Journal of
Food Process Engineering

Journal of Food Process Engineering ISSN 1745–4530

OPTIMIZATION OF MICROWAVE PRETREATMENT VARIABLES FOR CANOLA OIL EXTRACTION

L.B. RAMOS[1], R.J. SÁNCHEZ[1], A.K. DE FIGUEIREDO[1], S.M. NOLASCO[1] and M.B. FERNÁNDEZ[1,2,3]

[1]Núcleo TECSE, Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, Olavarría, Argentina
[2]CIFICEN, Universidad Nacional del Centro de la Provincia de Buenos Aires – CONICET, Tandil, Argentina

[3]Corresponding author.
TEL/FAX: +54 (2284)451055/56;
EMAIL: mbfernan@fio.unicen.edu.ar

Received for Publication February 24, 2016
Accepted for Publication May 18, 2016

doi:10.1111/jfpe.12431

ABSTRACT

The influence of microwave pretreatment on the oil yield (solvent extraction) and oil quality of canola was studied. Response surface methodology was used to analyze the variables of microwave pretreatment, working with two microwave powers 80 and 100% (457 and 607 W, respectively, referred absorbed power of 1 L of water). The independent variables were initial moisture content (5–10% dry basis) and pretreatment time (10–350 s), considering five levels. Second-order polynomial equations were used for oil yield, and first-order polynomial for final moisture content. The response models obtained were validated with independent experiments. Under optimal pretreatment conditions, no significant differences were detected in acidity, fatty acid profile and tocopherol content between the unpretreated and pretreated samples. However, significant differences were observed for peroxide index.

PRACTICAL APPLICATIONS

Canola oil is classified as one of the healthiest vegetable oils due to its fatty acid composition (low in saturated fatty acids and high in essential fatty acids). Vegetable oils are conventionally obtained by pressing or solvent extraction, the latter being the more efficient method. However, the use of organic solvents has some disadvantages such as health and safety issues, emission of volatile organic compounds, high operating costs and poor oil quality caused by the high temperatures of the process. Microwave pretreatment applied to canola seeds is a new technique that offers shorter processing times and lower energy consumption and provides better yields within short times and with reduced solvent use in the extraction step, maintaining the quality of the oil.

INTRODUCTION

Canola oil is considered one of the healthiest vegetable oils due to its fatty acid composition (low in saturated fatty acids and high in essential fatty acids). It also contains significant levels of phytosterols, which are well-known cholesterol absorption inhibitors, thus contributing to reduced cholesterol levels and high concentrations of tocopherols (700 ppm) (Fernández *et al.* 2012). Oil extraction from oilseeds is conventionally carried out by mechanical pressing and/or solvent extraction (hexane) methods. In the last few decades, there has been an increasing demand for new pretreatment and/or extraction techniques that shorten the extraction times and reduce the use of organic solvents, in turn reducing pollution. These pretreatments include microwave radiation, ultrasound technology and enzymatic pretreatments. In oilseeds, the oil is inside the membranes (Aguilera 2003) constituting the fatty bodies, and it is necessary to break up those membranes to release the oil. The purpose of the pretreatments is to modify or cause the rupture of that cellular structure in order to increase the extraction yield. Microwave radiation offers reduced processing times and energy savings, because the energy is delivered directly to materials through molecular interaction with the electromagnetic field, so that the heat is generated throughout the volume of the material

and it is possible to achieve rapid and uniform heating of relatively thicker materials (Uquiche *et al.* 2008). Uquiche *et al.* compared the microstructure of Chilean hazelnuts treated and untreated by microwave, and they found a change in the cellular walls of the treated nuts, which resulted in an increased porosity of the cells. Azadmard-Damirchi *et al.* (2010) reported that the microwave pretreatment increased the yield of canola oil extracted by pressing. Niu *et al.* (2012) studied the moisture-dependence of canola with microwave pretreatment time, and they observed an inverse relationship between the moisture content of the seed and exposure time to microwaves for a moisture range of 4.16–10% db (dry basis). However, no studies were found in the literature on the influence of microwave pretreatment on the yield of solvent extracted oil. On the other hand, recent studies reported the formation of a strong phenolic antioxidant and antimutagenic compound named canolol (4-vinyl 2,6 dimethoxyphenol) in canola pretreated by microwave radiation (Spielmeyer *et al.* 2009). It has been suggested that canolol is formed by decarboxylation of the sinapic acid during the thermal pretreatment, increasing its concentration up to two orders of magnitude (Wakamatsu *et al.* 2005). The presence of this compound in the extracted oil as a result of the microwave pretreatment brings an added value to the use of this technology.

In the present work, the effect of the microwave pretreatment of canola seeds on the yield of solvent extracted oil was studied, optimizing the process variables (initial moisture content and pretreatment time) by response surface methodology. Oil quality was determined by analyzing the acidity index, peroxide index, fatty acid profile and tocopherol content.

MATERIALS AND METHODS

Sample Characterization

Hornet variety canola sample (15 kg) was obtained from the local market. The seeds were stored at temperatures below 8°C until further use. They were characterized according to the standard methods for determining moisture (ASAE S352.2 DEC 97 [ASAE 1999] and AOCS Ba 2A-38) and protein content (AOCS Ai 4-91 [AOCS 1993]) using a BÜCHI distiller (Model 435, Switzerland).

The extracted oil was evaluated in terms of acidity according to IUPAC method 2.201 (IUPAC 1992), peroxide index according to AOCS method Cd 8 (AOCS 1993) and fatty acid composition (determined by gas chromatography (Izquierdo *et al.* 2002). Tocopherol concentration in the oil was determined by normal-phase ultra-high-performance liquid chromatography (UHPLC) following AOCS standard method Ce 8-89 (AOCS 1997). A Dionex Ultimate 3000 chromatographer (Thermo Scientific, Germany) with fluorescence detector (Agilent, 1100 Series Fluorescence Detector G1321A, Palo Alto, CA, Germany) with excitation/emission wavelength 290/330 nm, equipped with a Lichrosorb Si 60 column (250 × 4.6 mm i.d., particle size 5 mm; HicCHROM, United Kingdom) was used. Hexane°:°isopropanol (99.5:0.5 v/v) was used as mobile phase, with a column flow of 1.5 mL/min. All determinations were performed in duplicate. Results were analyzed by ANOVA followed by Tukey's test ($P < 0.05$), using Infostat software (INFOSTAT 2004, Argentina).

