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Influence of the type of olive-crusher used on the quality of extra virgin olive oils

An experimental investigation was carried out to evaluate the quality of virgin olive oils obtained when either a hammer-crusher or a disk-crusher were used for the olive paste preparation; the effect of the temperature rise caused by rapid olive crushing was also assessed. Oxidative degradation in the oils obtained from hammer-crushed olives was significantly higher than in those obtained from disk-crushed olives as shown by the levels of oxidised triacylglycerols and the results of the oven test. A significant inverse correlation ($p < 0.001$) was found between the Rancimat induction time values and the amounts of oxidised triacylglycerols as determined by the high-performance size exclusion chromatography analysis of polar compounds. These findings suggested that polar compound analyses, just as routine analyses, may be used as a suitable analytical tool to effectively evaluate the quality of virgin olive oils.

Keywords: Virgin olive oil, disk-crusher, hammer-crusher, temperature rise, quality.

1 Introduction

Major changes have taken place in the olive-oil industry in the past few years since mechanical crushers were first introduced to replace traditional stone mills in olive processing and since centrifugal decanters are being used to extract oil from the olive paste. The possibility of resorting to enzymatic treatments to improve the yields and to upgrade the oil quality has also been explored. Numerous experimental studies have also focused on defining the quality of the oils obtained using the different technologies proposed [1–5].

Olive paste preparation is the most important phase of the process whereby oil is mechanically extracted from the olives. The use of different machines in olive oil production has inevitable repercussions on the cost-effectiveness of the oil-making process, on the amounts of oil extracted and especially on the quality of the oil obtained. The traditional stone mills are characterised by batch-processing potentials while the mechanical crushers have different structural features with crushing devices that are designed and built in different ways to ensure continuous olive processing on-line with the decanters for oil extraction.

Previous papers of the present authors [1, 2, 6, 7] have emphasised the possibility of using a stone mill or a hammer-crusher for olive paste preparation depending on the type of cultivar involved. This is done to obtain extra virgin

olive oils with desirable organoleptic properties without jeopardising their shelf life. Amongst the minor classes of compounds present in virgin olive oil, phenolic substances play a key role in determining its typical “bitter pungent”- or “sweet”-taste, depending on their qualitative and quantitative properties they are also responsible for the resistance to oxidation and the shelf life of the oils [8–13].

Consumers now require products that reflect typical local features and yet present organoleptic and nutritional characteristics that cater to their expectations. This calls for a greater degree of consultation between the manufacturers of machinery for olive-oil production and the research community to propose innovative technologies capable of enhancing the quality of oils without curtailing yields.

The aim of this investigation was to provide helpful insights for choosing machines for oil production that meet consumers' expectations as well as the needs of olive oil producers. The action of hammer-crushers and of disk-crushers in olive paste preparation was compared and their effects on the quality of the oil yielded were evaluated.

2 Materials and methods

2.1 Samples

Coratina cultivar olives from Apulia, a region in Southern Italy, were hand-picked once they had reached an optimal degree of ripening. After washing and leaf-removal, a homogeneous batch of olives (about 250 kg) was divided into two portions. Each portion was processed separately either by a disk- or a hammer-crusher. Both crushers

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were laboratory scale pilot plants and their manufacturing characteristics reflected those of the corresponding crushers currently used in oil mills. Moreover, all the machine parts interfacing the olive paste were made of high quality stainless steel. The olives were processed about 12 h after harvesting.

The hammer-crusher (SK1, *Retsch*, Haan, Germany) consisted of a cylindrical crushing chamber ($\varnothing = 15$ cm) with 30 counterbeaters, a grid with 65 holes ($\varnothing = 5$ mm) in its lower part, as well as three fixed hammers positioned at 120° on a single plane and connected directly to the shaft of the motor with an angular velocity of 2850 rpm. The machine received an optimal inflow of 30 kg olives/h.

