OIL EXTRACTION KINETICS OF HYDROTHERMALLY PRETREATED CANOLA SEEDS

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In this work the kinetics of oil extraction from spring canola seeds subjected to a hydrothermal pretreatment with direct steam (393 K, 5 min) was studied. The differences between the seed internal structure generated by the application of this pretreatment and that of the untreated sample (ground sample) were observed by scanning electron microscopy. Oil from both samples was extracted with hexane at different times and temperatures using a stirred batch system. Oil yield increased up to 46 % due to the hydrothermal treatment. A model was proposed to explain the oil extraction process from hydrothermally pretreated and untreated canola seeds, taking into account two main mechanisms: a washing process of the surface oil from the seed, and a diffusion process. Parameters of the model were fitted, and values of the oil fraction extracted during the washing step (0.27 and 0.50 for untreated and hydrothermally treated canola seeds, respectively) and the effective diffusion coefficient (3.1–9.4.10-12 $m^2 s^{-1}$) were obtained. The latter value showed an Arrhenius-type temperature dependence in the untreated sample, but the diffusion coefficient did not vary with temperature when oil diffusion was analyzed using hydrothermally pretreated seeds.

Keywords: canola, oil extraction, kinetics, hydrothermal pretreatment, SEM

INTRODUCTION

Rapeseed (*Brassica napus* L.) is one of the world's major sources of edible vegetable oil. Rapeseed is often used as a general term to describe different species that are quite similar in appearance but are sometimes very different in their chemical composition or botanical origin. Canola was bred from rapeseed to reduce the concentration of erucic acid in its oil.[1] Canola oil is very low in saturated fats, and it contains linoleic (omega-6) and α-linolenic (omega-3) acids at 2:1 ratio, which is an even better ratio than olive oil. It has also significant levels of phytosterols, which are known to inhibit cholesterol absorption, reducing cholesterol levels in the organism.

The importance of canola oil resides not only in the nutritional aspect, but also in its physicochemical properties, which make it suitable for use as a feedstock for the production of alternative fuels to petroleum (biodiesel). In European countries and the USA, rapeseed, soybean, palm and canola oils are also being exploited for bio-lubricants.[2]

In the extraction process of canola oil, the seeds undergo a series of unit operations such as crushing, cleaning, flaking, conditioning, mechanical pressing and extrusion followed by solvent extraction.[3] During extraction, microstructural conformations play an important role affecting the permeability of solutes. There are reports that indicate that lignified cellular walls reduce the oil mass transfer and modify the physicochemical sorption. Furthermore, these materials contribute to the retention of moisture, preventing the access of the solvent to the active sites for the oil extraction.[4] Because of this fact, a conditioning of the seeds prior to extraction is required since the oil is inside the membranes and it is necessary to break the cellular structure to allow the release of the oil and make it more accessible to the solvent. Pretreatments are applied to seeds in order to modify or break their structure so as to facilitate the release of the oil. The extraction process is affected by many physical and chemical variables that are often difficult to assess quantitatively and qualitatively. In the literature, different models have been proposed to analyze the kinetics of oil extraction from canola seeds, sunflower (partially husked), sunflower collets, wild and cultivated sunflower, and olive foot cake, among others.[5–9] However, an exhaustive statistical analysis of the models is rarely performed.

It is known that theoretical equations fail when trying to explain the phenomena just for simple diffusion theory.[10] The most widely used models consider two main mechanisms: a washing process of the oil from the particle surface, and a diffusion process, which could be carried out in one or two stages, depending on the proportion of broken or intact cells that remain after the pre-extraction treatments.[8] The aim of this work was to evaluate the effect of a hydrothermal pretreatment on the kinetics of canola oil extraction, and to analyze models to explain the diverse phenomena involved in this process.