Sample Conditioning

The samples were conditioned to the selected moisture levels (5–10% db) by drying the seeds in a forced air oven at 35°C or by spraying with pre-calculated amounts of distilled water, and then thoroughly mixing and sealing them in separate polyethylene bags. The samples were then kept at 8°C in a refrigerator for at least 72 h to allow for a homogeneous moisture distribution. For each experiment, the required sample was taken out of the refrigerator and allowed to warm up to room temperature for approximately 2 h.

Scanning Electron Microscopy (SEM)

In order to detect structural differences, micrographs of the samples were taken with a MA10 variable pressure scanning electron microscope (Carl Zeiss SMT Ltd., United Kingdom) at 20 kV. The pressure was varied from 70 to 100 Pa as necessary.

Pretreatment With Microwaves

Equipment Calibration. For the application of the pretreatment by microwave radiation, a BGH Quick Chef microwave oven (model 36960, Argentina) was used. The microwave was calibrated to verify the powers by heating a fixed amount of water in the apparatus for 60 s, and then measuring the difference in temperature. The procedure was performed in triplicate.

The power absorbed by the water was calculated by Eq. (1):

$$W = m_w C_{pw} \frac{\Delta T}{\Delta t}, \tag{1}$$

where W is the power absorbed by the water (W), m_w is the mass of water (kg), C_{pw} is the specific heat (J/C kg), ΔT is the difference in temperature (°C) and Δt is the exposure time (s).

The mass of water used (approximately 1,000 g) was distributed into 5 Pyrex containers (10 cm diameter), in a similar manner as canola samples were arranged in the subsequent experiments. The absorbed powers by the water obtained were 457 and 607 W for 80 and 100% microwave nominal power, respectively (hereinafter referred to as 80 and 100% microwave power, respectively).

Pretreatment. An initial sample of 45 g was divided into 5 Pyrex containers and placed inside the microwave (BGH Quick Chef, model 36960, Argentina).

The samples were treated for 5 min at a frequency of 2,450 MHz and 100% microwave power to analyze the extraction rate. The temperature of the samples was measurement with an infrared thermometer (CEM DT-812, China).

For the analysis of the process variables, the samples were treated at the same frequency for two microwave powers (80 and 100%) according to the experimental design described in *Study of the Process and Optimization Variables* section. The seeds were ground in a blade grinder after both treatments.

Extraction Rate

The oil was extracted from the seeds by solvent extraction (hexane) according to IUPAC method 1.122 (1992) with a soxhlet equipment. Then the solvent was evaporated using a rotary evaporator (Büchi, R-3000, Switzerland) under vacuum at 45°C, removing the remaining solvent with a nitrogen stream.

Oil extraction yield was evaluated at different extraction times (2, 4, 6, 8 and 12 h) for a pretreatment of 100% microwave power and 300 s.

Study of the Process and Optimization Variables

Response surface methodology (Montgomery 1991; Meziane 2013) was used to analyze the effect of the process variables (moisture content and microwave pretreatment time) on oil yield. A central composite design (full 2^2 factorial design and a group of star points) with eight replicates at the center points was selected. The variables analyzed were treatment time (10–350 s) and moisture content of the seeds (5–10% db).

The order in which the experiments were performed was randomized (random function, Microsoft Excel 2010, USA). By properly randomizing the experiment, it is possible to average out the effects of extraneous factors that may be present (Montgomery 1991).

The software Statgraphics Centurión XVI.I, Spain was used for the statistical analysis of the responses, the development of models based on the experimental data, plotting of the response surfaces and the prediction of the conditions that would improve oil yield.

The experimental data were adjusted to a second-order general polynomial model using Eq. (2):

$$Yi = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2, \quad (2)$$

where Y_i (dependent variable) is the oil yield response ($i = 1$) or the final moisture content response ($i = 2$); X_1 (moisture content) and X_2 (treatment time) represent the independent variables in coded values. The variables were coded according to Montgomery (1991).

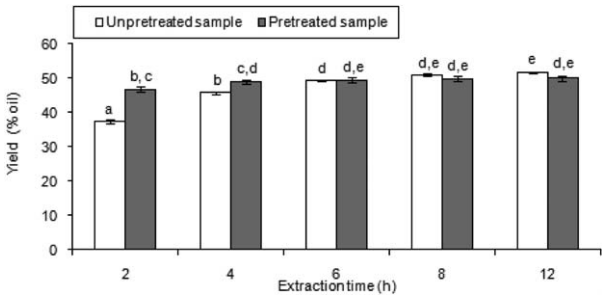

FIG. 1. CANOLA OIL YIELD (% DRY BASIS) OF THE UNPRETREATED SAMPLE AND SAMPLES PRETREATED AT 100% MICROWAVE POWER FOR 300 s. DIFFERENT LETTERS INDICATE SIGNIFICANT DIFFERENCES (TUKEY'S TEST, $P < 0.05$)

The extraction yield response was optimized by maximizing the variable using the model obtained from the response surface, finding a maximum value within the domain of the proposed experimental design. The demo version of software GAMS 23.5 (USA) was used for obtain the optimum values.

Oil extraction from the pretreated samples was carried out as described in *Extraction Rate* section, and the extraction time was selected based on the results of the extraction rate analysis.

RESULTS AND DISCUSSION

Characterization of the Raw Materials

The seeds used in the present work exhibited a moisture content 8.00 ± 0.01% db (dry basis) an oil content (51.50 ± 0.28 db) within the range reported in the literature (33–55%) (Windauer and Ploschuk 2006). The protein content (29.60 ± 0.02% db, in defatted meal) was lower than the values reported for rapeseed meal (38–43%) (Thakor *et al.* 1999).

