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Extraction of oil from chia seeds with supercritical CO_2

Jose Antonio Rocha Uribe[a,*], Jorge Ivan Novelo Perez[a], Henry Castillo Kauil[a], Gabriel Rosado Rubio[a], Carlos Guillermo Alcocer[b]

[a] FIQ, Universidad Autónoma de Yucatán, Periferico Norte km 33.5, C. P. 97203, Mérida, Yucatán, Mexico
[b] Oleox Industries S. A. de C.V. Anillo Periferico T.C. 13917 Int. 7 Col. Cholul, C. P. 97300, Merida, Yucatan, Mexico

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ABSTRACT

Chia (*Salvia Hispanic*, L.) is a crop that was used as food, medicine and paints by the Aztec Indians in Mexico before 1492, and now has a promissory future in several countries. Chia seeds oil is rich in polyunsaturated fatty acids, particularly omega-3 linolenic acid (54–67%) and omega-6 linoleic acid (12–21%) which pose great benefits for human and animal health.

The oil extraction from Chia seeds using supercritical CO_2 seems to be a good alternative because it operates at low temperature with good mass-transfer rates and with no solvent residual in the final product.

The objective of this work is to evaluate the extraction yield of oil from chia seeds and the concentration of omega-3 and omega-6 acids using supercritical extraction with CO_2 at three pressures: 136, 272, and 408 bar, and three temperatures: 40, 60, and 80 °C.

1. Introduction

Nowadays, national and international customers prefer natural products mainly in the food and cosmetic sectors. For this reason the extraction of essential oils and oleoresins of plants with supercritical CO_2 is being investigated in several institutions.

Chia (*Salvia hispanic*, L.) is a plant with high nutritional value that contains the polyunsaturated fatty acids (PUFAs): linolenic acid omega-3, and linoleic acid omega-6. These PUFAs have high international demand on the health sector. These nutraceutical compounds may be obtained using several methods: extrusion of the seeds, enzymatic extraction, solvent extraction and extraction with supercritical fluids. In all cases the researcher aims to shorten the extraction time, use less solvent, increase the yield and improve the quality of the extracted product.

The extraction of essential oils and oleoresins using supercritical fluids is of great importance due to the high purity of the final compounds, which increases the added value of the final products and their price in the international market. The supercritical fluid is usually CO_2 because is not toxic, no flammable, with low cost and mild critical conditions ($P \geq 74$ bar and $T \geq 31$ °C) allowing the recovery of thermolabile compounds.

The industrial manufacture of oils from oleaginous plants uses compression and solvent extraction from seeds. King and List [1] presented a good compilation of several procedures. At research scale CO_2 has been used at temperatures ranging from 40 to 80 °C and pressures from 50 to 600 bar [2–4] to extract oil from seeds. The fractionation of fat and oils with supercritical CO_2 result in products with improved functionality for specific applications or with higher nutritional value [1,5].

Differences in oil content and composition for chia from different parts of South America have been reported [6,7].

Recently, Ixtaina et al. [8] reported supercritical extraction of chia oil from seeds using three pressures (250, 350 and 450 bar), three temperatures (40 °C, 60 °C and 80 °C), and three retention times (60, 150, and 240 min). Another study, [9] reports supercritical extraction of omega-3 rich oil with CO_2 from a different seed.

According to Stahl cited in [10] there are three extraction modes with supercritical fluids: dynamic, static, and static-dynamic. In this research the static-dynamic mode was used. Fig. 1 shows the theoretical extraction profile of an analyte from a solid matrix using a dynamic system. The profile can be divided into three distinct regions: The initial extraction of material occurs rapidly and is dependent upon the solubility of the bulk analyte in the supercritical fluid (region I). Region II is an intermediate region where the extraction process occurs at a slower rate of extraction due to diffusion-controlled kinetics. Region III represent the portion of the extraction where the process is truly diffusion limited.

* Corresponding author. Tel.: +52 999 946 09 81.
E-mail addresses: antonio.rocha@uady.mx, rochaja21@hotmail.com (J.A.R. Uribe).

