solid statistical validation of these results, it would however be necessary to prepare specific comparative tests between mono-pump and peristaltic-pump without potential contamination points within the system, thus limiting the sources of variation to the pumps only.

Acknowledgments

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