MATERIALS AND METHODS

Characterization of Raw Material

Samples of canola seeds were characterized by standard techniques determining moisture (IUPAC 1.121), protein (AOCS Ai 4-91), neutral detergent fibre (NDF), acid detergent fibre (ADF), hemicellulose, lignin and cellulose.[11–13] The oil yield was

Table 1. Characterization of canola seeds

Determination	% (w/w, d.b.)
Moisture	7.4 ± 0.2
Oil	40.6 ± 0.6
Protein	25.9 ± 0.9
NDF	28.7 ± 0.7
ADF	23.6 ± 0.8
Lignin	7.9 ± 0.5
Cellulose	12.0 ± 1.4
Hemicellulose	5.1 ± 0.1

NDF: Neutral detergent fiber. ADF: Acid detergent fiber. w/w: weight/weight. d.b.: dry basis

Table 2. Yield and characterization of oil extracted by Soxhlet method

Determination	Untreated canola	Pretreated canola
Oil (%, w/w, d.b.)	40.6 ± 0.6[a]	56.6 ± 3.4[b]
Acidity value (% oleic, w/w)	0.49 ± 0.06[a]	0.44 ± 0.01[a]
Peroxide index (meq/kg oil)	ND	ND

ND: Not detected. Different letters in the same line indicate significant differences (Tukey Test, $p < 0.05$) w/w: weight/weight. d.b.: dry basis

determined following a modification of IUPAC 1.122 method (6 h, hexane, ANEDRA, 99.4 %).[11]

Oil Characterization

Oil was characterized by determining the acidity value (IUPAC 2.201) and peroxide index (AOCS Cd 8-53).[11,12]

Hydrothermal Pretreatments

Seeds were subjected to a hydrothermal pretreatment with water steam in an autoclave (VZ, Argentina) whose base had holes to facilitate the generation of steam from the bottom of the container. Samples were placed in trays with a metallic mesh base (149 μm opening). The hydrothermal treatment was carried out using broken seeds (particle size from 1.00 to 2.00 mm) at 393 K for 5 min. These operating conditions were selected because they were the optimum values found previously for hydrothermal pretreatments applied to canola seeds using the same system.[14] The samples were then dried up to a moisture content of 6.5-7.4 % dry basis (d.b.) at 25 °C in a forced circulation tunnel dryer (Armfield, England).

Kinetic Essays

A batch device stirred with a magnetic stirrer was used to study the kinetics of oil extraction from hydrothermally pretreated and untreated seeds. The extraction essays were carried out under various experimental conditions: at different times (from 300 to 64 800 s) and at different temperatures (313, 323 and 333 K). A negligible external mass transfer resistance was ensured by keeping a sufficiently high stirring rate (200 rpm). Five grams of ground sample and 85 mL of technical grade hexane (ANEDRA, 99.4 %) were mixed, after heating both separately to extraction temperature. The miscella was collected, subsequent to filtering the mixture through Whatman No. 42 filter paper and the solvent was separated using an R-3000 Büchi vacuum rotary evaporator (Switzerland) at 328 K. The remaining solvent was removed in a nitrogen (AIR LIQUIDE, 99.9 %) stream to constant weight. The oil content was determined gravimetrically using a Sartorius balance (model: PB211D, precision: 0.1 mg) and expressed as weight percent on a dry basis (% d.b.).

Mass of solute that diffuses at infinite time (M_∞) is the amount of oil obtained at 64 800 s because this time was considered long enough to attain the equilibrium state.[8]

Untreated and Pretreated Sample Characterization

Scanning electron microscopy (SEM) was used to determine the effect of the pretreatment on the structure of canola seed particles. SEM studies of the untreated and treated seeds were carried out using a scanning electron microscope (LEO, model EVO40 VP,

England). Before SEM, the samples were metallized with gold in a sputter coater (PELCO 91000).

