AgriEngineering

MDPI

Article

The Oil:Water Ratio in the Vertical Centrifuge Separator and Its Influence in Phenolic Compounds in the Virgin Olive Oil and the Olive Mill Wastewater (Alpechín)

Alfonso Montaño [1,*], Sofía Redondo-Redondo [1], Laura Moreno [1] and Manuel Zambrano [2]

[1] Agri-Food Technological Centre of Extremadura-CTAEX, 06195 Badajoz, Spain; sredondo@ctaex.com (S.R.-R.); lmoreno@ctaex.com (L.M.)
[2] S.C. Viñaoliva, 06200 Almendralejo, Spain; mzambrano@vinaoliva.com
* Correspondence: amontano@ctaex.com; Tel.: +34-924-44-8077

Abstract: The use of the vertical centrifuge in the olive oil production process is generally assumed to be habitual and necessary for the elimination of both the vegetation water and the small olive pulp particles that are not eliminated during solid–liquid separation (horizontal centrifugation). Trials were carried out with different oil:water ratios to study the influence of this variable on both the quality parameters of the olive oils obtained and the loss of oil with the olive wastewater. The trials were carried out at the industrial mill level with oil:water ratios between 0.6 and 5.5. While no differences were observed in the quality parameters of the oils obtained, correct adjustment of the oil:water flow rates reduced the loss of phenols present in the oils by around 30%. In addition, the results show a direct relationship between the soluble effluent and the conductivity of the olive mill wastewater (alpechín) with the loss of oil in the effluent. This work proves that both oil quality and the competitiveness of the olive oil value chain can be increased with energy savings, water consumption reduction, and environmental sustainability.

Keywords: phenolic compounds; vertical centrifuge; olive mill wastewater; conductivity; virgin olive oil

Citation: Montaño, A.; Redondo-Redondo, S.; Moreno, L.; Zambrano, M. The Oil:Water Ratio in the Vertical Centrifuge Separator and Its Influence in Phenolic Compounds in the Virgin Olive Oil and the Olive Mill Wastewater (Alpechín). *AgriEngineering* **2024**, *6*, 318–329. https://doi.org/10.3390/agriengineering6010019

Academic Editors: Giulia Angeloni, Piernicola Masella, Agnese Spadi and Ferdinando Corti

Received: 28 December 2023
Revised: 28 January 2024
Accepted: 31 January 2024
Published: 5 February 2024

1. Introduction

Worldwide consumption of olive oils (OOs) is increasing, reaching around 3.2 million tons at the beginning of this decade [1]. However, it still accounts for only 2.9% of global vegetable fat consumption [2]. Reduction in supply to the market in recent years due to naturally alternating yields, the consequences of climate change in the main producing countries (prolonged droughts and heat waves during fruit development), and crop diseases have led to a fall in production. But this fat, especially its top commercial category, extra virgin olive oil (EVOO), has a promising future. The health properties of EVOO are not only due to its monounsaturated fatty acid (MUFA) profile, but also to the presence of other substances such as phenolics.

The main phenolic compounds identified and quantified in OOs derive from oleuropein and ligstroside. They are generated during olive milling through various chemical reactions catalyzed by enzymes (β-glucosidases, esterases, lyases, etc.). In general, it can be summarized that the oleuropein molecule loses its linked glucose molecule, becoming more soluble in the lipophilic phase. Oleuropein without the glucose, called oleuropein aglycone, can acquire different complex molecular structures that are grouped according to the aldehyde groups they possess: dialdehydic forms of oleuropein aglycone (DOA) or aldehydic forms of oleuropein aglycone (AOA). Both types can in turn undergo hydrolysis, generating the simple phenols hydroxytyrosol and hydroxytyrosol acetate. Similarly, from ligstroside arise the dialdehydic forms of ligstroside aglycone (DLA), the aldehydic forms of ligstroside aglycone (ALA), tyrosol, and tyrosol acetate.

Phenolic compounds contribute very many properties to OOs, essentially related to their (1) sensory properties, i.e., the intensity of bitterness, pungency, and astringency owing to their capacity to stimulate the trigeminal nerve located in the palate [3–5], (2) oxidative stability and resistance to rancidity by acting as chain-breaking and free-radical scavengers chelating metals or binding to peroxyl and alkoxyl radicals [4], and (3) positive health and disease prevention effects, especially cardiovascular, anti-inflammatory, immunological, gastrointestinal, anticancer, chemopreventive, etc. [6,7].

The final presence of higher or lower phenol content in the oils depends on many factors and on good milling practices. The olive varietal is the most determining factor for the final phenol content [8], to which must be added the agro-climatic characteristics (availability of water, nutrients, agronomic practices, . . .), stage of ripeness, etc., so that the phenol pulp content in the olive may vary by a factor of 5–10 in the same varietal [8–11]. This final phenolic compound presence in oils is the result of a balance between "solubilization" and "oxidation". There are actions or factors that will either favor or reduce the solubilization of these amphiphilic molecules in the oil phase, and others that will favor their reaction with oxidants, causing them to lose their properties.

The next most studied factor of the varietal and crop management is the technological factor. Although one can assume a certain uniformity among olive oil industries in terms of machinery, in the last fifteen years, new technologies have been appearing that can improve the sensory and nutritional quality of the EVOO produced [12]. These technologies reduce phenol losses during the production process, and include vacuum olive paste preparation [13], ultrasound [14–17], control of the atmosphere inside the malaxer [14], electro-pulses [18], microwaves [19], use of heat exchangers [16,19,20], thermal flash conditioning [21], etc.

However, despite all the new technologies and selected varietals, there remain many gaps that call for improvement in the different phases of the EVOO extraction process which, without needing any economic investment but only adjustments to the process, could increase the final phenol content by about 25%. Optimization of the mill management (feed flow, use of variators [22], maintenance status of the screen and tablets, etc.), adjustment of the malaxer, control of temperature and of oil moisture and impurities, and proper use of water in the different stages of the process are actions available to staff that can improve the final contents before investing in expensive technologies that will have minimal effect if the practices that hinder the solubility of phenols in the EVOO are not corrected.