The disk-crusher (1987, *Retsch*, Haan, Germany) consisted of a rotor with an angular velocity of 2700 rpm which had three rings of prism-shaped picks coupled to another two rings of picks that were fixed onto the lid. The prism-shaped picks had cutting edges, 2 cm in length and 6 mm in width. The machine ensured an optimal inflow of 40 kg olives/h.

Real-time recordings of the olive paste temperature were taken every 5 s by a thermocouple connected to a computer placed at the outlet of the ground paste. Trials were conducted at three different starting temperatures (8, 10, and 15 °C).

Homogeneous samples of paste of at least 5 kg were then collected from each batch of olives and the oil was extracted by means of a laboratory basket centrifuge. All the oil samples were filtered through cotton before being analysed and were successively stored in a freezer at -18 °C until the analyses were performed. The flux diagram of the processing procedures is shown in Fig. 1.

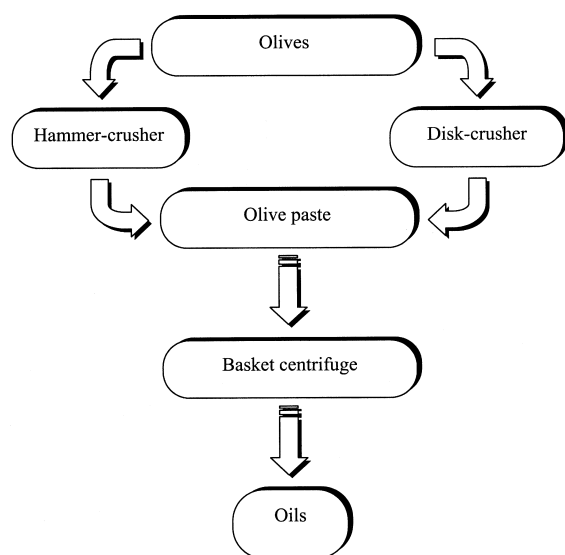


Fig. 1. Flux diagram of the processing procedure.

As a whole, nine independent crushing processes were carried out for each type of crusher.

2.2 Measurement of olive stone size

All the stone fragments were separated from the softer parts of the olives by decanting the unsifted olive paste after it had been appropriately diluted with water and separated. The portion thus obtained was dried in a ventilated oven at 60 °C and was sifted into different size groups by means of punched-plate screens (*Giuliani*, Turin, Italy) with mesh sizes of 0.75, 1.00, 1.40, 1.70, 2.00, 2.36, 3.35, and 4.00 mm.

2.3 Routine analysis

The titratable acidity as oleic acid, the peroxide value as meq of O₂ per kg of oil, and the coefficient of specific extinction at 232 and 270 nm (K_{232} and K_{270}) were determined for each oil sample according to the EC Regulation no. 2568/91 [14].

2.4 Phenolic compounds determination

The phenolic compounds were extracted according to the method described by *Cortesi* et al. [15] starting from 25 g of oil. After dilution of the oils with 50 ml of hexane, three consecutive extractions were carried out with 30 ml of methanol/water 60/40 (v/v) and the collected methanol/water phases were evaporated under vacuum, purified by washing with hexane and then with methanol, and finally dissolved in 5 ml methanol. Qualitative and quantitative evaluations of phenolic compounds were carried out by analysing the methanol phenolic extracts with high-performance liquid chromatography (HPLC) using gallic acid as an internal standard. The HPLC system was composed of a Beckman chromatograph (*Beckman*, Fullerton, CA, USA) equipped with a 250 mm × 4.6 mm C₁₈ Ultrasphere-ODS column (*Beckman*); the eluates were detected at 278 nm with a photodiode array detector (*Beckman*). The mobile phase used was 2% acetic acid in water (A) vs. methanol (B). The elution gradient applied at a flow rate of 1 ml/min was: 95%A/5%B for 3 min, 80%A/20%B in 15 min and isocratic for 2 min, 60%A/40%B in 10 min, 50%A/50%B in 10 min, 100%B in 10 min until the end of the run. Samples were dissolved in methanol, and 10 µl of this solution was injected into the column. The standards used and the quantitative assessment of each compound of interest were as described elsewhere [1]. The peaks were identified by comparing the retention time of each peak with that of the corresponding standard. The peaks that were more difficult to identify were verified by adding the corresponding standard. The repeatability of the method employed was

found to be 4%, as determined by three consecutive analysis carried out on the same sample.

