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Supercritical Extraction of Linseed Oil: Economical Viability and Modeling Extraction Curves

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*The aim of the present study was to use supercritical technology to recover linseed oil (*Linum usitatissimum *L.) using carbon dioxide (alone or modified with ethanol as solvent) to determine the influence of the technique on the chemical composition of the oil obtained, model the kinetic curves of extraction, and estimate the manufacturing cost of the process. The experiments were conducted at 323 K, pressure of 25 MPa, constant solvent flow of* 1.7×10^{-5} *kg/s, and extraction time of 5 h. The highest yield was obtained with the addition of cosolvent (28.8%). The SFE process of linseed oil manufacture proved to be economically viable, resulting in a product with a specific cost of 13.21 US$/*$kg_{oil}$*. As to oil composition, the main fatty acids detected were linolenic and oleic acid.*

Keywords Carbon dioxide; Flaxseed; *Linum usitatissimum* L.; Linseed oil; Manufacturing cost

Introduction

The market for functional foods and nutraceuticals has grown rapidly in recent years, which has stimulated research on bioactive lipid components such as polyunsaturated fatty acids (especially $\omega 3$), phytosterols, tocopherols, and tocotrienols (Temelli, 2009). Among the foods highlighted for this purpose is flaxseed, which has a high content of polyunsaturated fatty acids, especially α-linolenic acid (50–55% of total fatty acids), dietary fiber, lignans, and phenolic compounds to which are attributed many health benefits, including the reduction of risk factors for cardiovascular disease and cancer (Chen et al., 1994; Tarpila et al., 2005).

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Flaxseed is classified as an oil crop in terms of its high oil content (35–45%) (Tarpila et al., 2005). This oil has applications not only in the food industry, but also in cosmetics, pharmaceuticals, and oil chemistry, among others.

Among the most widely used industrial technologies for the production of vegetable oils are hydraulic pressing, screw pressing, and solvent extraction with organic solvents (Willems et al., 2008). In the case of linseed oil, cold mechanical pressing and extraction with organic solvents are the extraction techniques used by industry. Although it is widely used for processing good quality products, cold pressing only partially retrieves the oil present in seeds and is therefore usually followed by extraction with an organic solvent (usually hexane), at relatively high temperatures, in order to increase oil recovery (Bozan and Temelli, 2002). However, the use of organic solvents such as hexane is facing government restrictions due to environmental concerns and safety because its toxicity can lead to problems for human consumption, given the likely presence of residues in the obtained product. Furthermore, the growth of the natural products market (in particular, functional foods and nutraceuticals) has stimulated the search for alternatives to the use of organic solvents for the processing of oils and fats, which has pointed to supercritical technology as an excellent option (Temelli, 2009). Besides being a clean technology, a great advantage of the supercritical fluid extraction (SFE) is the high quality of the obtained product, resulting from the easy removal of the solvent of the final extract and the use of moderate process temperatures, which protects the product from thermal degradation (Pereira and Meireles, 2007; Mezzomo et al., 2011), which is very convenient in the case of linseed oil, rich in polyunsaturated fatty acids and thus highly susceptible to oxidative degradation (Giroux et al., 2010).

Supercritical technology has been widely studied around the world and has been successfully used in the extraction of various vegetable oils: soy (Reverchon and Osséo, 1994; Dobarganes Nodar et al., 2002), cottonseed (Bhattacharjee et al., 2007), canola (Temelli, 1992; Jenab et al., 2006), wheat germ (Zacchi et al., 2006), and sunflower (Andrich et al., 2001), among others. Despite SFE presenting unquestionable advantages, this technique still has not spread industrially in Brazil because of its high initial cost, since the main drawback of the SFE process is the cost of equipment, inherent in the fact of working with high pressures (Rosa and Meireles, 2005; Pereira and Meireles, 2007). However, the development of industrial-scale units is decreasing the cost of the equipment used in the SFE process (Chordia and Robey, 2000; Del Valle et al., 2005).

