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Experimental study of solid waste olive's mill: Extraction modes optimization and physicochemical characterization

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ABSTRACT

The main goal of this paper is to study the extraction of the oil from the solid waste after the extraction of virgin olive oil (pomace) of two various mills collected in Batna area. Also, two extractions modes are used: a physical extraction mode (Hydraulic press) and a chemical one. Olive pomace oil is a by-product from the olive oil industry that is still being used in the food industry as a low value vegetable oil. The results obtained are quantitative and qualitative. The first ones show that the best extracted oil quantity obtained is by the chemical way and especially with the mixture "Chloroform/Methanol". This result is the same (12,59-15,91%) with either samples of solid residues from traditional hydraulic pressing system or three-phase centrifugation separation process. The qualitative result obtained shows that the oil extracted by these two modes reveals the significant difference in all the physical and chemical parameters such as the relative density at 20°C, the refractive index, the acid value, the saponification value, the peroxide value and the iodine value. Except the unsaponifiable matter which haven't a difference Crude olive pomace oil needs to be refined and is blended with virgin olive oils before being used as edible oil.

Keywords: Extracted oil, pomace, mill, valorization, physicochemical, characterization, rate

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INTRODUCTION

The olive (*Olea europea* L.) is an evergreen tree, traditionally cultivated for the production of oil and table olives. As regards both wealth and tradition, the olive oil industry is a relevant one, especially in the Mediterranean countries where 97% of the world's olive production is harvested [1].

Olive oil is produced from olives either by means of conventional systems using hydraulic presses or by resorting to modern horizontal axis centrifuges. Both systems produce olive pomace [2]. Olive pomace is the solid residue resulting from the olive oil production process [3], it consists of olive skin, pulp and pits [4,5], containing approximately 5-8% of residual oil [2] that can be economically recovered in the pomace oil industry through extraction with n-hexane [3].

Nowadays, one of the most problematic olive oil waste products is pomace (also known as cake) generates a great environmental impact due to the production of high polluting residues [6]. Several studies have stated the negative effects of these forms of waste on soil's microbial populations [1], aquatic ecosystems [7] and even on the air [8], and constitutes one of the most polluting agricultural by-products in the Mediterranean region [3].

Actually, it is used for animal feed [9], a raw material for glycolipids biosynthesis [10] residual oil extraction, energy recovery, soil amendment or the extraction of valuable polyphenols [11]. Pomace oil is a non-edible oil and its low cost make it an important raw material for biodiesel production [12], also, it is considered an inferior grade and is used for soap [2].

Olive pomace oil is the oil obtained by treating olive pomace with solvents or other physical treatments to obtain crude olive pomace oil, which is not suitable to be used as edible oil. After this crude oil refining, a refined olive pomace oil is obtained, whose free acidity, expressed as oleic acid, has to be not more than 0,3 g per 100 g and other characteristics has to correspond to those defined in European Regulations [5].

The oil extraction is obtained by acting on the pomace with solvents. From where the problem of this work: What is the method of extracting the most effective pomace olive oil in terms of quantity and quality?

MATERIALS AND METHODS

Olive mill solid residue samples

The raw material used in this work was two different samples of solid residues, each from traditional hydraulic pressing system and three-phase centrifugation separation process for obtaining olive oil. They were collected from olive mills in N'gaous aera (Batna-Algeria) (Figure 1).

Figure 1: Area sampling « N'gaous » (Batna town, Algeria)

The olive residue was collected just after the pressing operation and immediately packaged plastic containers. This rustic variety represents more than 40% of the national orchard. It is characterized by its small fruits (2,5 g) and it is considered as being better quality oil. The initial moisture content was determined by drying in a oven at 70° C until reaching constant weight [13].

Reactants

The chemical reactants were used as well as their purity so, petroleum ether, hexane, ethanol, methanol and hydrochloric acid were purchased from "Biochem-Chemopharma", phenolphthalein and potassium hydroxide were obtained by "Fluka-Chemika".

Cyclohexane, Wijs reagent, thiosulfate sodium, chloroform, acetic acid and potassium iodide were purchased from "Fisher-Scientific", "Redel-de-Haën", "Windsor Laboratories Limited-Berkshire", "Cheminova International", "Sigma" and "Merk-Darmstadt".