2.5 Auto-oxidation stability

The resistance to auto-oxidation of the oils was evaluated on 2.5 g of oil using the Rancimat system (Metrohm Co., Herisau, Switzerland) at 120 °C with an air flow of 20 l/h. The results were expressed as induction time (hours, h).

2.6 Polar compounds analysis

The polar compounds (PC) were separated by silica gel column chromatography according to the IUPAC method [16]. The efficacy of separation was checked by thin-layer chromatography as recommended by the same method. Then, the PC recovered in CH₂Cl₂ were analysed by means of high-performance size-exclusion chromatography (HPSEC) using CH₂Cl₂ as eluant at flow rate of 1 ml/min. The HPSEC system consisted of a series 10 pump (Perkin-Elmer, Norwalk, CT, USA) with Rheodyne injector, a 50 µl loop, a PL-gel guard column (Perkin-Elmer, Beaconsfield, UK) of 5 cm length × 7.5 mm i.d., and a series of three PL-gel column (Perkin-Elmer, Beaconsfield, UK) of 30 cm length × 7.5 mm i.d. each. The columns were packed with highly cross-linked styrene-divinylbenzene copolymer with particle of 5 µm and a pore diameter of 500, 500 and 100 Å, respectively. The detector was a deflection type differential refractometer (RID 6A, Shimadzu, Kyoto, Japan) connected to an integrator. Peak identification in each chromatogram and quantitative determination of the classes of interest – triglyceride oligopolymers (TGP), oxidised triacylglycerols (ox-TG), diacylglycerols (DG) – were performed as described elsewhere [17, 18]. The precision of the method was expressed as relative percent standard deviation; it was calculated by repeating the analysis on the same sample three consecutive times and was: PC = 1.5; ox-TG = 1.4; DG = 1.7.

2.7 Statistics

One-way analysis of variance (ANOVA) was used to compare the oils obtained from the olive paste prepared by disk- or hammer-crushing.

3 Results and discussion

Given that fast olive crushing entails a considerable rise in temperature (6–10 °C) [19, 20], the difference in temperature between the olives going into the crusher and the paste coming out of it was assessed. The crushing process was effected at three different initial temperatures, with a long coil containing a coolant coated with insulating foam to minimise heat exchange with the outside.

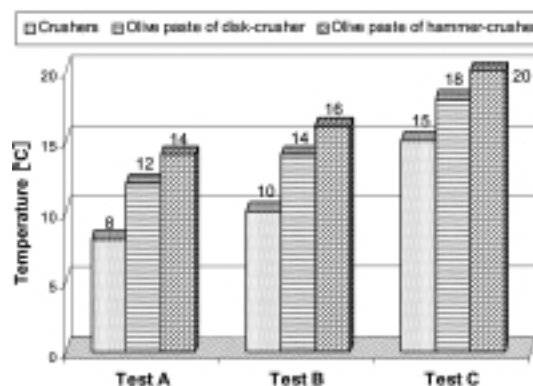


Fig. 2. Initial temperatures of the crushers and mean temperatures of the olive pastes obtained by disk-crushing and hammer-crushing for each test.

This set-up was chosen to determine the influence the two different types of crusher used for olive paste preparation (hammer- or disk-crushers) had on the quality of the extra virgin olive oils obtained. For the trials *Coratina* olives were used, because it is one of the more common cultivars in the Apulia region. Oil from *Coratina* olives is characterised by a high amount of phenolic compounds [1, 2] that may determine lesser oxidation of the oil due to temperature rises in the paste during crushing. In fact, more evident variations in the oxidation level are to be expected when utilising oils containing smaller amounts of phenolic compounds. Kneading of the olive paste was not performed to exclude the occurrence of any other variable linked to processing procedures that could produce analytical differences in the oils obtained which could not be solely ascribed to the olive-crushing method used.