Statistical Analysis

The experimental data were analyzed by means of analysis of variance (ANOVA) followed by Tukey's comparison test. Differences were considered significant at $p < 0.05$. For this purpose, the Infostat software package was used.[15]

Extraction Kinetics Modelling

Oil extracted by the stirring method

A diffusive model from a modified Fick's law was used. This model considered a non-stationary state and spherical particles suspended in a medium of constant concentration without volume restriction.[8] The solution of Fick's Second Law is given by Equation (1):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} A_n e^{-B_n t} \tag{1}$$

where t (s) is the diffusion time and M_t and M_∞ represent the mass of the substance (kg solute. kg dry defatted meal^{-1}) that diffuses at time t and infinite time, respectively. A_n and B_n (s^{-1}) are the model fitting parameters.

This model was used with modifications, where a washing stage was included in order to take into account the mass of oil M_0 extracted during the washing time t_0.[8] The proposed model is presented in Equation (2) and its simplified version in Equation (3), where only the first term of the series is considered, leading to an adequate simplification for long periods of time.

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{M_0}{M_\infty}\right) \sum_{n=1}^{\infty} A_n e^{-B_n(t-t_0)} \tag{2}$$

$$\frac{M_t}{M_\infty} = 1 - A e^{-Bt} \tag{3}$$

Table 3. Characterization of oil extracted by stirring method at 313, 323 and 333 K

T (K)	Determination	Untreated canola	Pretreated canola
313	Acidity value (% oleic, w/w)	0.54 ± 0.04[a]	1.08 ± 0.02[b]
	Peroxide index (meq/kg oil)	ND	ND
323	Acidity value (% oleic, w/w)	0.53 ± 0.02[a]	1.01 ± 0.11[b]
	Peroxide index (meq/kg oil)	ND	ND
333	Acidity value (% oleic, w/w)	0.54 ± 0.03[a]	0.94 ± 0.01[b]
	Peroxide index (meq/kg oil)	ND	2.72 ± 0.26

ND: Not detected. Different letters indicate significant differences (Tukey Test, $p < 0.05$) w/w: weight/weight

where the pre-exponential coefficient A is associated with the average value of the oil extracted in the washing step (M_0, kg solute. kg dry defatted meal^{-1}) and is given by

$$A = \left(1 - \frac{M_o}{M_\infty}\right)A_1 . e^{B_1 t_0}. \qquad (4)$$

A_1 is obtained from the following equation for spherical geometry:[16]

$$A_1 = \frac{6}{\pi^2} \qquad (5)$$

and B is associated with the effective diffusivity (D_{eff}, m^2/s)

$$B = \frac{D_{eff}.\pi^2}{R^2} \qquad (6)$$

with R (m) as the average particle radius. It was assumed that particle size and shape remained constant during the extraction process. The same assumption was made in a previous work in which sunflower seeds ground with the same grinding method as applied in the present work was used.[8] Since $B = B_1$, Equation (4) becomes

$$\frac{M_t}{M_\infty} = 1 - Ae^{-Bt}. \qquad (7)$$

The experimental data were fitted to the model using the Marquardt-Levenberg algorithm with the SIGMAPLOT software v. 11.0 (Systat Software, USA). Determinations were replicated.

Non-linear model comparison as a function of temperature

A comparison of the non-linear models was carried out by means of the extra sum of squares principle (ESS) in order to determine if coefficients A and/or B in Equation (7) were temperature dependent for the 313-333 K range. The proposed null (H_0) and alternative (H_1) hypotheses are expressed by the following statements:

H_0: Coefficients A and/or B do not depend on temperature (*Global* model in the case that both are not temperature-dependent; *Common A* model with only B varying with temperature, and *Common B* model if only A depends on temperature).

H_1: Both parameters A and B depend on temperature (individual parameters model).