Extraction modes

Physical process mode

The pomace oil is obtained with a vertical manual screw hydraulic press (Figure 2). The construction of this hydraulic press designs has been thoroughly studied and described in the literature [14], at our *Food Technology Department. Institute of Veterinary and Agronomic Sciences. Hadj Lakhdar University, Batna. Algeria*.

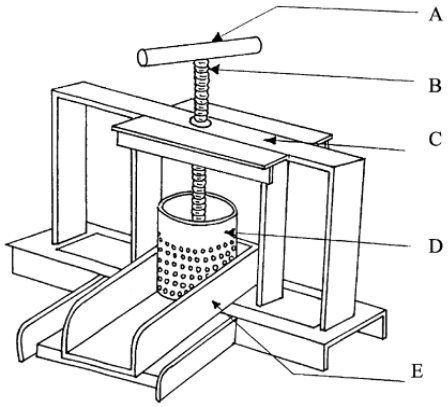

Figure 2: Manual screw press for oilseeds MC 2000 AUF (Scale: 1:7)
(a) Lever, (b) Spindle, (c) Framework, (d) Supply tank, (e) Oil collecting tray [14]

To press, the olive pomaces are left sodden in order to facilitate their pressing. This residue was put in a small cotton sack, introduced in the extraction component in the manual screw press (AC AUF 2000) and pressing was carried out as described by [14]. The characteristics of this press have been reported in a previous work [14]. The oil obtained was separated by decantation, and then the yield is calculated.

***Chemical process* mode**
The oil extraction is carried out by "Soxhlet" method for the determination of fat in dried solid foods [15] with a "Gerhardt Soxtherm 2000" device. It is done by repeat extraction with several non-polar organic solvents on dry olive residue.

As already stated, initial water content of three-phase mill pomace are lower than those of traditional hydraulic press mill residue 22,26±0,39% and 44,98±0,36% respectively (Figure 4).

The olive oil pomace (20 g) was defatted with petroleum ether, hexane and mixture of chloroform/ methanol with the following proportion respectively: 100-0, 75-25, 50-50, 25-75, 0-100%.

Physicochemical characterization of extracted oils
Physical parameters measurement
⅄ *Relative density* was measured according to Kohl Method [16]. It is the ratio of the oil's mass to the water's mass of a same volume under specified conditions of pressure and temperature.
⅄ *Refractive index* was determinate according to *NFT 60-212* [17]. Measurements are done using a suitable refractometer at a constant temperature of 20°C.

Chemical indices measurement
✦*Determination of the acid value*
For the determination of the total free fatty acid content in the oil, the titrimetric method described in Method *NFT 60-204* [18] was applied. The free fatty-acids were neutralized with potassium hydroxide (0,2 mol/l).

⅄ *Determination of the saponification value*
The determination was estimated according the *NFT 60-206* [19]. The oil pomace was poured into the bottle and heated in a boiling water-bath under reflux with an ethanolic solution of hydroxide potassium. The excess of hydroxide potassium is titrated with hydrochloric acid (0,2 mol/l).

✦*Determination of the iodine value*
It is measured according the *AOCS Cd Id-92* [20], by adding to the oil residue an excess of iodine monochlorure solution (or Wijs reagent) and a mixture (acetic acid and cyclohexane). After 15 minutes of the reaction time given in dark, the iodine released in a mixture of potassium iodide and water is titrated by a thiosulfate sodium solution.

✦*Determination of the peroxide value*
The peroxide value was determinate according the *NFT 60-220* [21]. Treatment of the oil in solution with acetic acid and chloroform by a potassium iodide solution. Then, titration of the released iodine with a thiosulfate sodium (0,01 N).

✦*Determination of unsaponifiables matter*
The term "unsaponifiable matter" refers to those substances present in oils that are not saponified by alkali hydroxides and are extractable into ether. They are estimated by the *NFT 60-205* [22]. After complete oil saponification, they were extracted using a solvent, and then evaporated under vacuum until obtaining a dry residue.