The initial working temperatures of the crushers and the mean temperature reached by the pastes after crushing the olives with the hammer- or disk-crusher, for each of the three tests performed, are reported in Fig. 2. Examination of the paste output temperatures shows that in each case crushing of the drupes caused a considerable temperature rise. The difference in temperature between the olives going into the machine and the paste coming out of it was greater when the olives were hammer-crushed (mean increase: +6 °C, SD = 1) than when they were disk-crushed (mean increase: +4 °C, SD = 1). So, in the experimental condition adopted, e.g. continuously cooling the crusher chamber, the rise in temperature in the hammer-crushed paste exceeded the temperature rise observed in the disk-crushed paste by an average of 2 °C, and there were also some trials in which a difference of 4 °C was recorded between olive pastes. If we had not ensured cooling of the chamber – which is the case in oil mills – the difference in temperature rise using the two types of crushers would surely have been more substan-

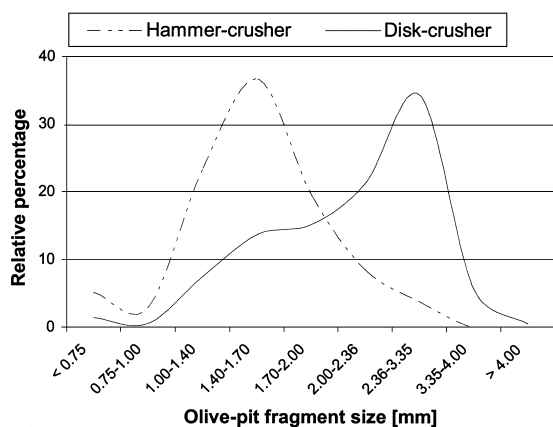


Fig. 3. Olive pit fragment size in the pastes obtained with different crusher system.

tial. Moreover, the average specific energy developed during olive crushing, calculated on the basis of both the manufacturing characteristics of the two types of crushers and on the mean dimension of the correspondingly obtained olive stone fragments, was of about 12.0 J/g for the hammer-crusher and about 8.5 J/g for the disk-crusher. This may affect the quality of the oil and, as shown in Fig. 3, it may be ascribed to the more intense fragmentation of the olive pits produced by the hammer-crusher than produced by the disk-crusher.

Tab. 1 contains the mean values and SD of the routine analyses as well as of the PC and the main classes of substances they are composed of, as analysed by HPSEC for the oils obtained by disk- or hammer-crushing. It also shows the values of the Rancimat induction times (indicative of resistance to forced oxidation), the results of HPLC analysis of phenolic compounds grouped in simple and hydrolysable phenolic substances, and the results of the statistical analysis.

Tab. 1. Analytical characteristics of the oils obtained by disk-crushing or by hammer-crushing (mean value \pm SD) and results of statistical analysis. NS - not significant.

Determination	ANOVA	Disk-crusher	Hammer-crusher
Free fatty acids [%]	$p < 0.01$	0.24 \pm 0.02	0.29 \pm 0.03
Peroxide values [meq O ₂ /kg]	$p < 0.001$	6.9 \pm 0.4	10.5 \pm 0.6
K ₂₃₂ (specific absorption at 232 nm)	$p < 0.05$	1.32 \pm 0.03	1.38 \pm 0.03
K ₂₇₀ (specific absorption at 270 nm)	$p < 0.05$	0.16 \pm 0.01	0.18 \pm 0.01
Polar compounds [%]	$p < 0.001$	1.66 \pm 0.03	1.79 \pm 0.05
Oxidised triacylglycerols [%]	$p < 0.001$	0.30 \pm 0.02	0.36 \pm 0.02
Diacylglycerols [%]	$p < 0.01$	1.06 \pm 0.04	1.12 \pm 0.04
Total simple phenols [mg/kg]	NS	8.1 \pm 0.2	8.1 \pm 0.3
Total complex phenols [mg/kg]	NS	318.8 \pm 11.1	315.0 \pm 9.4
Induction time [h at 120 °C]	$p < 0.01$	20.1 \pm 0.2	19.7 \pm 0.2