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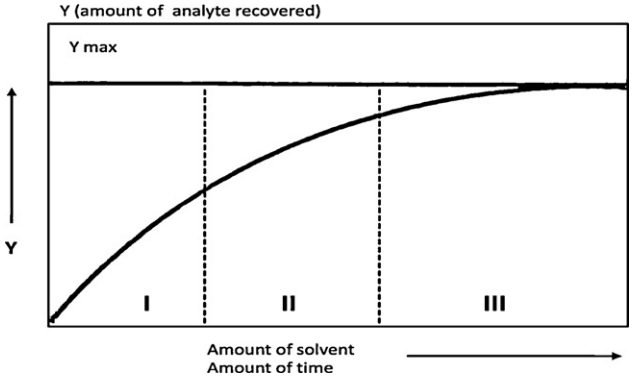

Fig. 1. Extraction yield versus time and mass of carbon dioxide.

For manufacturing cost estimation [11,12] only the first linear region, known as the constant extraction region is used. This corresponds to the extraction of the more accessible solute, and hence the mass transport is dominated by the convection in the solvent film surrounding the particles.

A mathematical model for the supercritical extraction of sage (*Salvia officinalis* L.) oil from leaves (as opposed to seeds) is reported [13] and the author considered region II and III.

The present work studied Mexican chia seeds measuring the oil yield and the concentration of PUFAs after extraction with carbon dioxide at pressures: 136, 272, and 408 bar, and temperatures of 40, 60 and 80 °C. The objective was to find good operational conditions (pressure and temperature) for the best yield. It is expected to call the attention of the industrial sector in Shoutern Mexico where there are many plants with a great potential as solid matrices for obtaining useful compounds with applications in the food, cosmetic and pharmaceutical industries.

2. Materials and methods

2.1. Chia seeds

The chia seeds were obtained from retailers at Merida Yucatan in November 2008. According to the sellers the seeds were grown in the state of Mexico (central part of the Mexican Republic). The seeds were ground using a conventional electric mill and sieved with mesh no. 30, giving an average size of 0.00054 m (0.54 mm).

2.2. Gases of operation

Industrial grade CO_2 with a purity of 99.9% and extra dry air with a purity of 99.99%, were supplied by Praxair, Merida-Mexico.

Fig. 2. Extraction system SFT-150 by Supercritical Fluid Technologies Inc., Newark, DE, USA.

2.3. Supercritical extraction

Fig. 2 shows a photograph of the experimental device. It is a 0.1 l cell which is charged with 30 g of ground chia seeds.

Fig. 3 shows a sketch of the experimental rig. The main steps of the process are:

(1) Filling of the extraction chamber with milled chia seeds (Fig. 3h).
(2) Changing the CO_2 from the conditions in the tank (b) to supercritical conditions. This is achieved by first cooling (g), increasing the pressure (f) and finally increasing the temperature (h).
(3) Static extraction (soaking). CO_2 at the chosen supercritical conditions is allowed to enter the extraction chamber for a pre-determined time (soaking time = 10 min).
(4) Dynamic extraction. CO_2 at the chosen supercritical conditions is allowed to flow through the fixed bed formed by the ground seeds (h). The CO_2 containing the extracted oil is directed to the first separation chamber (i) where the gas is expanded to atmospheric pressure.

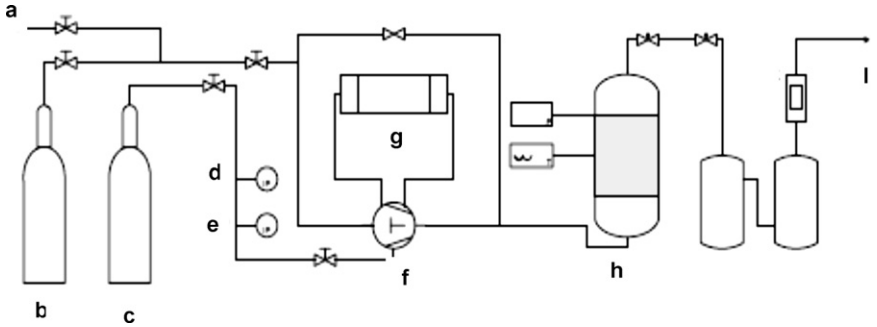

Fig. 3. Sketch of the supercritical extraction experiment: (a) purge, (b) CO_2 tank, (c) air tank, (d) and (e) manometers, (f) diaphragm pump, (g) cooler, (h) extraction chamber, (i) CO_2 separator and extract collector, (j) auxiliary separator and extract collector, (k) flowmeter, and (l) CO_2 to atmosphere.