Microwave Pretreatment

Oil Extraction Rate. The experimental data obtained for the extraction of oil from unpretreated and pretreated samples is presented in Fig. 1.

Solvent extraction of oil from the samples pretreated by microwave radiation was faster than that from the unpretreated sample, obtaining significantly larger oil yields at up to 4 h of extraction due to the pretreatment applied. At 2 h of extraction, an increase in oil yield of 25.1% as a result of the microwave pretreatment was observed, whereas at 4 h of extraction that increase was of 6.9%. After 6 h of extraction, no significant differences in oil yield were observed between the pretreated and unpretreated samples.

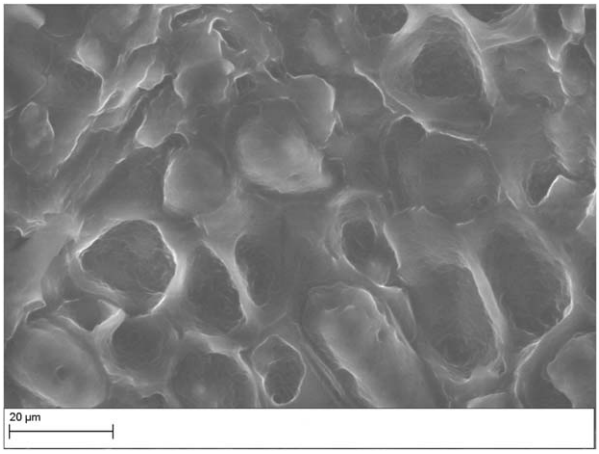

FIG. 2. MICROGRAPH OF THE UNPRETREATED CANOLA SAMPLE

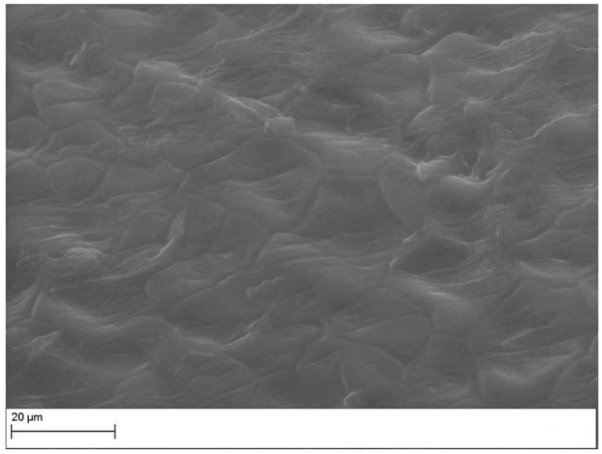

FIG. 3. MICROGRAPH OF A CANOLA SAMPLE PRETREATED BY MICROWAVE RADIATION

The higher yield observed for the initial times of the microwave-pretreated canola samples could be associated with the modification of the cellular structure due to the pretreatment, which could be causing a debilitation of the cell membranes so that the oil is more accessible to the solvent, and/or facilitating the subsequent breakdown of the membranes during seed grinding. Azadmard-Damirchi *et al.* (2010) also observed increases in oil yield obtained due to microwave treatment when extracted by press extraction, achieving an increment of up to 10% in the oil yield for treated rapeseed.

Scanning Electron Microscopy. Micrographs of the unpretreated and microwave-pretreated canola samples are shown in Figs. 2 and 3, respectively. Different structural configurations can be observed. The pretreatment by microwave radiation improves the availability of the oil because the solid matrix is modified due to the denaturalization of the protein, and it also reduces the viscosity of the oil by the effect of temperature (Uquiche *et al.* 2008). These observations are in agreement with those reported by those authors.

TABLE 1. EFFECT OF INITIAL MOISTURE CONTENT, AND MICROWAVE PRETREATMENT TIME ON TWO DEPENDENT VARIABLES FOR 80% OF MICROWAVE POWER

	Independent variables		Dependent variables	
	Initial moisture content (% db)	Microwave pretreatment time (s)	Yield (%)	Final moisture content (% db)
S. No.	$x_1(X_1)$	$x_2(X_2)$	Y_1	Y_2
1	5.7(−1)	60(−1)	45.9	6.1
2	5.7(−1)	300(1)	48.7	3.9
3	9.3(1)	60(−1)	43.2	8.1
4	9.3(1)	300(1)	43.3	5.1
5	7.5(0)	180(0)	47.0	5.4
6	7.5(0)	180(0)	46.6	5.3
7	7.5(0)	180(0)	47.2	5.7
8	7.5(0)	180(0)	46.8	5.4
9	7.5(0)	180(0)	46.9	5.9
10	7.5(0)	180(0)	46.7	5.7
11	7.5(0)	180(0)	46.6	6.0
12	7.5(0)	180(0)	46.0	5.5
13	10.0(1.4)	180(0)	42.8	6.3
14	5.0(−1.4)	180(0)	47.9	5.1
15	7.5(0)	350(1.4)	46.1	4.2
16	7.5(0)	10(−1.4)	43.4	7.4

X_i, represent the coded levels of variables; x_i represent the actual levels of variables.

TABLE 2. EFFECT OF INITIAL MOISTURE CONTENT, AND MICROWAVE PRETREATMENT TIME ON TWO DEPENDENT VARIABLES FOR 100% OF MICROWAVE POWER

	Independent variables		Dependent variables	
	Initial moisture content (% db)	Microwave pretreatment time (s)	Yield (%)	Final moisture content (% db)
S. No.	$x_1(X_1)$	$x_2(X_2)$	Y_1	Y_2
1	5.7(−1)	60(−1)	48.5	5.6
2	5.7(−1)	300(1)	51.0	2.9
3	9.3(1)	60(−1)	46.9	7.4
4	9.3(1)	300(1)	49.0	3.5
5	7.5(0)	180(0)	49.3	4.6
6	7.5(0)	180(0)	49.7	4.2
7	7.5(0)	180(0)	49.2	4.7
8	7.5(0)	180(0)	49.0	4.2
9	7.5(0)	180(0)	49.7	5.0
10	7.5(0)	180(0)	49.1	4.7
11	7.5(0)	180(0)	49.1	5.1
12	7.5(0)	180(0)	49.8	4.2
13	10.0(1.4)	180(0)	48.7	5.1
14	5.0(−1.4)	180(0)	49.8	4.0
15	7.5(0)	350(1.4)	51.0	2.7
16	7.5(0)	10(−1.4)	46.8	7.5

X_i, represent the coded levels of variables; x_i, represent the actual levels of variables.