Contrast statistics F_0 was obtained from the ESS of each model, which allowed for a comparison of the models associated with each one of the hypotheses.[5,17] Lack of fit was tested using a direct comparison method with the help of contrast statistics F_o^{dc}.[5,18]

RESULTS AND DISCUSSION

Canola Seed Characterization

The characterization of the original (untreated) sample is shown in Table 1. All the results are expressed d.b. oil content was within the range reported in the literature (33-55 %).[19] The protein content value obtained experimentally was 25.9 % (d.b.), corresponding to 40 % in defatted meal, which is in the range (38-43 %) observed by Thakor et al.[20]

Canola Oil Characterization

Table 2 shows the oil yield and quality indices for the untreated and pretreated canola seeds. The oil yield increased markedly with the hydrothermal treatment, whereas the acidity and peroxide values did not differ significantly between the treatments.

Table 3 shows a comparison between the quality indices (acid value and peroxide index) of canola oil obtained at 1080 min by stirring extraction using untreated and hydrothermally treated canola seeds as raw material.

For all the temperatures evaluated, pretreated samples presented the highest values of acidity index, while a peroxide index was only detected for pretreated canola oil at the highest tested temperature (333 K). Although the acidity value (AV) of pre-treated seeds seemed to decrease as temperature increased, statistical tests (Tukey's Test + ANOVA) showed no significant differences in AV among the temperatures studied (Table 3).

It can be observed that the analyzed quality characteristics were notably affected when oil was extracted by the stirring method (Table 3), whereas the quality characteristics of the Soxhlet-extracted oil were not significantly affected by the pretreatment (Table 2). This could be explained by the extraction time (360 min and 1080 min by Soxhlet and stirring methods, respectively) especially in pretreated samples, since their oil is more exposed to oxygen and the available water. In the case of peroxide index, the solvent/ground seed ratio could also be affected, since hexane could be favouring oxidation processes due to the oxygen that is dissolved therein.[21] Furthermore, being an agitated system, the amount of dissolved oxygen is greater than in a system without agitation such as in Soxhlet extraction.

Micrographs of Ground Untreated and Pretreated Seeds

Micrographs of ground (untreated) and hydrothermally pretreated canola seeds are shown in Figures 1a and b, respectively. Different conformations of the structure can be observed. The hydrothermal
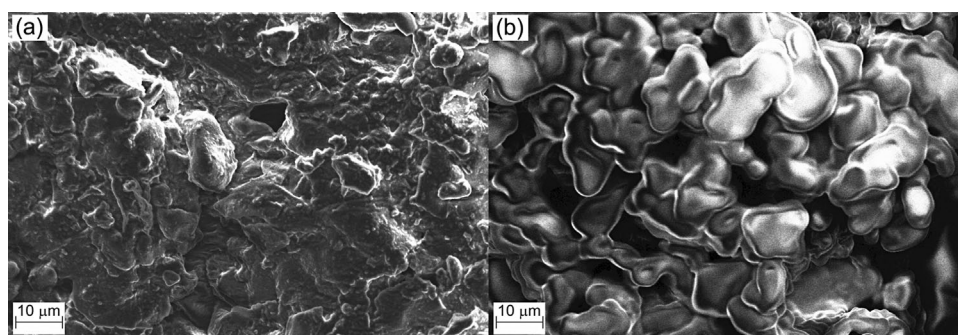

Figure 1. (a) Micrographs of untreated/ground canola sample and (b) hydrothermally pretreated/ground canola sample.

treatment improved the oil availability by changing the solid matrix due to the denaturalization of proteins, and it reduced the oil viscosity by the action of temperature during this treatment. This effect is evident in the micrographs, where a greater dispersion of the oil was detected in the hydrothermally treated sample, leading to greater oil availability. The pretreatment

distorted the original structure by destroying the membranes of the lipid bodies, causing the coalescence of oil droplets.[3]