Table 1
Experimental design for chia oil extraction with supercritical CO_2.

Temperature (°C)	Pressure (bar)
40	136
	272
	408
60	136
	272
	408
80	136
	272
	408

(5) Separation and collection of condensed extract. The decompressed CO_2 leaves the system flowing through a rotameter (k) and the extract condenses or precipitates in collectors (i) or (j).

2.4. Experimental conditions

In order to find the conditions of supercritical extraction of chia oil that result in the higher PUFAs concentration, the experimental design shown in Table 1 was performed.

Each experiment had 10 min of soaking time (static extraction) and 30 min of dynamic extraction with a CO_2 flow rate of 1.8 g/min. Each set of conditions was tested by triplicate. Kinetics test for the best yield was also performed, measuring the maximum content of oil in the samples.

2.5. Fatty acid analysis

The transesterification of fatty acids was performed according to reported procedures [14–16]. The lipid extracts were esterified with a mixture of boron trifluoride hexane and methanol (35:20:45 volume) according to [17]. The fatty acids composition was measured with gas chromatography in a GC Agilent Technologies (Model 6890N) with Coupled Mass Selective Detector (Model 5973N). The Column was a Supelco TM fused silica capillary column (100 m × 0.25 mm × 0.2 μm film thickness) Model SPTM-2560. The injector temperature was 250 °C. The oven initial temperature was 120 °C and then increased at a rate of 20 °C/min to 250 °C. The carrier gas was helium at a velocity of 1 ml/min. The samples were injected using an Agilent Automatic Injector (Model 7863 series) without split. The peak area was identified and quantified using pure methyl ester standards from Alltech Inc., USA.

3. Results and discussion

3.1. Experimental data

The yield is defined in Eq. (1). It was measured for each run and averaged for the three values.

$$y_1 = \frac{\text{g of oil extracted}}{\text{g of seeds charged in cell}} \quad (1)$$

The results obtained for the extraction of chia oil with supercritical CO_2 are plotted in Fig. 4. It is observed that with a temperature increase at constant pressure the yield tends to increase and this effect is more pronounced at higher pressures. In the same manner, for increasing pressure at constant temperature, the yield also increases. This behavior is due to the simultaneous increment of supercritical CO_2 density and oil solubility with pressure and temperature. This way, the flow of CO_2 carries more oil during the extraction process. It is also observed that effect of pressure on the yield increase is larger than the effect of temperature.

The highest yield was measured at 408 bar and looking at Fig. 4 it may be possible to further increase the yield by increments in the operational pressure or temperature; however an increase in temperature may degrade thermolabile compounds in the oil. Further experiments were performed at 80 °C and 544 bar achieving a yield of 10%.

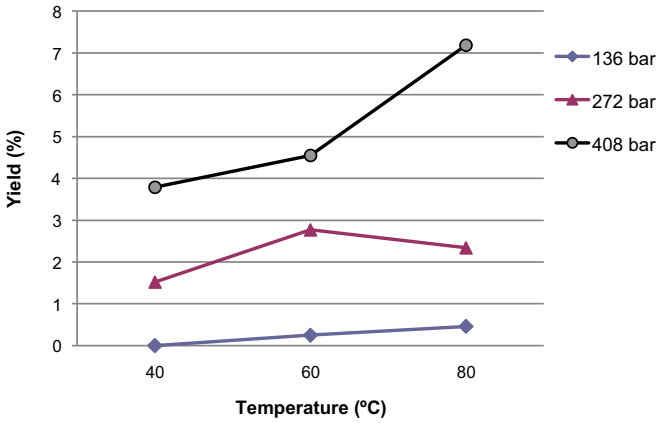

Fig. 4. Averaged yields obtained in chia oil supercritical extraction.

3.2. Kinetic study

Fig. 5 shows the results of the kinetic study. An asymptotic value for extracted oil is not observed and more time should be allowed to get the maximum amount of extraction. Comparing Figs. 1 and 5 it can be observed that the operation takes place up to region II only.

3.3. Comparison with other study [8]

From a comparison of the results reported in [8] and those in Fig. 4 show the same trends: Yield increases with pressure at the three temperatures; at low pressure, the yield remains constant or decreases with the increment of temperature; at pressures higher than 300 bar yield increase with temperature.