In the routine analyses, the values found correlated with the temperature reached during olive paste preparation in all the cases. The amounts of free fatty acids were significantly higher ($p < 0.01$) in the oils obtained by hammer-crushing than in those obtained by disk-crushing. Also the peroxide values and the specific absorption at 232 and 270 nm (K₂₃₂ and K₂₇₀) were significantly higher in the oils obtained from hammer-crushed pastes, with $p < 0.001$ for peroxides and $p < 0.05$ for K₂₃₂ and K₂₇₀.

Complex hydrolysable phenolic substances constituted the largest fraction of phenolic compounds, with mean values of 318.8 mg/kg for the oils obtained by disk-crushing and 315.0 mg/kg for the oils obtained by hammer-crushing. Simple non-hydrolysable phenolic substances, instead, accounted for about 2.5% of the total amount with mean values of 8.1 mg/kg in both the cases. No significant differences were observed in the amount of simple phenols and complex phenols depending on the different type of crusher used. As a consequence, considering that phenolic compounds are known to be the major compounds responsible for the resistance to oxidation of the oils [8, 9, 11], other substances having similar properties such as tocopherols were not examined.

The separation and determination of the PC – which comprise substances whose polarity was higher than that of unaltered triacylglycerols – always showed that they were present in rather small amounts. Fig. 4 shows the HPSEC analysis of the PC of one of the oils examined. The PC determined in the oils from the hammer-crushed olive paste were significantly higher ($p < 0.001$) than the levels measured in the oils from the disk-crushed paste with mean values of 1.79% (SD 0.05) and 1.66% (SD 0.03), respectively.

Traces of TGP were present in all the oil samples examined. Apart from the TGP, another class of oxidative com-

pounds present were the ox-TG. The levels of ox-TG measured in the oils from disk-crushed olives and in those from hammer-crushed olives proved to be statistically different ($p < 0.001$); they were higher when the hammer-crusher had been used with mean values of 0.30% (SD 0.02) for the disk-crusher and 0.36% (SD 0.02) for the hammer-crusher. The statistically greater oxidative degradation of the oils extracted from the hammer-crushed pastes was correlated to the different magnitude in the increase from the baseline crusher temperature to output paste temperature, as mentioned previously. The results from the oven tests also showed that the level of oxidative degradation of the oils obtained by hammer-crushing was greater than that of the oils obtained by disk-crushing (Fig. 5). The amounts of DG measured in the oils extracted from the hammer-crushed pastes were significantly higher ($p < 0.01$) than the amounts measured in the disk-crushed samples (with mean values of 1.12% for the hammer-crushed samples vs. 1.06% for the disk-crushed samples).

The induction time values determined for the oils obtained by disk-crushing were significantly higher ($p < 0.01$) than those measured in the oils extracted from hammer-crushed pastes, with mean values of 20.1 and 19.7, respectively. Moreover, as may be seen in Fig. 6, the induction time values for the oils analysed were significantly and inversely correlated with the levels of ox-TG. This inverse correlation may be ascribed to the different degree of oxidation which occurred during crushing, since the same batch of olives was used and it is in agreement with findings concerning the pro-oxidant activity of ox-TG reported in the literature [21].

