Microwave Assisted Extraction of Olive Oil Pomace by Acidic Hexane

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ABSTRACT: *In this study, Microwave Assisted Solvent Extraction (MASE) was used to recover oil residues from pomace olive using acidic hexane. Results obtained demonstrated that oil extraction yield increased with time, amount of acetic acid in hexane and power radiation. For both radiation powers used (170 and 510W), the optimal extraction time and most interesting content of acetic acid in hexane are 1.5 minutes and 5.0% respectively. Oil yield obtained at power 510 W was slightly higher than those corresponding to 170 W. Compared to results obtained with pure hexane, the yield increases were 8.4 % at 170 W and 6.0% at 510 W. However, the oil extracted from pomace olive was found to be of poor quality; indeed only phenolic compounds concentration increased significantly with acetic acid content.*

KEYWORDS: *Microwave; Oil extraction; Olive pomace; Oil characterization; Acidic hexane.*

INTRODUCTION

Mediterranean countries harbour nearly 98% of the world production of olive oil. Oil extraction by mechanical pressure generates large amounts of organic wastes of various compositions depending on the production process used. The obtained by-products are solid (olive cake) and liquid (olive mill wastewater)

Algerian olive cake production was estimated at 60,000 tons [1]. This waste, together with olive mill wastewaters can seriously spoil the environment because of their contents in phenolic compounds [2]. Waste residual oil (about 8%) usually recovered by solvent extraction is of significant economic interest [3-4]. Hexane is the main solvent used in solid-liquid extraction step [5].

Microwave heating is increasingly used for promoting solvent extraction of various compounds from solid wastes. The absorption of microwave energy in mixtures depends both on the nature of the solvent and the solids to be treated. When the solid phase does not absorb microwave radiation (because of a low dielectric constant) then a solvent is needed which effectively absorbs microwave energy (a high dielectric constant solvent). In the reverse case, the use of a microwave transparent solvent will let the solids absorb the radiation in a homogeneous way.

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The past decade has seen reports emerging on the successful use of MASE for oil extraction from vegetable biomass as an alternative to the conventional solvent extraction [6-8]. MASE is driven by several advantages including energy savings, reduced solvent consumption, more selective extraction, better yields and more homogeneous treatment. Addition of acetic acid in hexane is also known to improve efficiency of oil extraction from solids [9-10]. This work aimed to perform MASE on olive cake, combined with acetic acid addition to modify solvent polarity. The main objectives were to monitor the effect of acetic acid in hexane, to evaluate the role of microwave power on the yield and investigate the physicochemical parameters of the recovered oil.

EXPERIMENTAL SECTION

Materials

Olive pomace

Pomace olive samples used in this study were obtained from ''Ifri olive mill'' located at Bejaia (Algeria). This oil mill is equipped with centrifugation system with three phases. The olives processed were of the "Chemlal'' variety. The initial pomace humidity of 48.3 ± 0.4 % was brought down to 6.0 ± 0.5 % by gentle heating in an open air oven. The total residual oil content of 7.0 ± 0.3 % was determined by prolonged soxhlet extraction. The olive cake was used without further grinding. All extractions were carried out with technical grade hexane (95% purity).

Method

Microwave Assisted Solvent Extraction (MASE)

The microwave assisted solvent extraction system used [8] comprised an agitated reactor placed inside a microwave oven. The microwave oven (Whirlpool, model MWO611) operating at 2450 MHz had a maximum power of 850W adjustable by 170W increments and was modified by us to insert the mechanical agitator. The interior dimensions were 220 mm × 354 mm × 358 mm. Extractions were carried out in cylindrical glass vessels of 1000 mL volume. Solids were separated from the resulting oil miscella by vacuum filtration. Oil was recovered by solvent distillation under reduced pressure, the residual solvent being removed by oven drying at 103 ± 1°C.

Oil yield reported corresponds to the average of three experiments. Each batch consisted in 50 g of olive cake. The operating conditions were: Liquid to Solid ratio L/S =3 cm^3/g; stirring speed 400 rpm; radiation power 170 and 510 W; extraction times 0.25 to 3.0 mn and acetic acid content in hexane AA: 0.0 to 7.5 % (v/v). For microwave power 510 W and acetic acid content 7.5 %, the extraction time of 3 min could not be used because of solvent loss due to boiling

Oils analysis

Extracted oils were investigated for: acidity, specific absorbance, polyphenols content and peroxide index. Each result presented corresponds to the average of three experiments.