One of the points where most phenol losses occur is in the vertical centrifuge liquid–liquid separation, the last operation of the virgin olive oil extraction process. In it, part of the vegetation water extracted in the solid–liquid separation is removed from the oily must together with the remains of the olive pulp. This separation can be carried out in a natural way, with the resulting commercial advantages and disadvantages [23], but the slowness of the process can undoubtedly make the colloidal suspension in the vegetation water and in that from the decanter pose a risk in terms of both the oil's future commercial category and its sensory and nutritional characteristics.

The commonest system used in oil mills to take off the impurities (the vegetation water and solids in suspension) from oily musts is the vertical or disc centrifuge. While natural decanting or filtration systems have been investigated [24,25], they have not shown any at least equal working capacity to process the oily must with a low risk of loss of final oil quality. Although a vertical centrifuge forced decanting system may be a source of oxidation reactions, loss of substances of interest due to the use of warm water, and high water consumption, there exist no alternatives. It is the most efficient, with several functional advantages, and its disadvantages are more readily assumable than those of the other options that have been studied [26]. The system consists of a centrifuge with plates at a determined inclination, which rotates at high speed (6500–8000 rpm), and which, with the addition of warm water, quickly removes a large amount of impurities, and practically all of the vegetation water together with the water added in the process.

Good management of the vertical centrifuge in olive oil mills and its appropriate valuation are still unresolved topics. While much importance is given to choosing the characteristics of the equipment used in the production process, such as the crusher, malaxer, and decanter, in many cases there is no questioning of the requirements and functionality that a vertical centrifuge should have apart from its liters/hour flow rate being sufficient for a certain model of decanter. There is no valuation of its capacity to reduce the amount of water and solids in the suspension of the final oil. A reflection of this is that vertical centrifuges in oil mills are confined to a corner of difficult access, and the oil wash water outlet, one of the main control points of the process, is located at a point both difficult to access and to inspect. In our opinion, the vertical centrifuge should be located at an accessible point where any operator can easily manipulate it, not only for its disassembly but also for its control, and where the oil and water flows are visible from almost any point of the mill.

Factors such as water quantity and effluent temperature are critical for the presence of compounds such as phenols that are of nutritional and quality interest [26–29], as well as for the equipment's correct functioning. The amount of water usually added to the vertical centrifuge is highly variable. It depends firstly on the specific centrifuge model, and secondly on the perception of the oil mill staff who estimate the necessary amount by eye based on their experience and different subjective criteria. Only recently has some commercial brand installed flowmeters to show the quantity of oil and water being input into the equipment. Much of the blame for this lies in the generalized absence of flowmeters in vertical centrifuges and of objective measurements of the oily must's moisture and solids load. While the literature consulted [23,30,31] refers to the use of 1:1 or even 1:2 oil:water (O/W) ratios, in reality, the ratios usually employed are at least 2:1 and even up to 9:1 [25,29,32]. The most up-to-date equipment has achieved a reduction in water requirements, with the ratio being from 25:1 up to 50:1 in the so-called "minimum consumption" centrifuges. Different factors regarding cleaning, maintenance, proper adjustment of regulation rings, etc., will influence not only the loss of compounds of nutritional and quality interest such as phenols but even the commercial life of the oil due to the high level of oxygenation that it undergoes in the process [33].

The O/W ratio is set not only by the amount of water added to the centrifuge, but also by the regulation rings that many models have which, depending on this ratio, allow more or less water to be evacuated from inside the bowl. While the O/W ratio will depend on each model and the regulation ring used, an appropriate value to aim for would be 3:1.

Together with the addition of water, it is necessary to have absolute control of the temperatures of both the oil phase and the water. The difference should be maintained at around +2 °C to +4 °C water relative to oil. Higher values can cause the oil to burn if the water is very hot (this is clearly seen because the oil comes out transparent and shiny, not veiled), and lower values may lead to the formation of "margarines" (curdled oil) seen in the OMWW.

In the last twenty years, olive mill centrifuges have improved markedly in terms of their self-cleaning, optimization of water consumption with minimum consumption vertical centrifuges [30], etc. Even so, there still remain important points for improvement, some within the remit of the mill master, but others at the level of manufacturers when the sector demands solutions for the correction of easily identifiable quality loss points (oil heating, flow control, etc.). Recent research has sought to improve control by means of different devices monitoring the correct operation of the centrifuge and the quality of the centrifuged oil [31,34], and hence improve competitiveness.

This work aims to define the best working conditions and to establish tools and easily monitored references that will allow the mill staff to better control the process of vertical centrifuge forced decanting in order to make the process more sustainable, reduce the mill's water consumption, and improve the nutritional quality of the final EVOO produced.

2. Material and Methods

2.1. Industrial Mill Trials

The trials were carried out at S.C. Ntra. Sra. de Perales, Viñaoliva S.C.'s base cooperative. The olives tested were Picual varietal with a maturity index of 3.5–4.0. They were malaxed for 120 min, with an injection rate into the decanter of 6 t/h. The equipment used was an Amenduni model A-3500 vertical centrifuge (Figure 1), which is neither low-consumption nor has an automatic cleaning-in-place (CIP) system. Their theoretical working capacity is 1500 L/h, with easy regulation of the water flow, although they have no flowmeter to monitor the supply of oil and water to the equipment. For this reason, the flow rates in each trial were determined by weight. A total of 13 samples were taken, checking different ratios on each date. The water and oil samples were taken at the effluent outlet of the vertical centrifuge 20 min after each automatic discharge, which was programmed every 30 min to avoid distorting the data with the time of sampling.

Figure 1. Image of the two vertical centrifuges used in the tests.