Data processing
The data obtained after deferent analyses are treated statistically by analysis of variances and multiple comparison of Duncan test. Software SPSS Statistics 20 is used.

RESULTS AND DISCUSSION

Oil yield
The result showed that the oil content of the two residue samples are understood 4,36±0,45 and 15,91±0,13% for all extraction methods (Figure 4). These values are conformed to those published by the European Comission [23] (8-12%), (Table 1).

These results show that methanol, a polar solvent extracts more oil than, ether, hexane and chloroform. The oil yield increases with the addition of methanol in chloroform. This yield is better with the mixture "Chloroform/Methanol 25-75%" for both samples: 15,91±0,13% for the three-phase mill pomace and 12,59±0,16% for the traditional hydraulic press one.

It was found that the most effective process (Method) is the chemical one.

Table 1: Humidity and extraction rate of the pomace olive

Residue origin	Humidity	Extraction methods	Extraction rate
Three-phase mill	22,76±0,26	Physical	05,21 ± 0,33
		Chemical	
		• Hexane	12,05 ± 0,11
		• Petroleum ether	08,31 ± 0,35
		• Mixture« Chloroform/Methanol »	
		✦ 100/0	09,25 ± 0,22
		✦ 75/25	12,60 ± 0,66
		✦ 50/50	13,97 ± 0,18
		✦ 25/75	15,91 ± 0,13
		✦ 0/100	13,35 ± 0,29
Traditional hydraulic press mill	44,64±0,40	Physical	04,36 ± 0,45
		Chemical	
		• Hexane	09,90 ± 0,20
		• Petroleum ether	05,94 ± 0,17
		• Mixture « Chloroform/Methanol »	
		✦ 100/0	07,52 ± 0,43
		✦ 75/25	09,40 ± 0,15
		✦ 50/50	10,39 ± 0,19
		✦ 25/75	12,59 ± 0,16
		✦ 0/100	11,47 ± 0,17

Physicochemical characteristics of extracted oils
This physicochemical characterization was carried for oils extracted by hydraulic press (Physical method) (Figure 2) and the mixture "Chloroform/Methanol 25-75%" (Chemical method). This characterization is presented in Table 2.

Table 2: Several oils extracted

Oils	Signification
E.O.1	Oil extracted by pressing the pomace coming from the three-phase mill
E.O.2	Oil extracted by pressing the pomace coming from the traditional hydraulic press mill
E.O.3	Oil extracted by the mixture "Chloroform/Methanol 25-75%", the pomace coming from the three-phase
E.O.4	Oil extracted by the mixture "Chloroform/Methanol 25-75%", the pomace coming from the traditional hydraulic press mill

Physical parameters: Relative density and refractive index
The results of relative density and refractive index of the four oils studied were presented in Table 3. In the analyzed oils, the refractive indices at 20◦C were 1,4680 to 1,4655 ($p<0,05$). While referring to the vegetable oils classification [24] , we note that this index fell in the range of (1,468-1,472) oils rich in oleic acid, major fatty acid in olive oil, which ranges between 63,5 and 77,5% (IOC, 2001) [25].

These values are consistent with those found for conventional oils such as cotton (1,458–1,466) and maize (1,465–1,468) [26].

They revealed a significant difference ($p<0,05$) at the interval [0,910-0,916] for the relative density and at the interval [1,4680-1,4707] for refractive index of the olive-residue oil [27].

The values of the relative density of the extracted oils by press (Mechanical method) for (E.O.1 and E.O.2) both of them presented the higher value compared to the two other oils (E.O.3) and E.O.4) extracted by chemical process ($p<0,05$) (Figure 5).

Chemical parameters

Table 3 and figure 6 present the evaluated chemical characteristics in oils extracted from solid waste olive.