Oil Extraction Kinetics

Figures 2a–c show oil yield as a function of time using untreated and pretreated ground canola seeds at 313, 323 and 333 K,
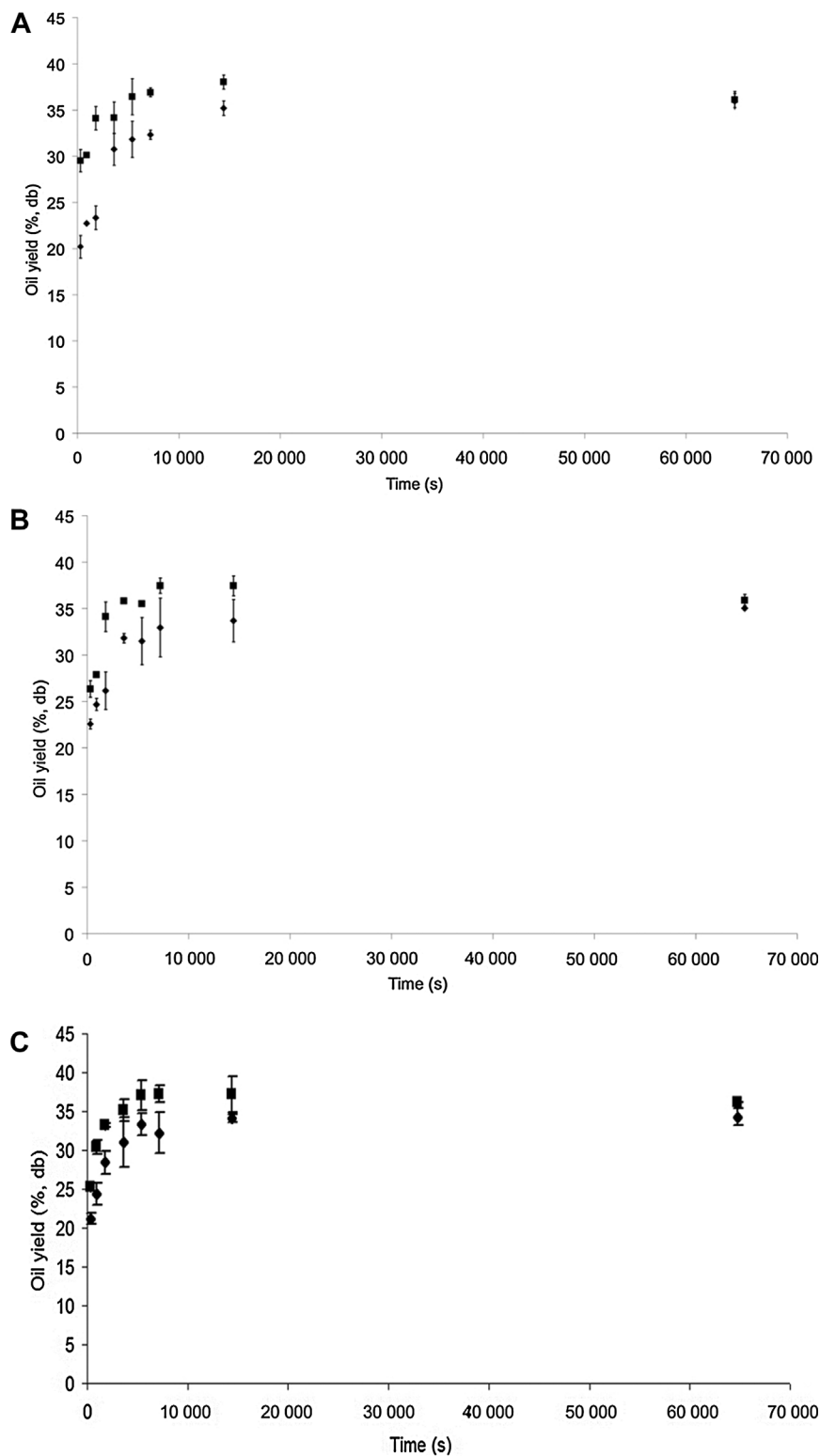
Figure 2. (A) Oil yield (%, w/w, d.b.) of pretreated (■) and untreated (◆) canola seeds in dry basis at 313 K of extraction temperature. (B) Oil yield (%, w/w, d.b.) of pretreated (■) and untreated (◆) canola seeds in dry basis at 323 K of extraction temperature. (C) Oil yield (%, w/w, d.b.) of pretreated (■) and untreated (◆) canola seeds in dry basis at 333 K of extraction temperature.