2.2. Quality Parameters of the Virgin Olive Oils

The free acidity, peroxide value, spectrophotometric absorptions (K232, K270), and ethyl esters of the oils were determined in accordance with the European Union standard method [35].

2.3. Suspended Solids

Determined via gravimetry by filtering the OMWW through a glass fiber filter paper 0.45 µm in size; the retained residue is dried at 105 °C.

2.4. OMWW Oil Content

Determined through the extraction of the fat using the Soxhlet [36]. The sample was completely oven-dried at 110 °C for 24 h. Hexane was used as the solvent.

2.5. Determination of Phenolic Compounds

Phenols were evaluated following the method described by Mateos [4] and Mateos et al. [37]. All reagents were HPLC grade from Panreac (Barcelona, Spain). Distilled water was de-ionized in a Milli-Q system (Millipore, Bedford, MA, USA). Phenols were extracted through an SPE Diol column (Sep-Pak® Vac 3cc, Waters) with 6 mL hexane and 2.5 mL hexane:ethyl acetate (9:1) per 2.5 g of oil, using 10 mL of methanol as eluent. The resulting extract was vacuum evaporated, and the residue dissolved in 0.5 mL methanol:water (1:1). The clear solution was kept at room temperature for 4 h before the HPLC assay.

The HPLC system consisted of an Agilent 1200 Series isocratic and binary gradient pump, Agilent 1200 Series autosampler, Agilent 1200 Series thermostatted column compartment, and Agilent 1200 Series diode array and multiple wavelength detector managed by Agilent ChemStation. The analytical column was an Eclipse XDB-C18 (Agilent Technologies, Santa Clara, CA, USA), particle size 5 µm, length 150 mm, and internal diameter 4.6 mm. The HPLC assay parameters were as follows: injection volume 5 µL, column temperature 30 °C, flow rate 1 mL/min. The total run time was 55 min. Two eluents were used: orthophosphoric acid:water (99.5:0.5) and methanol:acetonitrile (50:50) with gradients 95:5 at t = 0 min, 30:70 at t = 25 min, 38:62 at t = 40 min, 45:55 at t = 45 min, 52:48 at t = 50 min, and 100:0 at 55 min.

Phenols were assayed at 280 nm using syringic acid and at 335 nm using *o*-coumaric acid as internal standards, both of which were purchased from Sigma-Aldrich (St. Louis, MO, USA). The response factors were determined following Mateos et al. [4,37]. The results are expressed as mg/kg.

2.6. Oxidative Stability

Evaluated using a Rancimat 743 apparatus (Metrohm Co., Basel, Switzerland), measuring the oxidative induction time. A flow of air (15 L/h) was bubbled through 2.5 g of oil heated to 100 °C. The Rancimat stability was taken to be the time needed for an abrupt change in conductivity of an aqueous solution in which the volatile compounds resulting from oxidation of the oil were collected.

2.7. Chlorophylls and Carotenoids

Determined through spectrophotometry using the method of Mínguez-Mosquera et al. [38]. The absorbance at 670 nm is specific to the chlorophyll fraction, and at 470 nm for carotenoids. The applied values of the specific extinction coefficients were Cp= 613 for pheophytin as a major component in the chlorophyll fraction, and Cc = 2000 for lutein as a major component in the carotenoid fraction.

2.8. Statistical Analysis

All statistical analyses were performed using the IBM® SPSS® vn 21.0 Statistics software package (SPSS Inc., Chicago, IL, USA). Mean values obtained for the variables studied in the different groups were compared by one-way ANOVA (Duncan's multiple range test), taking differences to be significant at the level of $p < 0.05$. Pearson's linear correlation analysis was applied to study the possible relationships between the variables.

3. Results and Discussion

The results reported in this work were obtained in different trials carried out on two days (16/12 and 27/12) in the oil mill of the Ntra. Sra. de Perales cooperative. Sampling was conducted under normal working conditions from homogeneous batches of Picual varietal olives.

The conditions and establishment of the flow rates during each trial were adjusted to the extreme parameters at each time of the trials, not exceeding the threshold of usual conditions in the oil mill and realistic in the conventional production process. Under this premise and agreed upon with the mill's technical staff, different O/W (oil-to-water) ratios were tested ranging between 0.6 and 5.5 (Table 1). To simplify the presentation of the results, the trials are grouped into LOW flow (O/W ratio 0.6–1.7), MEDIUM (2.4–2.8), and HIGH (4.7–5.5), corresponding to respective average O/W ratios of 1.1 ± 0.5, 2.5 ± 0.2, and 5.1 ± 0.4. The oil flow rate remained unchanged in all the trials, being controlled by a buffer tank maintaining a constant gravity-fed supply to the centrifuge. The temperature of the oil depended on the outlet temperature of the oily must from the decanter, being in the range 25.3–27.1 °C. The temperature of the water added to the centrifuge can be considered optimal quality-wise if it is 1–3 °C higher than that of the oil. This temperature remained on average slightly higher (by 0.7–3.6 °C) than that of the oil, with average values

in the range of 26.8–28.8 °C (Table 1). This high amplitude and divergence in the water temperatures was caused by the demand for hot water at different points in the oil mill and not by poor regulation of the equipment. Industries ought to have different water supply networks due to the unequal water requirements within the mill, as well as to maintain adequate pressure for optimal effect in the face of different types of needs.

Table 1. Conditions of the vertical centrifuge during the trials. Mean of two trials with 13 samples in total. Different letters indicate significant differences at $p < 0.050$ according to Duncan's test. The absence of a letter indicates that there was no significant effect between treatments by ANOVA.