Analysis of the Variables. Taking into account the results obtained in *Oil Extraction Rate* section, an extraction time of 4 h was selected for pretreated samples since up to this time the oil yield showed a significant increase compare to the untreated sample.

The experimental values of extraction yield, final moisture content and final temperature for the various pretreatments are shown in Tables 1 and 2.

The regression coefficients for the second-order polynomial equations are presented in Tables 3 and 4 for the full and simplified model, respectively. In the case of the simplified models, only the significant terms were considered (ANOVA, $P \leq 0.05$).

The R^2adj values indicate a good correlation between the experimental values and those predicted by the models, showing that more than 80% of the variability of responses can be explained by these models. The lack-of-fit test with P values exceeding 0.05 in all the cases, together with the R^2adj values greater than 0.8, in principle would suggest that the proposed models are adequate to describe the values of oil yield, final moisture content and final temperature within the experimental range studied (Ixtaina et al. 2010); however, it is necessary to perform a confirmation test to verify the validity of the models.

Equations (3) and (4) represent simplified models for responses oil yield (Y_1, %db) and final moisture (Y_2, %db) for pretreatment at 80% of power, respectively. x_1 represents the variable initial moisture in current variables (% db) and x_2 represents the variable time of pretreatment (min) in current variables.

$$Y_1 = 44.4 + 1.3227x_1 - 0.1956x_1^2 + 0.4503x_2 - 0.2364x_2^2 + 0.1850x_1x_2, \quad (3)$$

$$Y_2 = 4.9 + 0.3611x_1 - 0.6500x_2 \quad (4)$$

Also Eqs. (5) and (6) represent simplified models for responses oil yield (Y_1, % db) and Final moisture (Y_2, % db) for pretreatment at 100% of power, respectively.

$$Y_1 = 49.3 - 0.3463x_1 + 1.0935x_2 - 0.0725x_2^2, \quad (5)$$

$$Y_2 = 5.2 + 0.2778x_1 - 0.850x_2 \quad (6)$$

The response surface plots for oil yield and final moisture content in actual variables are shown in Figs. 4 and 5.

At 80% of microwave power, the factors time and initial moisture content, the interaction between them and the quadratic terms were significant for oil yield according to the results obtained by ANOVA ($P \leq 0.05$), whereas at 100% microwave power, the interactions were not significant and the initial moisture factor was significant in the linear term. For both power conditions, increasing pretreatment time (X_2) had a positive effect on extraction yield, whereas the increase in initial moisture content (X_1) had a negative effect on the extraction yield.

A linear model with a significant effect of the studied factors on the final moisture content response was obtained both with the pretreatment at the lower (80%) and higher microwave power (100%). No interaction between the variables was observed, and in both cases, the factor with the greatest influence was pretreatment time. Final moisture

TABLE 3. REGRESSION COEFFICIENTS, R^2_{adj}, AND LACK OF FIT FOR TWO DEPENDENT VARIABLES FOR MICROWAVE PRETREATMENT FOR THE SOLVENT EXTRACTION OF CANOLA OIL

Microwave power (%)	Regression coefficient	Yield (%)	Final moisture content (% db)
80	b_0	46.7***	5.6***
	b_1	−1.9020***	0.6202***
	b_2	0.8378***	−1.2680***
	b_{11}	−0.6338**	0.0631
	b_{22}	−0.9458***	0.1647
	b_{12}	0.6659**	−0.2729
	R^2_{adj}	0.96	0.91
	Lack of fit	0.5982	0.1136
100	b_0	49.4***	4.7***
	b_1	−0.62***	0.50**
	b_2	1.32***	−1.70***
	b_{11}	−0.140	−0.013
	b_{22}	−0.2900*	0.2417
	b_{12}	−0.1050	−0.2866
	R^2_{adj}	0.88	0.95
	Lack of fit	0.0900	0.9054

*Significant at 0.05 level; **Significant at 0.01 level; ***Significant at 0.001 level.
Subscripts: 1 = initial moisture content, 2 = time of pretreatment.

TABLE 4. REGRESSION COEFFICIENTS, R^2_{adj}, AND LACK OF FIT OF SIMPLIFIED MODELS FOR TWO DEPENDENT VARIABLES FOR MICROWAVE PRETREATMENT FOR THE SOLVENT EXTRACTION OF CANOLA OIL

Microwave power (%)	Regression coefficient	Yield (%)	Final moisture content (% db)
80	b_0	46.7***	5.7***
	b_1	−1.9020***	0.6500***
	b_2	0.8378***	−1.3000***
	b_{11}	−0.6338**	–
	b_{22}	−0.9458***	–
	b_{12}	0.6659**	–
	R^2_{adj}	0.96	0.91
	Lack of fit	0.5982	0.0801
100	b_0	49.3***	4.7***
	b_1	−0.6234*	0.5000**
	b_2	1.317***	−1.700***
	b_{22}	−0.29	–
	R^2_{adj}	0.89	0.93
	Lack of fit	0.1647	0.3845

*Significant at 0.05 level; **Significant at 0.01 level; ***Significant at 0.001 level.
Subscripts: 1 = initial moisture content, 2 = time of pretreatment.

content decreased with increasing pretreatment time and when the initial moisture content was lower. A similar effect was reported by Niu *et al.* (2012), who observed a decreasing linear dependence of final moisture with time of exposure to the microwaves.