Table 4. Effect of temperature and time and their interaction on the oil yield increase due to hydrothermal pretreatment. P-values of the factors and their interaction.

Variation source	p
Temperature	<0.0001
Time	<0.0001
Temperature*time	<0.0001

respectively, by the stirring technique. Oil yield increased with extraction time. Curves shown in Figure 2 present a very short initial stage, in which most of the oil fraction was removed, then the oil extraction was slow, as it was also observed in previous work.[5,8] This behaviour can be attributed to the treatments (grinding or hydrothermal pretreatment and grinding) that facilitate oil extraction by washing, due to the disruption of the structures where the oil is located. This first stage was much faster than the diffusion one. This phenomenon was explained by Aguilera and Stanley in terms of the high diffusion resistance of the cell walls and membranes attached.[22]

It was also observed that, at the first extraction times (up to 240 min), the hydrothermal pretreatment favoured oil release, whereas at 1080 min the difference in oil yield between untreated and pretreated seeds was not significant. ANOVA followed by Tukey's test ($p < 0.05$), carried out at the three analyzed temperatures, corroborated this trend. When comparing the oil yields, significant differences can be detected at all the temperatures and at all the extraction times, with the exception of very long times (1080 min).

On the other hand, the effects of both factors (temperature and time) and their interaction on the percentage of oil yield increase were estimated. P values (ANOVA) are presented in Table 4. Considering a critical significance level equal to 0.05, it can be observed that both temperature and extraction time had significant effects on oil yield, being the interaction between them also significant (temperature x time).

Oil yield increased significantly due to the hydrothermal pretreatment and with extraction time. The increase in oil extraction due to the hydrothermal pretreatment could be associated with the greater dispersion of oil detected in the micrograph of the treated sample (Figure 1b), since the availability