Table 3: Physicochemical characterization of extracted olive pomace oils

Origin	Extraction method	Extracted oil	Physicochemical characterisation						
			RD	**RI**	**AV**	**SV**	**IV**	**PV**	**UR**
	Physical	E.O.1	$0,914^{a}$ ± 0,00	$1,470^{c}$ ± 0,00	$6,76^{d}$ ± 0,02	$185,72^{c}$ ± 0,15	$76,91^{b}$ ± 0,12	$6,5^{c}$ ± 0,16	$1,00^{a}$ ± 0,02
Three-phase mill	Chemical	E.O.2	$0,910^{b}$ ± 0,00	$1,469^{b,c}$ ± 0,00	$6,86^{c}$ ± 0,05	$186,29^{c}$ ± 0,77	$77,86^{c}$ ± 0,08	$7,12^{d}$ ± 0,13	$1,07^{a}$ ± 0,06
Traditional hydraulic press mill	Physical	E.O.3	$0,914^{a}$ ± 0,001	$1,467^{a}$ ± 0,00	$6,31^{a}$ ± 0,02	$180,58^{a}$ ± 0,16	$78,43^{d}$ ± 0,12	$5,99^{ab}$ ± 0,12	$1,06^{a}$ ± 0,03
Significance level	Chemical	E.O.4	$0,913^{b}$ ± 0,00	$1,469^{b}$ ± 0,00	$6,50^{b}$ ± 0,00	$184,08^{b}$ ± 0,56	$76,29^{a}$ ± 0,14	$5,25^{a}$ ± 0,09	$1,14^{b}$ ± 0,01
			0,001	0,001	0,000	0,000	0,000	0,000	0,13

RD : Relative Density at 20°C, RI : refractive Index, AV: Acid Value, SV: Saponification Value, PV: Peroxide Value, IV: Iodine Value, UR: Unsaponifiables Matter

Acid value is an important index of physicochemical properties, being indicative of age, quality, edibility and suitability of oils [28]. The oils (E.O.1) and (E.O.2) content showed free fatty acids significantly higher than that of the oils (E.O.3) and (E.O.4) ($p<0.05$).

The determined acid value was less than 6,51 mg KOH/g, for (E.O.3) and (E.O.4) oils, and it is in accordance with the Codex Alimentarius Committee [26], which allows a maximum of 6,6 mg KOH/g to crude vegetable oils, although, (E.O.1) and (E.O.2) oils.

Their high acid value is indicative of oil becoming rancid due to the degradation of triacylglycerols caused mainly by enzymes, and catalyzed by physical agents such as light energy and/or heat, or injuries in the fruits from which the oil was extracted [29].

Saponification value (mg KOH/g) gives an idea of the average molecular weight or the chain length of all the acids present. Higher the molecular weight, the lower the saponification value and being inversely related [28]. The saponification value of the four oils was in accordance with the Codex Alimentarius Committee [26], which defines an interval [182-193] for refined olive-pomace oil. This high saponification value is suggestive of the presence of high molecular weight fatty acids in it.

The iodine value is an empirical test that indicates the unsaturation degree of oil [29]. The variation of this value due to the samples origin and the extraction mode, is highly significant ($p<0,01$). The four extracted oils present different unsaturation values are below than 79 g I_2/100g oil.

The peroxide value (mEq/kg) of oil is used as a measurement of the extent of rancidity reactions. Air, or specially oxygen in the air, can react with the oil and form various peroxide components which eventually affect odor, flavor and quality. Lower the peroxide value, the fresher the oil would be [29].

The International Olive Council [25] determines for refined olive-pomace oil a maximum peroxide value of 10 meq O_2/kg. The all analyzed oils presented peroxide value below 10 meq O_2/kg (5,25 to 7,12 meq O_2/kg). So, all oils didn't expose to oxidative process either during the preparation of the raw material, extraction or storage.