Both works report kinetic tests at the best extraction conditions (80 °C and 408 bar for this work and 80 °C and 450 bar for the reference). Here a mass flow rate for CO_2 of 1.8 g/min was used in a 0.1 l cell. Whereas the reference work used 30 g/min in a 0.5 l cell. The differences in the CO_2 flowrate explains why the maximum yield (region III of Fig. 1) was achieved in the reference work within 5 h of extraction and in the present work only the region II was achieved in 6.5 h of extraction.

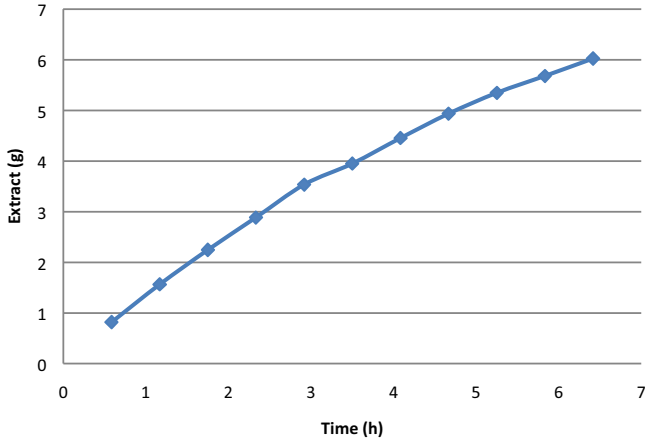

Fig. 5. Kinetic test for supercritical extraction, with $T = 80$ °C and $P = 408$ bar.

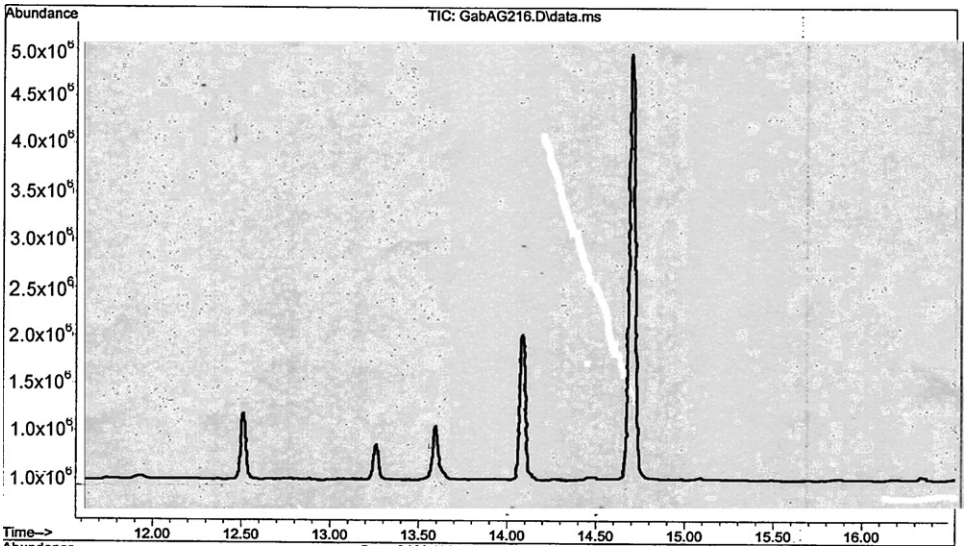

Fig. 6. Profile of fatty acids from chia oil obtained with gas chromatography/mass spectrometer.

Table 2
Fatty acid content (g/g of total acids) * 100 at different extracting conditions.

Extracting conditions	40 °C, 544 bar	60 °C, 408 bar	60 °C, 482 bar	60 °C, 544 bar	80 °C, 408 bar	80 °C, 544 bar
(g specific acid/g of total fatty acids) * 100						
Palmitic acid	7.12 ± 0.64[a]	7.96 ± 0.19	7.32 ± 0.28	7.52 ± 0.57	8.03 ± 1.51	7.16 ± 0.97
Stearic acid	3.09 ± 0.57	3.62 ± 0.18	3.81 ± 0.27	3.24 ± 0.44	4.09 ± 0.34	4.06 ± 1.35
Oleic acid (omega-9)	6.28 ± 0.48	6.87 ± 0.24	7.28 ± 0.48	6.70 ± 0.20	7.06 ± 0.37	6.97 ± 1.18
Linoleic acid (omega-6)	17.51 ± 0.36	17.67 ± 0.56	18.15 ± 0.10	18.07 ± 0.76	17.59 ± 0.42	17.37 ± 0.36
Linolenic acid (omega-3)	66.00 ± 1.56	63.88 ± 0.61	63.45 ± 1.12	64.47 ± 1.00	62.23 ± 3.85	64.44 ± 3.64

[a] Percentage ± standard deviation.