The obtained results showed that the different amounts of mechanic energy, transformed into thermal energy, caused by the two different crushers is the major cause of the different behaviour of the oils with respect to oxidation. Besides, it can be assumed that the results may also be influenced by the activity of the enzymes released as a consequence of the rupture of the cells. However, considering that the crushing experiments were carried out on the same batch of olives and that the oils were extracted immediately after the paste was obtained, any difference in the enzyme activity in the two types of oil would be solely due to the different ways of preparation of the olive paste. With the hammer-crusher, in fact due to the presence of a grid in the bottom of the crushing chamber, a greater extent of rupture of the cells is achieved. This can determine a different level of enzymatic activity justifying a higher degree of hydrolytic degradation in the oils obtained using the hammer-crusher than in those obtained by the toothed disk-crusher. Finally, it could also be hypothesised that there is an influence on the results obtained by metals having pro-oxidant activity. With regard

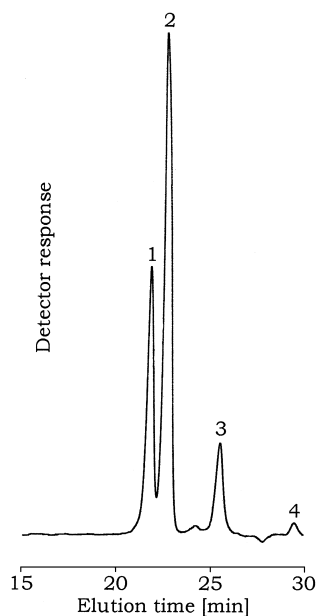


Fig. 4. HPSEC analysis of the polar compounds from one of the virgin olive oil examined.

1) Oxidised triacylglycerols; 2) diacylglycerols; 3) free sterols and triterpene diols; 4) free fatty acids.

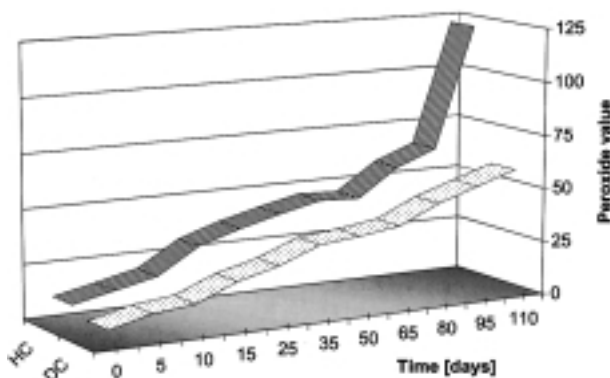


Fig. 5. Accelerated auto-oxidation (60 °C in the dark) of the oils extracted from disk-crushed olive pastes (DC) and hammer-crushed olive (HC) pastes: mean peroxide values of the nine tests performed for each crushers.

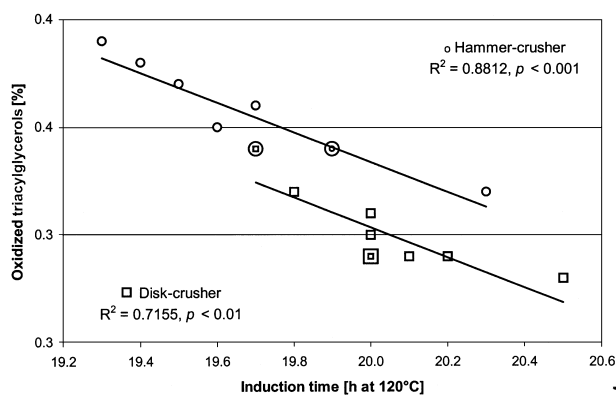


Fig. 6. Induction time versus oxidised triacylglycerols.

to this, it can be assumed that the release of metals from the crushers to the oil is negligible and in any case not significantly different from one crusher to the other due to the following: all parts in contact with the olive paste were stainless steel of high quality; the time of contact between the olive paste and the crushers is very short; the olives were of good quality with a very low free fatty acid levels so that an important corrosion was not to be expected; the temperature of processing during the trials was rather low.

4 Conclusions

The experimental results obtained showed that fast olive crushing with mechanical crushers produces a substantial increase between olive input temperature and paste output temperature. The parameters examined were affected by the rise in temperature and paste preparation by hammer-crushing caused a greater level of oxidative degradation of the oils than did disk-crushing.

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