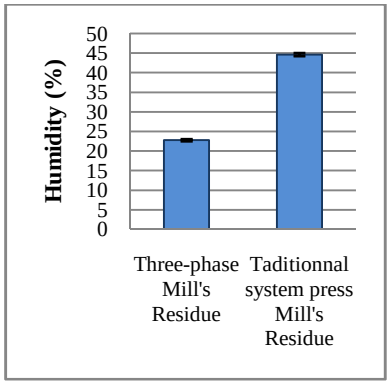

Figure 3: Humidity of olive residue

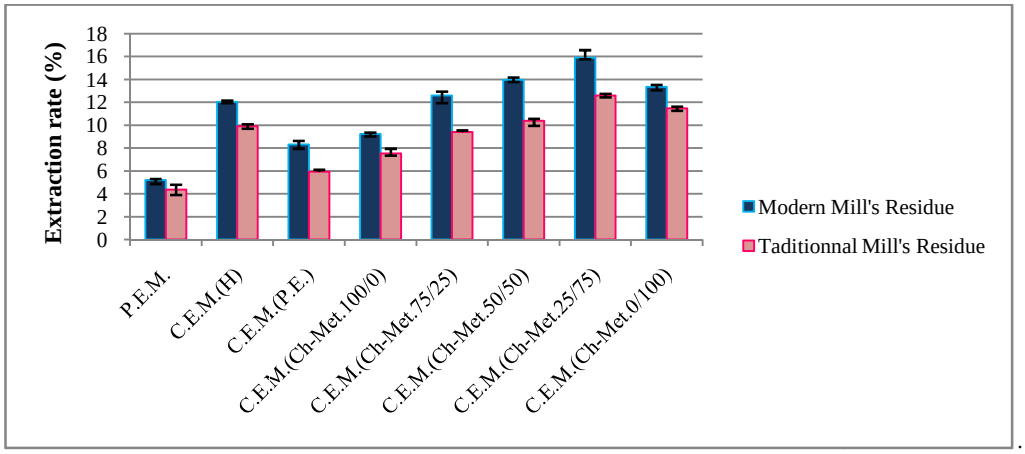

Figure 4: Oil yield (%) of olive residue

P.E.M.: Physical extraction method using hydraulic press
C.E.M.(H): Chemical extraction method using hexane
C.E.M.(P.E.): Chemical extraction method using petroleum ether
C.E.M.(Ch.-Met.100/0): Chemical extraction method using the mixture "Chloroform-Methanol" with 100/0
C.E.M.(Ch.-Met.75/25): Chemical extraction method using the mixture "Chloroform-Methanol" with 75/25
C.E.M.(Ch.-Met.50/50): Chemical extraction method using the mixture "Chloroform-Methanol" with 50/50
C.E.M.(Ch.-Met.25/75): Chemical extraction method using the mixture "Chloroform-Methanol" with 25/75
C.E.M.(Ch.-Met.0/100): Chemical extraction method using the mixture "Chloroform-Methanol" with 0/100

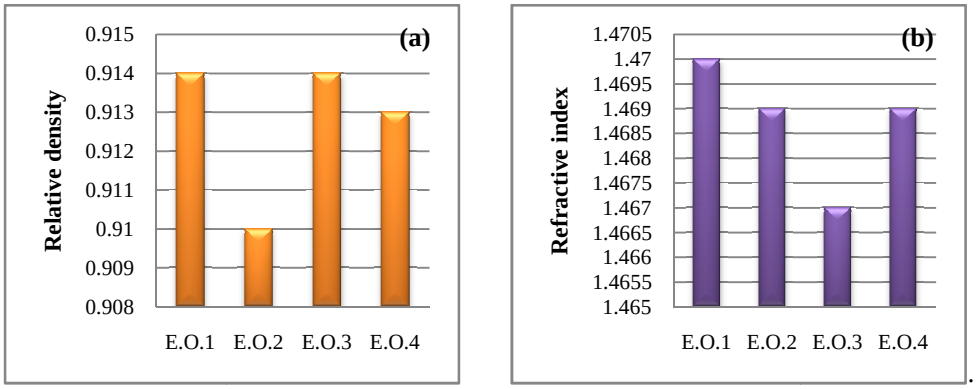

Figure 5: Physical parameters of extracted oils
(a) Relative density at 20°C, (b) Refractive index

The unsaponifiable matter corresponds to compounds present in oils which after saponification with alkali are insoluble in aqueous solution. These compounds may include impurities, such as mineral oil or substances naturally present in oils as sterols, tocopherols and carotenoids [29].

The minor compounds composition do not reveal a significant difference (p>0,05). All oils present a content less than 2,5% in according with the International Olive Council [25].