Another difference between these works is the definition of yield. Whereas in this work the yield is based on the total weight of raw seeds, the reference work defines yield in terms of the total amount of oil contained in the raw seeds, therefore their yield is calculated by

$$y_2 = \frac{\text{g of oil extracted}}{\text{g of total oil in charged seeds}} \quad (2)$$

In this study the time of extraction was 30 min for most of the runs, and the 0.1 l cell was charged with 30 g of chia seeds.

On the other hand, the reference study worked extraction times ranging from 60 to 240 min, charged 120 g of chia seeds containing 33% of oil, giving 39.6 g of total oil (denominator in Eq. (2)). With this one may recalculate the yields reported in the reference work to give comparable yields to those reported herein, by dividing grams of extracted oil by the mass of chia seeds charged in their cell (120 g). Regarding the comparison of the extraction times, a time correction factor is needed, which can be derived using the kinetic time data of Fig. 5. Thus for 0.5–1.0 h we get a correction factor of 1.3/0.8 = 1.625; for 0.5–2.5 h we get 3.0/0.8 = 3.75. Using this procedure the reported runs 15–18 performed at 60 °C, 350 bar and 2.5 h provide an averaged y_2 = 48.125: the weight of extracted oil was (0.48125)(39.6) = 19.06 g; dividing by the mass of chia seeds (120 g) gives $y_{1-2.5h}$ = 0.158; converting to an extraction time of 0.5 h gives $y_{1-0.5h}$ = 0.158/3.75 = 0.042 and plotting this value in Fig. 4 it falls between 272 and 408 bar. From this, one may conclude that the extraction yields in both works are comparable.

3.4. Fatty acids composition

Fig. 6 shows an example of the gas chromatography results and Table 2 presents the concentration of the five main components.

From these data it is observed that there are no interferences between the five fatty acids; Linolenic acid omega-3 and Linoleic acid omega 6 are the more abundant of the fatty acids with 80–84% of the total; the ratio omega-3/omega-6 varies between 3.49 and 3.77.

Fig. 7 shows the concentrations of omega-3 and omega-6 at several operating condition for the supercritical extraction of oil from chia seeds. In some cases the increase in temperature decrease the amount of the compound of interest due to thermal degradation.

It seems that at the temperatures and pressures tested, the degradation of the fatty acids of interest, i.e. omega-3 and omega-6, is very small or none.

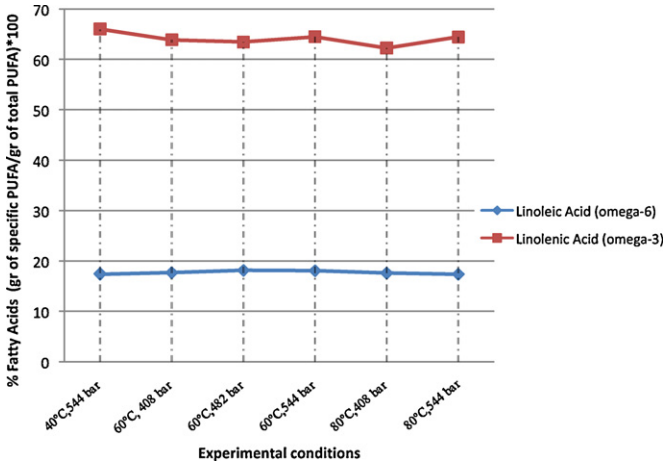

Fig. 7. Percentage of omega-3 and omega-6 at different operating conditions.

4. Conclusions

Oil from chia seeds is rich in fatty acids omega -3 and omega-6 and these may be obtained by supercritical extraction with CO_2. Using this method the final extract is free of solvent. The combination of $P = 408$ bar and $T = 80\,^{\circ}C$, provided the best yield (7.18%) among the tested conditions. Pressure has a more significant effect than temperature on the extraction yield. The kinetic curve obtained let us suppose a maximum yield of 25% with an extraction time of 10 h. The concentration of key compounds omega-3 and omega-6 do not decrease with the increment of temperature and pressure in the tested range.

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