Acidity

French standard assay used [11] was based on dissolution of an aliquot in a 1/1 v/v mixture of ethanol and diethylether followed by titration with sodium hydroxide to reach the end point for free fatty acids.

Specific absorbance

An UV-visible spectrometry (Shimadzu 1601 PC double beam) was used to measure the absorbance at 270 and 232 nm for oils dissolved in pure hexane, according to the French standard [12].

Peroxide index

Peroxide index was determined according to French standard [13]. The method consisted in treating a test sample dissolved in solution constituted by acetic acid and chloroform with potassium iodide. The liberated iodine was then titrated with a sodium thiosulfate solution in presence of starch as end point indicator.

Phenolic compounds

Determination of the total phenolic compounds level in extracted oils was realized using Folin-Ciocalteu colorimetric reaction method [14]. The reagent consists of phosphotungstic acid and phosphomolybdic acid mixture. The oxidation of phenols reduces this reagent into tungsten and a mixture of molybdenum blue oxides.

Variance analysis (ANOVA)

In order to identify the factors and the interactions which have a significant effect at level 5% on the yield and the oil analysis (acidity, specific absorbance,

peroxide index…), the two-way variance analysis based on Fisher test was used [15, 16]. The two-way analysis of variance (ANOVA) is an extension of the one-way ANOVA that examines the influence of two different categorical independent variables on one continuous dependent variable. The two-way ANOVA not only aims at assessing the main effect of each independent variable but also if there is any interaction between them.

RESULTS AND DISCUSSION

Oil extraction

Extraction yield results are illustrated in Figs. 1 and 2. Both figures demonstrate that oil yield increased with extraction time and acetic acid content in hexane. Also, whatever the radiation power used, the acetic acid content AA = 5% and a contact time t =1.5 min was sufficient to attain the best performances.

The results reported in Fig. 3 indicated that the radiation power barely had a positive influence on the oil yield.

Also, it can be noted that, at t = 1.5 min, the increase in the yield at P = 170W was 8.4 % when pure hexane (without acid) was replaced by acidic hexane (5%). This increase was only 6% at P = 510W.

Table 1 gives the two-way ANOVA corresponding to the experimental data given in Figs. 1 and 2 (every result is the average of three experiments). These results confirm the effect of extraction time t and acetic acid content (AA) on the yield for the two radiation powers used. The interaction t-AA is only significant for P= 170 W (F= 7.45 and Fc= 1.99).

The independence tests (data no reported) indicate that the yield depends on the radiation power P (F= 153.94 and Fc= 4.20). The interaction effect t-P is not significant (F= 0.84 and Fc= 2.45).

As proposed in previous reports [8, 17], the yield increases due to microwaves can be explained by the sudden increase in temperature causing cellular disruption resulting in release of oil entrapped in cells and easier dissolution in solvent. Increased power accentuates the cell wall destructions thus releasing more oil [18-20].

In our case, the microwave radiations effects were combined with those of acetic acid, thus accelerating disruption of cells and oil release [21]. Hensarling and Jacks [9-10] similarly observed that an addition of acetic acid to hexane increased oil extraction yield from oilseeds.

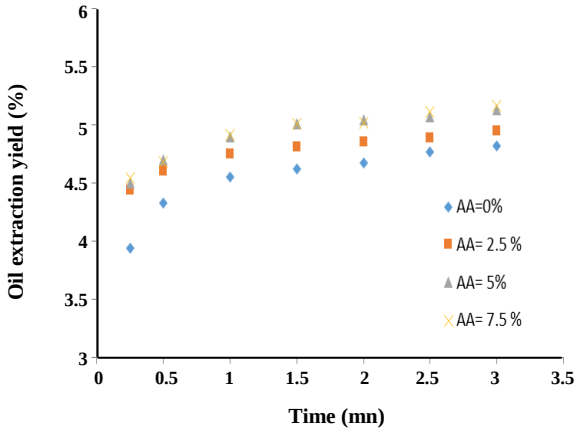

Fig. 1: Oil extraction yield according to time (mn) at P = 170 W.

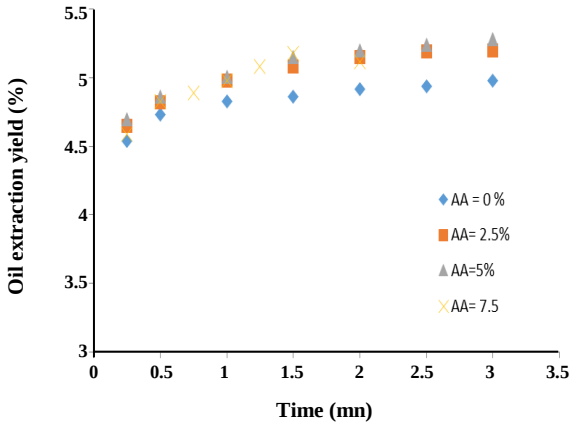

Fig. 2: Oil extraction yield according to time (mn) at P = 510 W.