Parameters	**LOW**	**MEDIUM**	**HIGH**
	Mean ± S.D.	**Mean ± S.D.**	**Mean ± S.D.**
Number of trials	5	5	3
Oil flow rate (kg/h)	902 ± 81	829 ± 81	883 ± 59
Oil temperature (°C)	27.1 ± 1.1	25.3 ± 1.4	25.8 ± 2.2
Water flow rate (kg/h)	991 ± 504 a	329 ± 39 b	173 ± 3 c
Water temperature (°C)	27.7 ± 0.6	25.9 ± 0.2	28.8 ± 4.0
Oil/water ratio	1.1 ± 0.5 c	2.5 ± 0.2 b	5.1 ± 0.4 a
Water–oil temperature difference (°C)	0.6 ± 0.2	0.7 ± 1.3	3.6 ± 5.4

The use of different O/W ratios did not affect the physicochemical quality parameters of the oils produced (Table 2). Indeed, the use of different ratios should not positively affect the quality parameters (acidity, K232, K270, or peroxide index). For instance, Jebabli et al. [39], in a study in which the oily must was compared with the oil after it had passed through the vertical centrifuge, observed no statistically significant differences in quality parameters, with even the major variations they observed in acidity being explicable as due to the interference of organic acids in the aqueous phase. Nonetheless, it has been found that the use of a low O/W ratio could reduce the ethanol and alkyl ester contents [33]. Also, Vidal et al. [30] observed a slight decrease in acidity (from 0.19% to 0.15%), K232, and K270 between the oily must and the oil resulting from passage through the vertical centrifuge, with a slight increase in peroxides, although the variations in quality parameters were minimal and insufficient to change the commercial category of virgin olive oil. However, those workers tested just a single 5 t batch of olives, compared with the 15 t tested during each of the two days of the present work, with the greater variability between these two batches on different days, and hence the greater value of the standard deviation, meaning that any such influence would not have been observed.

The pigment content of the resulting oils was unaffected by the use of different O/W ratios (Table 2). The average values obtained had large standard deviations, with the chlorophyll content being that which varied most among the samples resulting from the trials. This large variation in the results could be more influenced by other elaio-technical parameters such as the mixing temperature or the characteristics of the mills.

With respect to oxidative stability (Table 2), although there were no statistically significant differences between the three groups ($p = 0.060$), there was an apparent trend reflecting what had been referred to in previous work in which a low O/W ratio might favor the loss of oxidative resistance due to a reduction in phenol content (Table 3).

Table 2. Quality and composition parameters of oils tested in two trials at different oil:water flow rates. Mean of two trials with 13 samples in total.

Quality Parameters of the Virgin Olive Oils	**LOW**	**MEDIUM**	**HIGH**
	Mean ± S.D.	**Mean ± S.D.**	**Mean ± S.D.**
Free fatty acids (%)	0.16 ± 0.02	0.15 ± 0.03	0.16 ± 0.03
Peroxide index (mEq O_2/kg)	8.3 ± 2.5	5.5 ± 2.5	7.3 ± 2.7
K232	0.96 ± 0.38	0.45 ± 0.39	0.84 ± 0.52
K272	0.08 ± 0.02	0.06 ± 0.03	0.07 ± 0.04
Delta K	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Chlorophylls (mg/kg)	10.22 ± 3.98	5.40 ± 4.47	8.73 ± 6.01
Carotenoids (mg/kg)	7.60 ± 1.65	5.76 ± 1.98	7.10 ± 2.55
Ethyl esters (mg/kg)	<10	<10	<10
Oxidative stability (hours)	83.9 ± 19.7	110.5 ± 9.7	98.9 ± 14.6

Table 3. Phenolic composition of oils obtained at different oil:water ratios. Mean of two trials with 13 samples in total. Different letters in the same row indicate significant differences at $p < 0.050$ according to Duncan's test. The absence of a letter indicates that there was no significant effect between treatments by ANOVA.

Phenolic Compounds (mg/kg)	**LOW**	**MEDIUM**	**HIGH**
	Mean ± S.D.	**Mean ± S.D.**	**Mean ± S.D.**
Hydroxytyrosol	1.1 ± 0.4	2.6 ± 1.8	3.0 ± 2.5
Tyrosol	2.5 ± 0.2	2.9 ± 0.9	3.2 ± 0.8
Vaníllic acid	0.3 ± 0.0 ab	0.2 ± 0.1 b	0.4 ± 0.1 a
Vanillin	<0.1	<0.1	<0.1
p-Coumaric acid	0.4 ± 0.0	0.3 ± 0.0	0.4 ± 0.1
Hydroxytyrosol acetate	1.4 ± 1.3	1.7 ± 1.4	2.0 ± 0.4
DOA	29.7 ± 8.1	16.6 ± 12.9	32.9 ± 15.9
Tyrosol acetate	34.9 ± 12.0	34.4 ± 16.4	33.4 ± 13.1
DLA	24.1 ± 11.8	27.5 ± 36.7	20.1 ± 12.5
Pinoresinol	0.9 ± 0.4	0.6 ± 0.1	0.9 ± 0.4
Cinnamic acid	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Acetoxypinoresinol	1.6 ± 1.1	2.3 ± 1.4	1.8 ± 1.1
AOA	124.2 ± 13.0 b	157.8 ± 18.9 ab	169.3 ± 37.8 a
ALA	29.5 ± 4.7	46.4 ± 29.4	61.1 ± 40.1
Ferulic acid	0.1 ± 0.2	0.2 ± 0.2	0.2 ± 0.1
Luteolin	7.5 ± 8.2	16.9 ± 6.9	10.2 ± 10.5
Apigenin	3.0 ± 2.8	6.0 ± 2.2	3.8 ± 3.6
Total phenols	261.3 ± 18.2 b	316.8 ± 38.3 ab	342.7 ± 53.3 a
o-Diphenols	163.9 ± 15.5 b	195.7 ± 17.7 ab	217.4 ± 34.6 a
Secoiridoid derivatives	207.6 ± 20.2	248.4 ± 52.5	283.4 ± 49.8