Table 5. Model fitted parameters and determination coefficients

Model	T (K)	Untreated canola			Hydrothermally pretreated canola		
		$A \times 10^2$	$B \times 10^4$	R^2	$A \times 10^2$	$B \times 10^4$	R^2
Global	313–333	45.46 ± 2.04	3.40 ± 0.32	0.88	30.39 ± 2.53	7.34 ± 1.08	0.85
Individual parameters	313	48.08 ± 1.91	2.60 ± 0.24	0.95	23.23 ± 3.80	5.79 ± 1.78	0.81
	323	41.03 ± 2.39	3.58 ± 0.46	0.94	36.70 ± 4.62	8.33 ± 1.80	0.90
	333	48.66 ± 5.07	6.08 ± 1.00	0.91	31.48 ± 4.16	7.61 ± 1.77	0.88
Common A	313		2.37 ± 0.17	0.94		8.46 ± 1.52	0.77
	323	45.46	4.16 ± 0.40	0.93	30.39	6.73 ± 1.11	0.88
	333		5.59 ± 0.58	0.91		7.27 ± 1.07	0.88
Common B	313	50.14 ± 1.47		0.94	25.45 ± 2.78		0.80
	323	38.88 ± 1.75	3.40	0.93	34.55 ± 2.68	7.34	0.89
	333	34.46 ± 3.26		0.81	30.92 ± 2.52		0.88
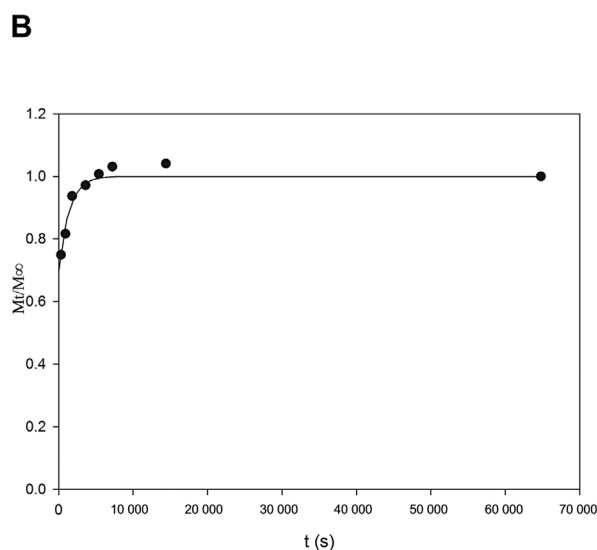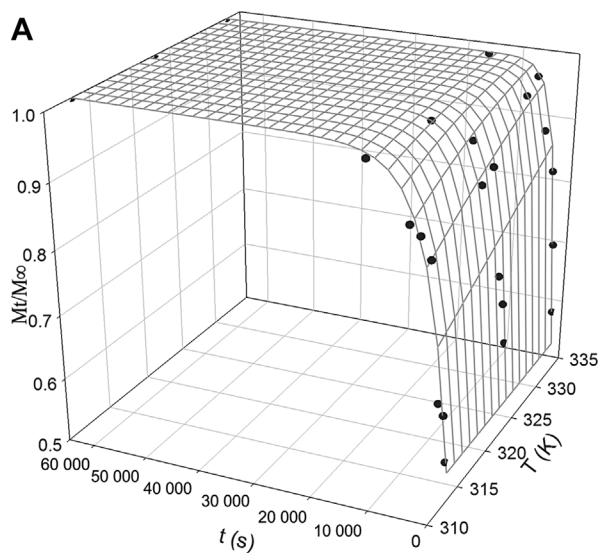
Figure 3. (A) Untreated (ground) canola oil extraction: extracted oil fraction (M_t/M_∞) as a function of extraction time and temperature. Full dots represent experimental data and the mesh, the simulated data by means of the Common A model. (B) Pretreated (hydrothermally pretreated and ground) canola oil extraction: extracted oil fraction (M_t/M_∞) as a function of extraction time. Full dots represent experimental data and the line, simulated data by means of Global model. T = 313–333 K.

of oil could be improved. This increase was more marked for the lower temperature used during the extraction process. At 313 K, the yield increased up to 46 % at 5 min. At 323 K, the extraction yielded up to 30 % more in the pretreated sample than in the untreated one at 30 min, whereas at 333 K, 26 % more of oil was obtained with the hydrothermal pretreatment at 15 min of extraction.

Oil Extraction Kinetics Modelling

Table 5 shows the fitted parameters and the determination coefficient R^2 of the different models for untreated and hydrothermally pretreated canola seeds.

When analyzing the kinetics of oil extraction from untreated seeds, and taking into account the proposed hypotheses, it was found that only the *common A* model did not present significant differences in comparison with the individual parameters model ($p < 0.05$). Therefore, both models represent similarly the canola oil extraction. Since the F_o^{dc} calculated by comparing experimental data with the data predicted by the *common A* model was 0.76, lower than the corresponding critical value at a confidence level of 95 % ($F_c^{dc} = 1.84$), lack of fit was not significant, indicating that this model is adequate. Therefore, the model selected to represent ground canola oil extraction was the *common A* model. Considering that washing time was very short (t_0 tending to 0) the M_o/M_∞ ratio can be calculated from coefficient A. The value obtained was 0.27, showing that a significant amount of oil was removed during the washing stage.