The temperatures reached for the pretreatments were in the range of 32–86 and 33–101°C for 80 and 100% microwave power, respectively. The maximum yield was obtained at a temperature of 74.5°C for 80% and at 82°C for 100% of microwave power. It was observed that at higher microwave power and pretreatment time, the samples reached a higher final temperature.

Model Validation. In order to validate the models, it is necessary to select a point that does not belong to the experimental design proposed. The selected points are presented in Table 5.

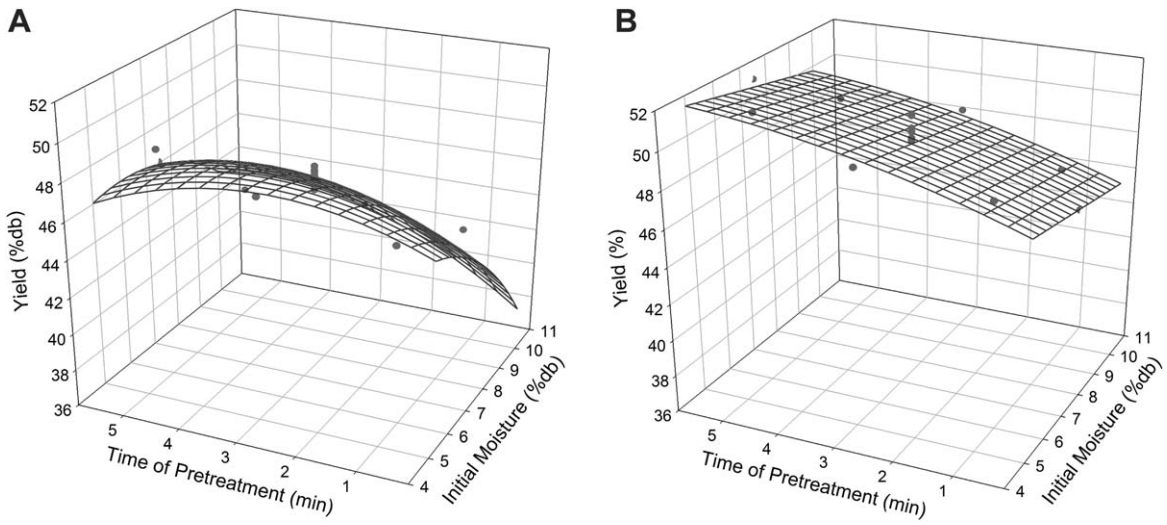

FIG. 4. RESPONSE SURFACE. RESPONSE: OIL YIELD (% db). (A) MICROWAVE POWER 80% AND (B) MICROWAVE POWER 100%

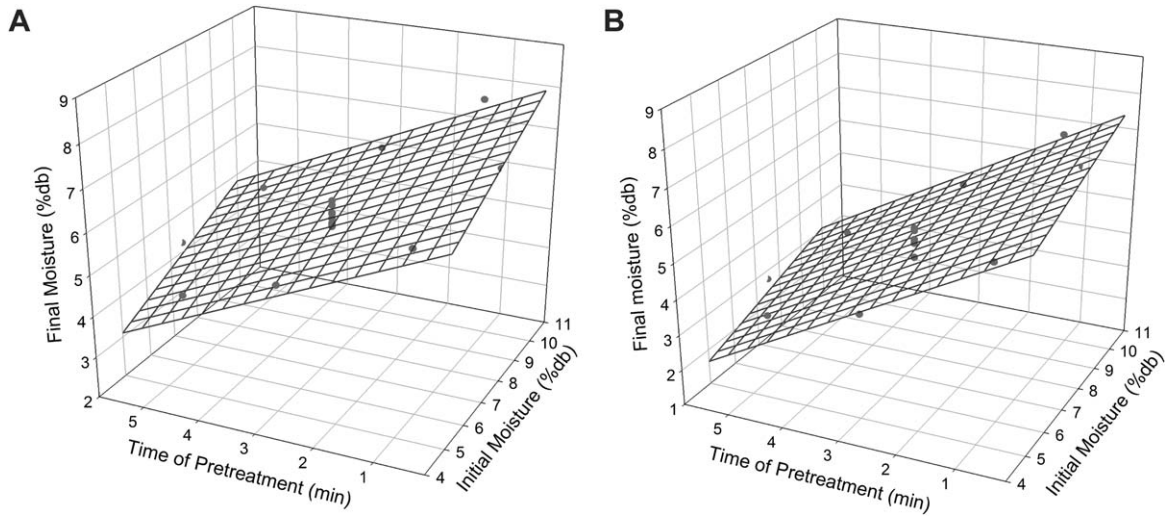

FIG. 5. RESPONSE SURFACE. RESPONSE: FINAL MOISTURE CONTENT (% db). (A) MICROWAVE POWER 80%. (B) MICROWAVE POWER 100%. MICROWAVE POWER 100%

A comparison for extraction yield and final moisture content between the values predicted by the model and those observed experimentally for both microwave powers, respectively, are shown in Table 6.

Considering the errors obtained, the results seem to suggest that the models are adequate to predict the responses for extraction yield (error 0.1 and 0.7%) and moisture (error 2.3 and 1.0%).

Optimization. The optimum values obtained from the models, and the values for the extraction yield and final moisture responses are presented in Table 7.

An increase in oil extraction yield was observed with microwave pretreatment. The increase in oil yield was achieved at the optimal conditions, determined by maximizing the models. In order to confirm that the increase in oil yield with the pretreatment is obtained due to a structural change of the seeds and not only due to their final moisture content, the seeds were stove-dried at 35°C to a final moisture (3.90 and 2.88% db) equal to that obtained under optimal conditions for the samples pretreated at both microwave powers, respectively, and then the oil was extracted. The oil extraction yields of unpretreated samples with optimum initial moisture levels were also analyzed. The results are shown in Table 7.