The compounds that were most affected by the use of different O/W ratios were the phenols since their amphiphilic characteristics give them greater solubility in polar solvents (the water used in the oil production process) than in nonpolar solvents (the extracted oil). Statistically significant differences were obtained when analyzing the total phenolic compounds in the resulting oils (p = 0.024), although not all compounds were affected to the same intensity. Specifically, *o*-diphenols were affected (p = 0.017), although only the AOA form gave statistically significant differences (p = 0.037). Previous studies had already indicated that the main phenolic compounds affected in this process would be *o*-diphenols [25,33,39], the justification being the different partition coefficients of the various forms of oleuropein derivatives (i.e., hydroxytyrosol 0.010, tyrosol, 0.077, DOA, 0.189, AOA 1.490) [28]. According to Rodis et al. [28], optimizing the reduction of water consumption in the vertical centrifuge will affect the phenolic compounds differently depending on their polarity. Similar results have been observed in tests that added water at pH 4.5 in which the phenol with the greatest observed increases in the final oil was AOA [40].

With respect to the composition of the OMWW, it is notably affected by the conditions of use: the amount of water added and the characteristics of the initial oils of the oily must. At a low O/W ratio, the OMWW pH would be higher due to the dilution of the vegetation water in the oily must because of the added tap water, as well as the remains of the fruit in that must (Table 4). The case is similar to the other quality parameters analyzed in the OMWW (phenols, solids, and conductivity), which will vary in direct relation to the water added.

Table 4. Characteristics of the vertical centrifuge water. Means of two trials with 13 samples in total. Different letters in the same row indicate significant differences at $p < 0.050$ according to Duncan's test. The absence of a letter indicates that there was no significant effect between treatments by ANOVA.

OMWW Characterization	**LOW**	**MEDIUM**	**HIGH**
	Mean ± S.D.	**Mean ± S.D.**	**Mean ± S.D.**
pH	5.3 ± 0.4 a	4.9 ± 0.1 b	4.8 ± 0.0 b
Conductivity (µS/cm)	2699 ± 778 b	5411 ± 1.290 a	6912 ± 1.685 a
Fat content (%)	0.28 ± 0.15 b	0.99 ± 0.52 a	0.76 ± 0.24 a
Fat loss (L/h)	1.92 ± 0.36 ab	3.14 ± 1.31 b	1.30 ± 0.40 a
Total phenols (mg/L gallic acid)	2154 ± 974 b	6676 ± 2570 a	7669 ± 1545 a
Phenol loss (kg/h)	1.52 ± 0.13 ab	2.12 ± 0.61 a	1.33 ± 0.31 b
Suspended solids (mg/L)	6358 ± 4492 b	26 726 ± 15 531 a	20 210 ± 2648 ab

The fat content present in the OMWW, if expressed as a percentage (Table 4), indicates a lower value with a lower O/W ratio. However, expressing the values in kilograms of oil lost per hour of work indicates that with a high O/W ratio, lower oil losses would be obtained, of 1.3 kg/h compared with 1.9 kg/h if the ratio is excessively low.

Despite these results, it is important to stress that the highest oil loss values during the process seem to be more related to the characteristics of the oily must and the state of internal cleanliness of the machine itself than to the amount of water added to the centrifuge. Thus, a correlation analysis showed the OMWW's oil content to be directly correlated with its electrical conductivity (r = 0.766) (Figure 2) and its soluble solids content (r = 0.947) (Figure 3), which would allow the oil loss that would take place in the centrifuge to be predicted based on these parameters.

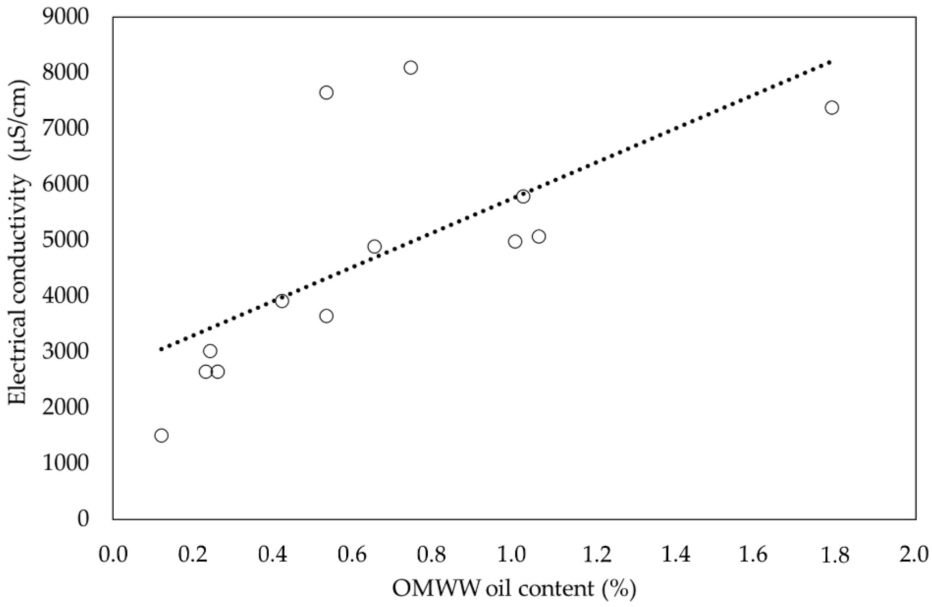

Figure 2. Relation between electrical conductivity (µS/cm) and oil content in OMWW (%).