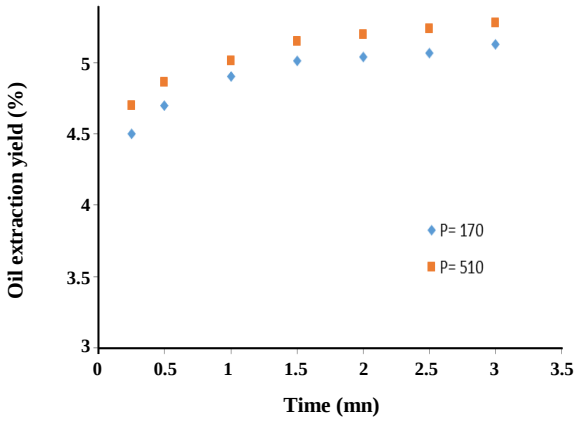

Fig. 3: Oil extraction yield according to time (mn) for acetic acid content of 5 %.

Table 1: Two-way analysis of interaction between time extraction and acetic acid content at P= 170W.

Source	Sum of Squares	Degrees of Freedom	Mean of Squares	F	F critical
Rows	1.600	2	0.800	400.00	3.22
Columns	2.969	6	0.495	247.50	2.32
Cells (interaction)	0.192	12	0.016	8.00	1.99
Within groups	0.090	42	0.002		
Total	3.849	62			

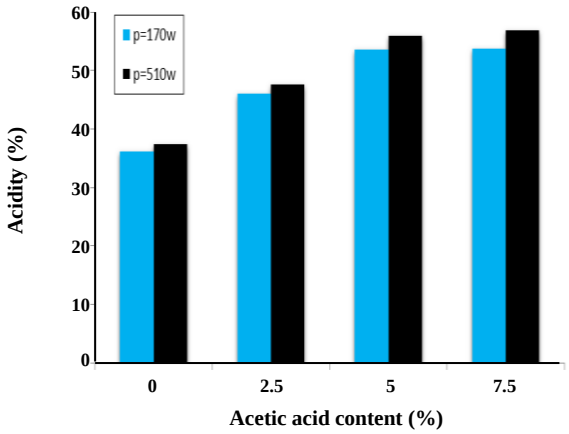

Fig. 4: Acidity (%).

Extracted oils analysis

Acidity

The acidity of extracted oil increased with acetic acid content in hexane solvent. At AA= 5%, the oil acidity increased by 48% at P=170W and 50% at P=510W. These results shown in Fig. 4 illustrates this tendency. The two-way ANOVA confirms that the acidity depends on AA (F=5.77, Fc= 4.49) and P (F= 105.10, Fc= 4.49). The interaction AA-P is not significant (F= 0.25 and Fc= 3.24).

Increased acidity was probably due to triglycerides hydrolysis by presence of acetic acid in hexane and to temperature elevation caused by irradiation time. These observations were reported by earlier studies conducted on oil extracted from olive foot cake by acidified solvent in soxhlet apparatus and stirred reactor [22-23].

The acidity increase with microwave radiation power was also found [20] in oils extracted from castor bean. Increasing acidity of extracted oils from soybean in soxhlet apparatus with acetic acid content [24] was less important than that observed in our study.

Specific absorbance

The specific absorbance values at 232 and 270 nm are given in Tables 2 and 3. These values increase at the same time with acetic acid content and microwave radiation power.

When acetic acid content in hexane was greater than 2.5 %, the absorbance at 232 nm (Table 1) did not show any variation. On other hand, absorbance at 270 nm (Table 2) increases significantly with acetic acid content and microwave power.

The independence tests confirm that the specific absorbance at 232 and 270 nm depends on the P and AA. The interaction effect P-AA is only significant for P= 170 W.

Portuguese olive oils have the same characteristic after heating under microwave radiation [25].

Peroxide index

Peroxide index values are given in Fig. 5. These values increase with acetic acid content in hexane and microwave radiation power. The two-way ANOVA confirms that the peroxide index depends on AA (F= 134.65, Fc= 3.24) and P (F= 161.55, Fc= 4.49). The interaction AA-P is also significant (F= 4.05 and Fc= 3.24).