It is worth mentioning that the extraction yield obtained with the pretreatment at 100% was significantly larger than that obtained at 80% of microwave power. This could be associated with a more pronounced effect of the pretreatment due to the application of a higher microwave power, which entails a lower final moisture content and also a greater modification in the cellular walls (Azadmard-Damirchi *et al.* 2010). The decrease in moisture content in the pretreated samples could make the cell membranes weaker and thus facilitate the extraction of the oil. The SEM micrographs (Figs. 2 and 3) help to better explain the increase in oil yield.

Analysis of the Oil Obtained at the Optimum Values

Quality indices, free acidity, peroxide index, fatty acid profile and tocopherol content for the canola samples pretreated at 80 and 100% at the optimum values for the variables are shown in Table 8.

When comparing the oils extracted from the pretreated samples and with the oil from the unpretreated sample

TABLE 5. VALUES OF INITIAL MOISTURE CONTENT AND PRETREATMENT TIME SELECTED TO VALIDATE THE MODELS

Microwave power (%)	X_1	X_2	Moisture (% db)	Time of pretreatment (s)
80	−1.3	0.67	5.2	252
100	−1.3	0.67	5.2	252

X_1, initial moisture content in coded level; X_2, microwave pretreatment time in coded level.

TABLE 6. COMPARISON BETWEEN THE VALUES PREDICTED BY THE MODEL AND THOSE OBSERVED EXPERIMENTALLY

	Microwave power (%)	Predicted value	Observed value	Relative error (%)
Yield (%)	80	48.9	48.8	0.2
	100	50.9	51.4	1.0
Final moisture (% db)	80	4.0	3.9	2.6
	100	2.9	2.9	0.0

TABLE 7. EXPERIMENTAL OPTIMAL VALUES FOR OIL EXTRACTION YIELD AT 80 AND 100% OF MICROWAVE POWER. COMPARISON WITH UNPRETREATED SAMPLES FOR MOISTURE LEVELS CORRESPONDING TO THE INITIAL CONTENT AND THE FINAL VALUE OBTAINED AFTER THE PRETREATMENT

Microwave power (%)	X_1	X_2	Initial moisture (% db)	Time of pretreatment (s)	Final moisture (% db)	Yield (%)
80	−1.30	0.67	5.2	252	3.9	48.8
Unpretreated	–	–	3.9	–	3.9	43.7
Unpretreated	–	–	5.2	–	5.2	44.2
100	−1	1	5.7	300	2.9	51.0
Unpretreated	–	–	2.9	–	2.9	42.9
Unpretreated	–	–	5.7	–	5.7	45.6

TABLE 8. QUALITY INDICES, ACIDITY COMPOSITION AND TOCOPHEROL CONTENT FOR CANOLA SAMPLES UNPRETREATED, PRETREATED AT 80 AND 100% MICROWAVE POWER

Determination	Unpretreated	Pretreated at 80%	Pretreated at 100%
C16:0 (%)	$4.36^a \pm 0.38$	$4.48^a \pm 0.39$	$4.55^a \pm 0.40$
C18:0 (%)	$1.70^a \pm 0.12$	$1.47^a \pm 0.10$	$1.46^a \pm 0.10$
C18:1 (%)	$68.24^a \pm 5.87$	$68.14^a \pm 5.86$	$67.88^a \pm 5.84$
C18:2 (%)	$18.51^a \pm 0.35$	$18.62^a \pm 0.35$	$18.60^a \pm 0.35$
C18:3 (%)	$7.18^a \pm 0.50$	$7.30^a \pm 0.50$	$7.48^a \pm 0.52$
Free acidity (% oleic)	$0.81^a \pm 0.02$	$0.77^a \pm 0.01$	$0.79^a \pm 0.00$
I.P (meq/kg)	$1.75^a \pm 0.03$	$1.92^b \pm 0.01$	$1.81^a \pm 0.01$
Total tocopherols (μg/g oil)	$731.6^a \pm 15.7$	$698.2^a \pm 4.5$	$715.3^a \pm 1.3$
α-tocopherol (μg/g oil)	$292.5^a \pm 6.1$	$280.4^a \pm 1.6$	$287.5^a \pm 0.9$
β-tocopherol (μg/g oil)	$1.8^a \pm 0.2$	$2.1^a \pm 0.1$	$1.7^a \pm 0.1$
γ-tocopherol (μg/g oil)	$437.3^a \pm 9.5$	$415.6^a \pm 2.9$	$426.1^a \pm 0.6$

Means followed by the same letter in the same line are not significantly different (Tukey's test, $P > 0.05$). db, dry basis; C16:0, palmitic acid; C18:0, stearic acid; C18:1, oleic acid; C18:2, linoleic acid; C18:3, linolenic acid; AV, acidity value in % oleic; PV, peroxide value in meq peroxides/kg oil; TTC, total tocopherol; α-TC, α-tocopherols; β-TC, β-tocopherols; γ-TC, γ-tocopherols. All tocopherols content in μg tocopherols/g oil.

(Table 8) it can be observed that there were no significant differences in the quality indices evaluated, fatty acid composition or tocopherol content, except for the peroxide index for the sample pretreated at 80% of microwave power.

Similar results were reported in previous works, where for a microwave pretreatment for rapeseed oil at 500 W for 0–360 s, a decrease in tocopherol content of less than 10% was obtained (Yoshida *et al.* 1991). Other authors observed that there was an increase not only in extraction yield but also in oil quality, for example for rapeseeds (Azadmard-Damirchi *et al.* 2010) and hazelnuts (Uquiche *et al.* 2008) that had been pretreated with microwave radiation prior to mechanical pressing.

Total tocopherol content (μg/g oil) in the oil extracted from pretreated samples did not present significant differences with that extracted from unpretreated samples (Table 8).