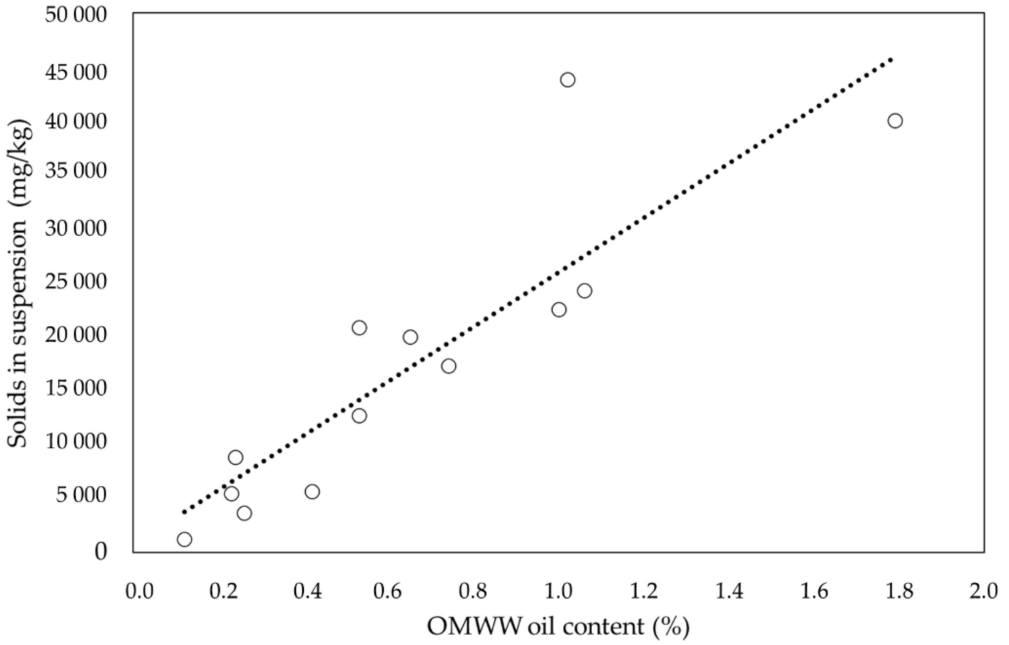

Figure 3. Relation between the solids in suspension of the vegetable meal and oil content in the OMWW.

These first results would, by means of a straightforward system of measurement, allow a control system to be set up that would reduce oil losses in the mill. The conductivity results obtained in this work are comparable to those obtained in another Badajoz oil mill with a Pieralisi model *P*-6000 vertical centrifuge, in which the suspended solid values were between 68 ± 83 mg/kg and 4615 ± 633 mg/kg and oil content between 0.23 ± 0.02 and 0.67 ± 0.04, respectively, with an exponential relationship (n = 6) in the said range, a trend that would be similar to the lower ranges of Figure 3. In those trials, no statistically significant direct relationship was obtained, but there was a similar relationship between the OMWW's oil content and conductivity because the conductivities were in the range of 400–700 µS/cm and the oil values 0.2–0.7%. The deviation could be due to intrinsic factors of the trial.

4. Conclusions

In oil mills, the vertical centrifuge is a piece of equipment which, despite its importance in the olive oil production process owing to the fact that it allows the load of moisture and impurities to be reduced to levels for optimal conservation before filtering, is usually given insufficient control and supervision. Greater dedication and control in the management of this equipment would lead to major improvements in the sensory, nutritional, and commercial quality of the oily musts extracted in the decanter, as well as savings in water consumption and reduction of oil losses.

This work has underscored that, in an oil mill working with industrial flows in full campaign, appropriate adjustment of the O/W flows would allow the loss of phenols present in the oils to be reduced by around 30%. In the trials that used ripe olives of the Picual varietal, adjusting the O/W ratio from 1 to 5 increased the total phenol content from 261 mg/kg to 343 mg/kg. The phenol that increased the most with the increased ratio was an *o*-diphenol, specifically the compound AOA which increased by 36%.

Moreover, this adjustment of the O/W ratio from 1 to 5 allowed the oil content of the OMWW to be reduced, quantified as being in the range of 0.6–2.5 kg/h. There was also a decrease in the polluting capacity of this effluent and a reduction in the oil mill's economic losses. This potential oil loss during the operation of the vertical centrifuge could be controlled or monitored by simply measuring the OMWW's conductivity, as has been shown in this work. Thus, high values would be related to greater oil losses, which would also be related to the greater presence of suspended solids.

This study has shown that, with basic adjustments, and without any need to implement high technologies, not only would better EVOO quality be achieved, but there would also be better use of resources, a reduction in losses, and greater competitiveness of the mill. The sector must be aware that there is significant room for improvement in the management of vertical centrifuges in oil mills, not only at the level of a small or a large mill, but also at the level of research and innovation. In the mills themselves, in addition to the visual inspection of the OMWW, specific controls should be implemented such as the installation of water and oil flowmeters (which do not exist as standard in the vast majority of models marketed by the principal firms), and control of conductivity and/or soluble solids by nephelometry, which could help monitor potential oil loss, efficiency of the process of reducing humidity and impurities, and losses of phenolic compounds carried away in the OMWW.

Author Contributions: Conceptualization, A.M. and M.Z.; methodology, A.M. and S.R.-R.; validation, A.M. and S.R.-R.; formal analysis, A.M., M.Z. and S.R.-R.; investigation, M.Z. and S.R.-R.; resources, M.Z. and L.M.; data curation, L.M. and S.R.-R.; writing—original draft preparation, A.M. and M.Z.; writing—review and editing, L.M., M.Z. and S.R.-R.; visualization, A.M., L.M., M.Z. and S.R.-R.; supervision, A.M., L.M. and M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been carried out thanks to the AGROMATTER: Establishment of a Cervera network for the development of highly sustainable technical materials derived from by-products or waste from the agricultural industry and from the conservation operations of natural spaces. The project is funded by the CDTI (Centre for Industrial Technological Development), through the Ministry of Science and Innovation, in the framework of aid for Technology Centres of Excellence "Cervera". CER-20211013.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: Thanks are due to the S.C. Ntra. Sra. de Perales (Arroyo San Serván, Badajoz, Spain) and Viñaoliva S.C. (Almendralejo, Badajoz, Spain) for the use of their facilities to carry out these trials.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