The oxidation state of oils extracted with microwaves was higher at power P= 510 W than at 170 W. The increase of peroxide index with 510 W remained weak for 2.5 % of acetic acid in hexane.

The negative effect of microwave heating on olive oil quality was observed by Malheiro and co-workers [25]. These authors investigated the effect of microwave heating duration on the peroxide index values of three Portuguese olive oils.

Phenolic compounds content

As shown in Fig. 6, phenolic compounds content in extracted oil increased with acetic acid content in solvent and with microwave radiation power. At AA= 5 %

Table 2: Specific absorbency at 232 nm.

	Acetic acid content (%)			
Power radiation (W)	0.0	2.5	5.0	7.5
170	1.48	3.23	3.94	3.97
510	2.86	3.68	3.94	3.97

Table 3: Specific absorbency at 270 nm.

	Acetic acid content (%)			
Power radiation (W)	0.0	2.5	5.0	7.5
170	0.34	0.60	2.11	2.64
510	0.60	0.64	2.24	2.91

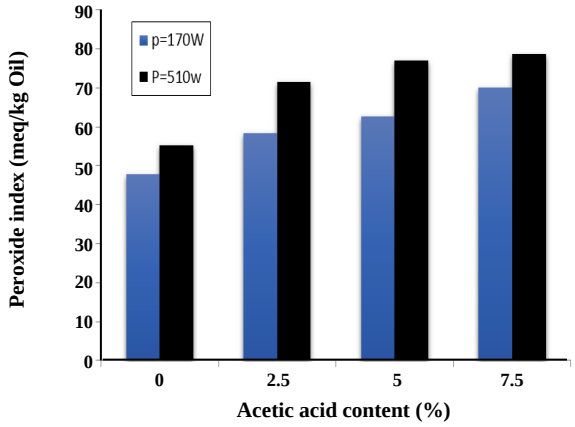

Fig. 5: Peroxide index (meq/Kg Oil).

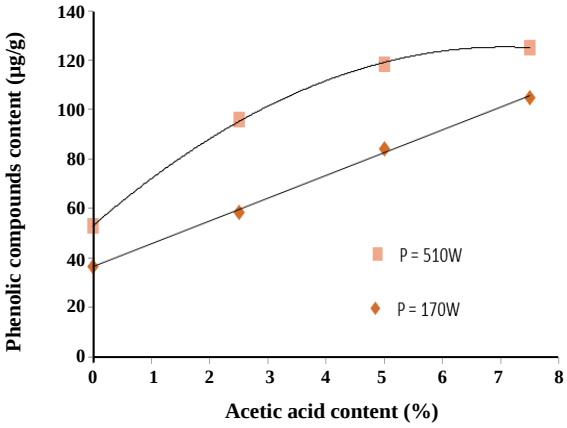

Fig. 6: Phenolic compounds content (ppm).

(which reaches maximum oil yield), phenolic compounds content increased by 130% at P=170W and 223% at P=510W. Additionally, phenolic compounds content is proportional to acetic acid content at P=170W. For P=510W, beyond AA=5%, phenolic compounds content increase is not significant.

The independence tests (results no shown) indicate that the phenolic compounds content depend on P (F= 1471.49, Fc= 4.49) and on AA (F= 1898.96, Fc= 3.24). The interaction effect P-AA was also significant (F= 53.12 and 3.24).

The increased content of phenolic compounds could be related to solvent polarity which increases with addition of acetic acid in hexane. Phenolic compounds being more polar, their extraction is then favored by polar solvents.

Total polyphenols content obtained in our case was within the range (44 - 157 µg/g of oil) reported by *Gutfinger* [14] for Israeli oils extracted by pressing. In contrast, our values were lower than those reported by *Ramezani Kharazi* [26] (261- 453µg/g of oil) for three olive oils of different cultivars. In addition, as reported previously [27], *Rafiee et al.* [26] showed that phenolic compounds extraction under microwave was more effective than conventional extraction.

CONCLUSIONS

The time, acetic acid content in hexane and irradiation power has positive influence on performance of olive oil extraction from pomace. The increase in extraction yield is attributed both to microwave heating which causes rupture of vegetable cells to release oil, and to solvent polarity which increases with acetic acid presence.

For both irradiation powers used, the more interesting acetic acid content allowing best oil yield was 5.0 %.

Oil quality was altered by presence of acetic acid in hexane and by microwave irradiation power as found by acidity, specific extinctions at 232 and 270 nm and peroxide index values.

Despite their low quality, such oils, rich in polyphenols, could be valorised in non-food uses such as in cosmetics, soap manufacturing and pharmacology.

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