On the other hand, when studying oil extraction from hydrothermally pretreated canola seeds, no significant differences were found between the *individual parameters* model and the *global* model ($F_0 < F_c$), suggesting that neither coefficients A nor B depend on temperature. Based on the statistical analysis used to test the goodness of fit of the selected model (*global* model), a F_o^{dc} value of 1.55 was obtained, lower than the corresponding critical value at a confidence level of 95 % ($F_c^{dc} = 1.98$). The responses of M_t/M_∞ simulated with the selected models are shown in Figures 3a and b. It is worth mentioning that, from 60 min (3600 s) to 1080 min (64 800 s), ANOVA and Tukey's Test showed no significant differences in extraction among times at all the tested temperatures.

Diffusive effective values (D_{eff}) obtained from parameter B are shown in Table 6. These values were similar to those reported by Perez et al. for oil extracted with hexane from oilseed sunflower (1.43 10^{-12}-1.96 10^{-12} m^2/s) and wild sunflower seeds (1.49 10^{-12} - 2.07 10^{-12} m^2/s).[8]

The Arrhenius function was used to represent the dependence of the effective diffusivity D_{eff} on temperature in the case of the data obtained for the untreated sample. The solution of the linearization of this expression is given in Equation (6):

$$\ln(D_{eff}) = -15.5(\pm 2.24) - \frac{4484(\pm 723)}{T} \tag{6}$$

with a determination coefficient R^2 equal to 0.97. The pre-exponential coefficient and the activation energy were 5.25 10^{-6} m^2.s^{-1} and 37.3 kJ.mol^{-1}, respectively.

Table 6. Effective diffusivity coefficients (m^2/s)			
Temperature (K)	313	323	333
Untreated canola	3.15 10^{-12}	4.90 10^{-12}	7.44 10^{-12}
Pretreated canola		9.37 10^{-12}	

CONCLUSIONS

Oil yield increased with extraction time, presenting a very fast initial stage where a significant amount of oil was removed from the seed, followed by a slower extraction step (diffusion step). This behaviour can be attributed to the pretreatment applied to canola seeds (grinding, hydrothermal pretreatment), which facilitated oil extraction by washing due to the distortion of the structures where the oil is located.

For all the studied temperatures (313, 323 and 333 K), the hydrothermal pretreatment favoured oil extraction, the increase being more noticeable for the lower temperature. Pretreated samples exhibited an oil yield increase of up to 46 %. However, at long times (1080 min) the influence of temperature or the hydrothermal treatment on the oil yield was not detected.

Canola oil extraction by a stirring method was satisfactorily described by the modified diffusive model, which involves two parameters: A, associated with the extracted fraction during the first washing stage, and B, related to the effective diffusion coefficient. In the case of untreated (ground) canola seeds, the model selected was *common A* (where only B varied with temperature). However, when analyzing the pretreated samples, neither parameter A nor B were temperature-dependent, therefore the global model was adopted.

On the other hand, the relation of the diffusivity coefficient with temperature in the untreated sample was represented with an Arrhenius type expression. However, for pretreated canola seeds this coefficient remained constant in the 313-333 K range.

NOMENCLATURE

A, B	Model-fitting parameters (A, dimensionless; B, s^{-1})
A$_n$, B$_n$	Model-fitting parameters (A$_n$, dimensionless; B$_n$, s^{-1})
D$_{eff}$	Effective diffusion coefficients (m^2.s^{-1})
F$_0$	Contrast statistics for parameter comparison
F$_o^{dc}$	Contrast statistics for direct comparison
F$_c$	Critical value of Snedecor's F distribution for the comparison of the parameters
F$_c^{dc}$	Critical value of Snedecor's F distribution for direct comparison
M	Mass of solute that diffuses (kg solute. kg dry defatted meal^{-1})
R$_p$	Average particle radius (m)
R^2	Determination coefficient
t	Diffusion time (s)
T	Absolute temperature (K)

Subscripts

1, 2,..., n	Series terms
0	Washing stage
∞	Infinite time
t	At time t

Superscripts

dc	Direct comparison

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