ALA	Aldehydic forms of ligstroside aglycone
AOA	Aldehydic forms of oleuropein aglycone
DLA	Dialdehydic forms of ligstroside aglycone
DOA	Dialdehydic forms of oleuropein aglycone
EVOO	Extra virgin olive oil
OMWW	Olive mill wastewater

References

1. IOC. Available online: https://www.internationaloliveoil.org/what-we-do/economic-affairs-promotion-unit/#figures (accessed on 11 August 2023).
2. Statista. Available online: https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/ (accessed on 11 August 2023).
3. Mateos, R.; Cert, A.; Pérez-Camino, M.C.; García, J.M. Evaluation of virgin olive bitterness by quantification of secoiridoid derivates. *J. Am. Oil Chem. Soc.* **2004**, *81*, 71–75. [CrossRef]
4. Mateos, R. Caracterización de Componentes Fenólicos del Aceite de Oliva y su Relación con la Estabilidad Oxidativa y el Amargor. Ph.D. Thesis, University of Seville, Seville, Spain, 2002.
5. Gutiérrez-Rosales, F.; Perdiguero, S.; Gutiérrez, R.; Olías, J.M. Evaluation of the bitter taste in virgin olive oil. *J. Am. Oil Chem. Soc.* **1992**, *69*, 394–395. [CrossRef]
6. Obied, H.K.; Prenzler, P.D.; Omar, S.H. Pharmacology of olive biophenols. In *Advances in Molecular Toxicology*; Fishbein, J.C., Ed.; Elsevier: Oxford, UK, 2012; Volume 6, pp. 195–242.
7. Servili, M. The phenolic compounds: A commercial argument in the economic war to come on the quality of olive oil? *OCL* **2014**, *21*, D509. [CrossRef]
8. Miho, H.; Moral, J.; Barranco, D.; Ledesma-Escobar, C.A.; Priego-Capote, F.; Díez, C.M. Influence of genetic and interannual factors on the phenolic profiles of virgin olive oils. *Food Chem.* **2021**, *342*, 128357. [CrossRef] [PubMed]
9. Mousavi, S.; Stanzione, V.; Mariotti, R.; Mastio, V.; Azariadis, A.; Passeri, V.; Valeri, M.C.; Baldoni, L.; Bufacchi, M. Bioactive compound profiling of olive fruit: The contribution of genotype. *Antioxidants* **2022**, *11*, 672. [CrossRef] [PubMed]
10. Medina, G.; Sanz, C.; León, L.; Pérez, A.G.; de la Rosa, R. Phenolic variability in fruit from the 'Arbequina' olive cultivar under Mediterranean and subtropical climatic conditions. *Grasas y Aceites* **2021**, *72*, e438. [CrossRef]
11. Polari, J.J.; Crawford, L.M.; Wang, S.C. Cultivar determines fatty acids and phenolics dynamics for olive fruit and oil in super-high-density orchards. *Agronomy* **2021**, *11*, 313. [CrossRef]
12. Pérez, M.; López-Yerena, A.; Lozano-Castellón, J.; Olmo-Cunillera, A.; Lamuela-Raventós, R.M.; Martin-Belloso, O.; Vallverdú-Queralt, A. Impact of emerging technologies on virgin olive oil processing, consumer acceptance, and the valorization of olive mill wastes. *Antioxidants* **2021**, *10*, 417. [CrossRef] [PubMed]
13. Taticchi, A.; Esposto, S.; Veneziani, G.; Minnocci, A.; Urbani, S.; Selvaggini, R.; Sordini, B.; Daidone, L.; Sebastiani, L.; Servili, M. High vacuum-assisted extraction affects virgin olive oil quality: Impact on phenolic and volatile compounds. *Food Chem.* **2020**, *342*, 128369. [CrossRef] [PubMed]
14. Iqdiam, B.; Abuagela, A.; Yagiz, Y.; Goodrich-Schneider, R.; Baker, G.; Welt, B.; Marshall, R. Combining high power ultrasound pre-treatment with malaxation oxygen control to improve quantity and quality of extra virgin olive oil. *J. Food Eng.* **2019**, *244*, 1–10. [CrossRef]
15. Navarro, A.; Ruiz-Méndez, M.-V.; Sanz, C.; Martínez, M.; Rego, D.; Pérez, A.G. Application of pulsed electric fields to pilot and industrial scale virgin olive oil extraction: Impact on Organoleptic and Functional Quality. *Foods* **2022**, *11*, 2022. [CrossRef] [PubMed]
16. Clodoveo, M.L.; Crupi, P.; Corbo, F. Olive sound: A sustainable radical innovation. *Processes* **2021**, *9*, 1579. [CrossRef]
17. Nardella, M.; Moscetti, R.; Nallan Chakravartula, S.S.; Bedini, G.; Massantini, R. A review on high-power ultrasound-assisted extraction of olive oils: Effect on oil yield, quality, chemical composition and consumer perception. *Foods* **2021**, *10*, 2743. [CrossRef] [PubMed]
18. Leone, A.; Tamborrino, A.; Esposto, S.; Berardi, A.; Servili, M. Investigation on the effects of a pulsed electric field (PEF) continuous system implemented in an industrial olive oil plant. *Foods* **2022**, *11*, 2758. [CrossRef] [PubMed]
19. Tamborrino, A.; Veneziani, G.; Romaniello, R.; Perone, C.; Urbani, S.; Leone, A.; Servili, M. Development of an innovative rotating spiral heat exchanger with integrated microwave for the olive oil industry. *LWT* **2021**, *147*, 111622. [CrossRef]
20. Veneziani, G.; Nucciarelli, D.; Taticchi, A.; Esposto, S.; Selvaggini, R.; Tomasone, R.; Pagano, M.; Servili, M. Application of low temperature during the malaxation phase of virgin olive oil mechanical extraction processes of three different italian cultivars. *Foods* **2021**, *10*, 1578. [CrossRef]
21. Veneziani, G.; Esposto, S.; Taticchi, A.; Selvaggini, R.; Urbani, S.; Di Maio, I.; Sordini, B.; Servili, M. Flash thermal conditioning of olive pastes during the oil mechanical extraction process: Cultivar impact on the phenolic and volatile composition of virgin olive oil. *J. Agric. Food Chem.* **2015**, *63*, 6066–6074. [CrossRef]