Chu (1995) observed that tocopherol content increases when microwave pretreatment is applied to soybean samples with an initial moisture content between 15 and 18%; however, when the initial moisture is lowered to 12%, tocopherol content does not change significantly with the pretreatment. This observation would seem to suggest that at low moisture content, as is the case in the present work, tocopherol content remains approximately constant. The chromatograms obtained in the determination of tocopherol content in the oil extracted from the unpretreated sample, and from the samples pretreated at 80 and 100% of microwave power

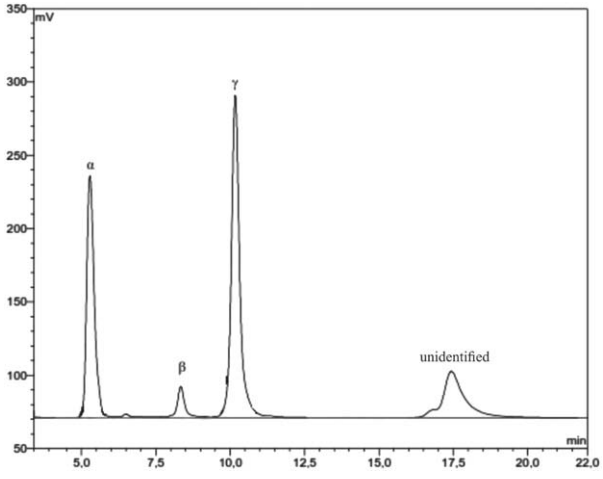

FIG. 6. CHROMATOGRAM OF THE OIL EXTRACTED FROM THE UNPRETREATED SAMPLE. DETERMINATION OF TOCOPHEROL CONTENT. á: á-TOCOPHEROL, â: â-TOCOPHEROL, ã: ã-TOCOPHEROL, UNIDENTIFIED: UNIDENTIFIED COMPOUND

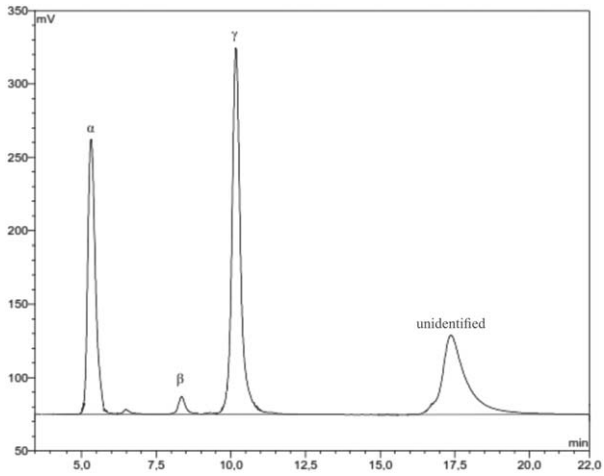

FIG. 7. CHROMATOGRAM OF THE OIL EXTRACTED FROM THE SAMPLE PRETREATED AT 80% MICROWAVE POWER. DETERMINATION OF TOCOPHEROL CONTENT. á: á-TOCOPHEROL, â: â-TOCOPHEROL, ã: ã-TOCOPHEROL, UNIDENTIFIED: UNIDENTIFIED COMPOUND

(under optimum conditions, Table 8) are presented in Figs. 6–8, respectively. It is worth mentioning that at 17.5 min of retention time, a peak that does not correspond to tocopherols can be observed, and it is larger for the pretreatment at higher microwave power. For similar conditions of analysis, Shrestra *et al.* (2012) determined the presence of canolol (4-vinyl 2,6 dimethoxyphenol), with a retention time of tocopherols similar to that obtained in the present work. The canolol compound is formed during heating of the rapeseeds by decarboxylation of sinapic acid (Matthaüs 2012). Canolol could be responsible for the greater stability of canola oil due to its antioxidant properties and considerable presence in the oil extracted from pretreated seeds (Koski *et al.* 2003), which would be consistent with the significantly lower peroxide value observed in the oil obtained from seeds pretreated at 100% compared to those pretreated at 80%.

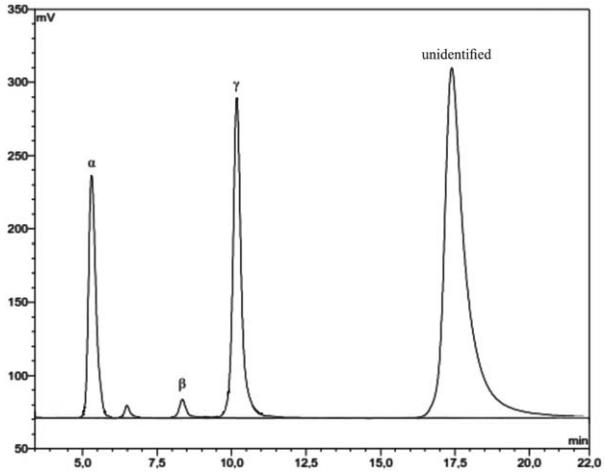

FIG. 8. CHROMATOGRAM OF THE OIL EXTRACTED FROM THE SAMPLE PRETREATED AT 100% MICROWAVE POWER. DETERMINATION OF TOCOPHEROL CONTENT. á: á-TOCOPHEROL, â: â-TOCOPHEROL, ã: ã-TOCOPHEROL, UNIDENTIFIED: UNIDENTIFIED COMPOUND

CONCLUSIONS

The pretreatment by microwave radiation applied to canola seeds, prior to the solid-liquid oil extraction, enabled a faster oil extraction compared with the unpretreated sample, giving significantly higher oil yields at the first 2 and 4 h of extraction (increase of 25.1 and 6.9%, respectively).

The increase in pretreatment time (80 and 100% of microwave power) had a positive effect on the extraction yield, whereas the increase in initial moisture content had a negative effect.

A lower final moisture content was observed with increasing pretreatment time and a low initial moisture content within the range studied.

The mathematical models obtained for oil extraction yield and final moisture content of the seeds based on pretreatment time and initial moisture content adequately represented the pretreatment process and enabled the optimization of its variables.

An increase of 10.4 and 11.8% in oil yield was observed for the samples pretreated at 80 and 100% of microwave power at the optimum process values compared with the unpretreated samples, respectively, being larger for the higher microwave power. It is worth noting that the oil yield obtained was significantly higher for the pretreatment at 100 than at 80%.