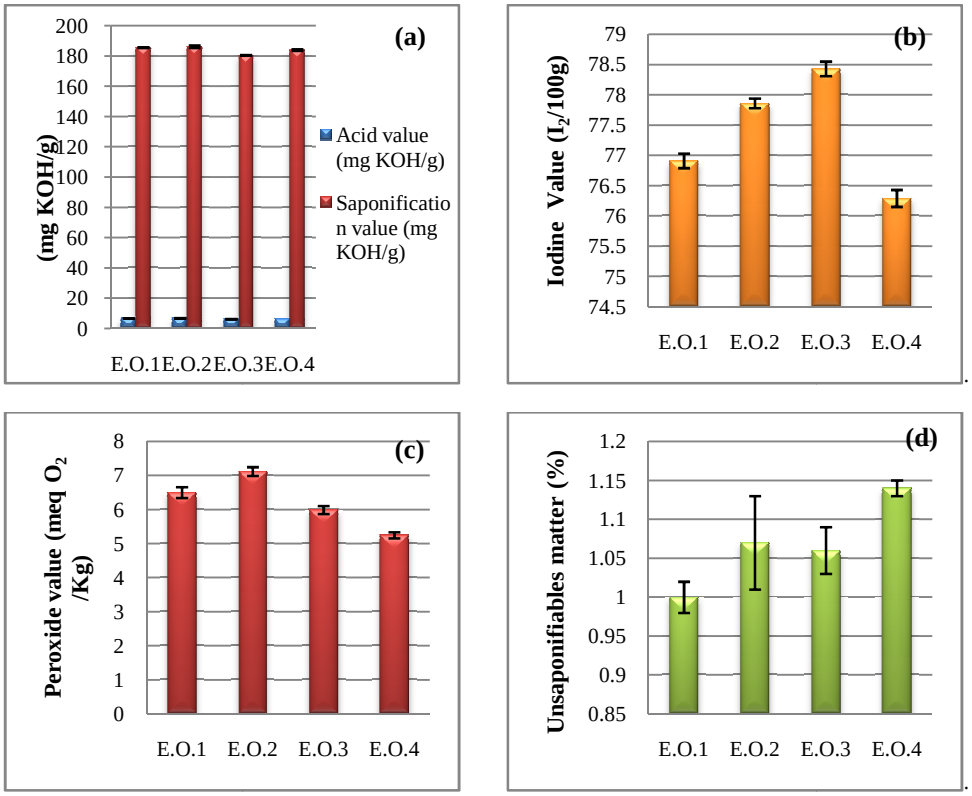

Figure 6: Chemical parameters of extracted oils
(a) Acid and Saponification value, (b) Iodine Value, (c) Peroxide Value, (d) Unsaponifiables Matter

CONCLUSION

From the results of the present study, it may be concluded that the variations in % oil yield and physicochemical parameters of the extracted essential oils could be attributed to the extraction methods.

Compared the two oil extraction methods from solid-waste olive residue; physical mode (Hydraulic press “AC AUF 2000”) and chemical one (using petroleum ether, hexane and mixture "Chloroform / methanol"), the chemical way provided high extraction yield.
In fact, the highest quantity is obtained by the mixture "Chloroform / Methanol 25-75%" is 15,91 ± 0,13 and 12,59 ± 0,16 for the three phase centrifugation and hydraulic system press residues respectively, against 05,21 ± 0,33 and 04,36 ± 0,45 of the three phase centrifugation and hydraulic system press residues extracted by “AC AUF 2000” press.

Despite the performance development exhaust systems for olive oil extraction, pomace still contains a significant amount of oil, which can go up to 15,91 ± 0,13, which makes their valorization necessary and very interesting.
Physicochemical parameters analysis of olive residue oils extracted reveals a significant difference (p <0,05) between these results, which reveals the heterogeneity of the two extraction methods. Parameters (relative density at 20°C, refractive index, acid value, saponification value, peroxide value, iodine value) influence the quality of these oils.

Also, this analysis indicates that the only parameter that showed no significant difference (p <0,05) is the unsaponifiable matter for all the extracted oils. The effort of valorization of this vegetable oil must be continued, because it would allow positive impact of economic benefit to local populations.

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