22. Polari, J.J.; Garcí-Aguirre, D.; Olmo-García, L.; Carrasco-Pancorbo, A.; Wang, S. Impact of industrial hammer mill rotor speed on extraction efficiency and quality of extra virgin olive oil. *Food Chem.* **2018**, *242*, 362–368. [CrossRef]
23. Gila, A.; Sánchez-Ortíz, A.; Beltrán, G.; Bejaoui, M.A.; Aguilera, M.P.; Jiménez, A. Effect of clarification system on the conservation of virgin olive oil during its storage. *Eur. J. Lipid Sci. Technol.* **2020**, *172*, 1900426. [CrossRef]
24. Altieri, G.; Genovese, F.; Tauriello, A.; Di Renzo, G.C. Innovative plant for the separation of high quality virgin olive oil (VOO) at industrial scale. *J. Food Eng.* **2015**, *166*, 325–334. [CrossRef]
25. Guerrini, L.; Pantani, O.L.; Parenti, A. The impact of vertical centrifugation on olive oil quality. *J. Food Process Eng.* **2017**, *40*, e12489. [CrossRef]
26. Costagli, G. The use of disc stack centrifuge in the virgin olive oil industry. *J. Agric. Sci.* **2018**, *49*, 75–80. [CrossRef]
27. Di Giovacchino, L.; Sestili, S.; Di Vincenzo, D. Influence of olive processing on virgin olive oil quality. *Eur. J. Lipid Sci. Technol.* **2002**, *104*, 587–601. [CrossRef]
28. Rodis, P.S.; Karathanos, V.T.; Mantzavinou, A. Partitioning of olive oil antioxidant between oil and water phases. *J. Agric. Food Chem.* **2002**, *50*, 596–601. [CrossRef]
29. Vidal, A.M.; de Torres Alcalá, S.A.; Moya, M.; Espínola, F. Centrifugation, storage, and filtration of olive oil in an oil mill: Effect on the quality and content of minority compounds. *J. Food Qual.* **2019**, *2019*, 7381761. [CrossRef]
30. Gila, A.; Beltrán, G.; Bejaui, M.A.; Aguilera, M.P.; Jiménez, A. How clarification can affect virgin olive oil composition and quality at industrial scale. *Eur. J. Lipid Sci. Technol.* **2017**, *119*, 10. [CrossRef]
31. Gila, A.; Bejaoui, M.A.; Beltrán, G.; Jiménez, A. Rapid method based in computer vision to determine the moisture and insoluble impurities content in virgin olive oils. *Food Control* **2020**, *113*, 107210. [CrossRef]
32. Beltrán, G.; Bejaoui, M.A.; Sánchez-Ortíz, A.; Jiménez, A. Water addition during oil extraction affects on virgin olive oil ethanol content, quality and composition. *Lipid Sci. Technol.* **2021**, *123*, 2000400. [CrossRef]
33. Masella, P.; Parenti, A.; Spugnoli, P.; Calamai, L. Influence of vertical centrifugation on extra virgin olive oil quality. *J. Am. Oil Chem. Soc.* **2009**, *86*, 1137–1140. [CrossRef]
34. Funes, E.; Allouche, Y.; Beltrán, G.; Aguilera, M.P.; Jiménez, A. Predictive ANN model for the optimization of extra virgin olive oil clarification by means of vertical centrifugation. *J. Food Process Eng.* **2018**, *41*, e12593. [CrossRef]
35. European Commission Regulation (EEC) No 2568/91 of 11 July 1991 on the Characteristics of Olive Oil and Olive-Residue Oil and on the Relevant Methods of Analysis. *Off. J. Eur. Community* **1991**, *248*, 1–102.
36. IOC. COI/OH/Doc. No 1—Guide for the Determination of the Characteristics of Oil-Olives. Available online: https://www.internationaloliveoil.org/what-we-do/chemistry-standardisation-unit/standards-and-methods/ (accessed on 11 August 2023).
37. Mateos, R.; Espartero, J.L.; Trujillo, M.; Rios, J.J.; León-Camacho, M.; Alcudia, F. Determination of phenols, flavones and lignans in virgin olive oils by solid-phase extraction and high performance liquid chromatography with diode array ultraviolet detection. *J. Agric. Food Chem.* **2001**, *49*, 2185–2192. [CrossRef] [PubMed]
38. Mínguez-Mosquera, I.M.; Rejano-Navarro, L.; Gandul-Rojas, B.; Sanchez-Gómez, A.H.; Garrido-Fernandez, J. Color-pigment correlation in virgin olive oil. *J. Am. Oil Chem. Soc.* **1991**, *68*, 809–813.
39. Jebabli, H.; Nsir, H.; Taamalli, A.; Abu-Reidah, I.; Álvarez-Martínez, F.J.; Losada-Echevarria, M.; Barrajón-Catalán, E.; Mhamdi, R. Industrial-scale study of the chemical composition of olive oil process-derived matrices. *Processes* **2020**, *8*, 701. [CrossRef]
40. Montaño, A. Medida de Diferentes Parámetros Fisicoquímicos de Aceitunas y Aceites Vírgenes de las Variedades Principales Cultivadas en Extremadura y Desarrollo de Técnicas Elaiotécnicas para la Mejora de la Comerciabilidad de los Aceites de Oliva Vírgenes. Ph.D. Thesis, University of Extremadura, Badajoz, Spain, 2016.