In general, the quality characteristics, acidity, fatty acid profile and tocopherol content determined for the samples pretreated at optimum values did not show significant differences compared to the unpretreated samples, except for peroxide index. The variations observed for peroxide index could be attributed to the production of a potent antioxidant (canolol), but further research is needed in this respect.

NOMENCLATURE

C_{pw}	heat capacity (J/C kg)
x_1	initial moisture content (% d.b.)
X_1	initial moisture content in coded variable (dimensionless)
m_w	mass of water (kg)
b_n	model-fitting parameters (dimensionless)
W	power absorbed by water (W)
Y_i	response (Y_1, %; Y_2, % d.b.)
x_2	time of microwave pretreatment (s)
ΔT	temperature difference (°C)
X_2	time of microwave pretreatment in coded variable (dimensionless)
Δt	time of microwave treatment

ACKNOWLEDGMENTS

The authors acknowledge the financial support from ANPCyT (Agencia Nacional de Promoción Científica y Tecnológica), CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and Universidad Nacional del Centro de la Provincia de Buenos Aires, Argentina.

REFERENCES

AGUILERA, J.M. 2003. Solid–liquid extraction. In *Extraction Optimization in Food Engineering* (C. Tzia and G. Liadakis, eds.), Food Science and Technology Series. Marcel Dekker Inc., New York, US.

AOCS. 1997. *Official Methods and Recommended Practices of the American Oil Chemists Society* (D. Firestone, ed.) 5th Ed., AOCS Press, Champaign, IL.

ASAE. 1999. *Standard Engineering Practices Data*, 46th Ed., American Society of Agricultural Engineers, St. Joseph, MI.

AZADMARD-DAMIRCHI, S., HABIBI-NODEH, F., HESARI, J., NEMATI, M. and ACHACHLOUEI, B.M. 2010. Effect of pretreatment with microwaves on oxidative stability and nutraceuticals content of oil from rapeseed. Food Chem. *121*, 1211–1215.

CHU, Y. 1995. Effects of soybean pretreatments on crude oil quality. J. Am. Oil Chem. Soc. *72*, 177–181.

FERNÁNDEZ, M., PÉREZ, E., CRAPISTE, G. and NOLASCO, S. 2012. Kinetic study of canola oil and tocopherol extraction: Parameter comparison of nonlinear models. J. Food Eng. *111*, 682–689.

INFOSTAT. 2004. Grupo Infostat. Universidad Nacional de Córdoba: Facultad de Ciencias Agropecuarias, Córdoba.

IUPAC. 1992. *Standard Methods for the Analysis of Oils, Fats and Derivatives* (C. Paquot and A. Hautfenne, eds.) 7th Ed., International Union of Pure and Applied Chemistry, Blackwell Scientific, Oxford, UK.

IXTAINA, V. Y., VEGA, A., NOLASCO, S. M., TOMÁS, M. C., GIMENO, M., BÁRZANA, E., and TECANTE, A. 2010. Supercritical carbon dioxide extraction of oil from Mexican chia seed (Salvia hispanica L.): characterization and process optimization. J. Supercrit. Fluid. *55*, 192–199.

IZQUIERDO, N., AGUIRREZÁBAL, L., ANDRADE, F. and PEREYRA, V. 2002. Night temperature affects fatty acid composition in sunflower oil depending on the hybrid and the phenological stage. Field Crop. Res. *77*, 115–126.

KOSKI, A., PEKKARINEN, S., HOPIA, A., WÄHÄLÄ, K. and HEINONEN, M. 2003. Processing of rapeseed oil: Effects on sinapic acid derivative content and oxidative stability. Eur. Food Res. Technol. *217*, 110–114.

MATTHAÜS, B. 2012. Effect of canolol on oxidation of edible oils. In *Canola and Rapeseed Production, Procesing, Food Quality and Nutrition* (U. Thiyam-Holländer, N. Eskin and B. Matthaüs, eds.) AOCS Press, Urbana, IL.

MEZIANE, S. 2013. Optimization of oil extraction from olive pomace using response surface methodology. Food Sci. Technol. Int. *19*, 315–322.

MONTGOMERY, D.C. 1991. Diseño y Análisis de experimentos. Editorial Grupo Editorial Iberoamérica, México.

NIU, Y., JIANG, M., WAN, C., YANG, M. and HU, S. 2012. Effect of microwave treatment on sinapic acid derivatives in rapeseed and rapeseed meal. J. Am. Oil Chem. Soc. *90*, 307–313.

SHRESTRA, K., STEVENS, C. and DE MEULENAER, B. 2012. Isolation and identification of a potent radical scavenger (canolol) from roasted high erucic mustard seed oil from nepal and its formation during roasting. J. Agric. Food Chem. *60*, 7506–7512.

SPIELMEYER, A., WAGNER, A. and JAHREIS, G. 2009. Influence of thermal treatment on the canolol content. Food Chem. *112*, 944–948.

THAKOR, N.J., SOKHANSANJ, S., SOSULSKI, F.W. and YANNACOPOULOS, S. 1999. Mass and dimensional changes of single canola kernels during drying. J. Food Eng. *40*, 153.

UQUICHE, E., JEREZ, M. and ORTIZ, J. 2008. Effect of pretreatment with microwaves on mechanical extraction yield and quality of vegetable oil from Chilean hazelnuts (*Gevuina avellana* Mol). Food Sci. Emerging Technol. *9*, 495.

WAKAMATSU, D., MORIMURA, S., SAWA, T., KIDA, K., NAKAI, C. and MAEDA, H. 2005. Isolation, identification, and structure of a potent alkyl-peroxyl radical scavenger in crude canola oil, canolol. Biosci. Biotechnol. Biochem. *69*, 1508–1574.

WINDAUER, L.B. and PLOSCHUK, E.B. 2006. Cultivos Industriales. Editorial Facultad de Agronomía, Argentina.

YOSHIDA, H., HIROOKA, N. and KAJIMOTO, G. 1991. Microwave heating effects on relative stabilities of tocopherols in oils. J. Food Sci. *56*, 1042–1046.