In SFE, the cost of manufacturing (COM) is influenced by factors that can be divided into three categories: direct costs, such as equipment depreciation, taxes, and insurance; fixed costs that do not depend directly on production capacity; and general expenses, which are items necessary to maintain the business such as administrative costs, sales expenses, and research and development, among others (Turton et al., 1998; Pereira et al., 2007; Mezzomo et al., 2011). According to Rosa and Meireles (2005), to estimate COM one must know the extraction time and extract yield obtained during this time. An industrial-scale supercritical extraction unit should have the same performance as that of a laboratorial-scale unit, if the particle size, bed density (mass of particles per unit of column volume), and ratio between the mass of solid and the CO_2 flow rate are kept constant. This assumption should be precise if the scale-up is done by increasing the column diameter and the CO_2 is distributed similarly.

Thus, the purpose of this study is to determine the costs involved in the use of supercritical technology for extracting oil from flaxseed (*Linum usitatissimum* L.)

based on simulations of a scale-up conducted from data obtained experimentally. The economic viability of the SFE process was evaluated by comparing the costs with the market values of extracts obtained by low-pressure techniques. Moreover, literature models were applied in the modeling of extraction curves, and the effect of adding cosolvent on the chemical composition of the oil obtained was investigated.

Materials and Methods

The costs estimate of the SFE process for recovery of linseed oil was based on tests performed at the Laboratory of Supercritical Technology at UFRN (Brazil) in an extraction unit at laboratory scale. Carbon dioxide (alone or modified with ethanol) was used as extraction solvent and the brown variety of linseed was chosen for the experiments, as this is more common in Brazil.

Raw Material Preparation

The samples of brown linseed (*Linum usitatissimum* L.) used in the experiments were obtained from a market in Natal (Brazil), homogenized, stored in vials, and maintained below 278 K until use. Moisture content of the samples was determined according to AOCS Method 2–54 (American Oil Chemists' Society, 1993). To prepare the particle bed, the seeds were ground in a domestic multiprocessor (Arno, Brazil) for 20 s and separated in a Tyler sieve shaker (Bertel-Brazil). The granulometry of the samples was composed of a particle mixture with 30% of 24 mesh, 30% of 28 mesh, 20% of 32 mesh, and 20% of 48 mesh.

Supercritical Extractions

The SFE assays were conducted in a laboratory-scale extraction unit containing a 0.145 L extraction column. For each SFE assay, 138 ± 2 g of ground seed was used to make up the fixed particle bed.

A schematic drawing of the extraction unit used in the experiments is shown in Figure 1.

The parts of the unit are: RCO2 = CO_2 containing a siphon with capacity of 23 kg (99.5% pure, White Martins Gases Industriais); FL = stainless steel line filter (HOKE); RT = jacketed cylinder to keep the solvent as a subcooled liquid with capacity of $0.4 \times 10^{-3}\,m^3$; MP1 = Bourdon gauge (Record, 004-99, with capacity of $100 \pm 1\,kgf/cm^2$, Brazil); MP2 and MP3 = gauges (Zürich, Class A1, ABNT, 0–60 MPa); BT1 and BT2 = thermostatic bath (Tecnal, model TE 184); B1 and B2 = HPLC pumps (Constametric 3200, LDC Analytical, USA); FS = cosolvent vial; CE = jacketed equilibrium cell (stainless steel extractor, length of 0.60 m, diameter of 0.0216 m, and wall thickness of 0.028 m); VM = micrometric valve (Autoclave Engineers, stainless steel 316, 1/8″ OD, 15.000 psi, ref. 10VRMM2812) with heating system (NOVUS, model N480D, Brazil); G = 25 mL glass vial and glass recipient with ice cubes and water; MV = flow totalizer (LAO, model G1, Brazil); BM = glass glass bubble meter; VA = relief valve (Swagelok); V1,V2,V3,V4,VS = needle valves (Autoclave Engineers, stainless steel 316, 15.000 psi, ref. 10V2071).

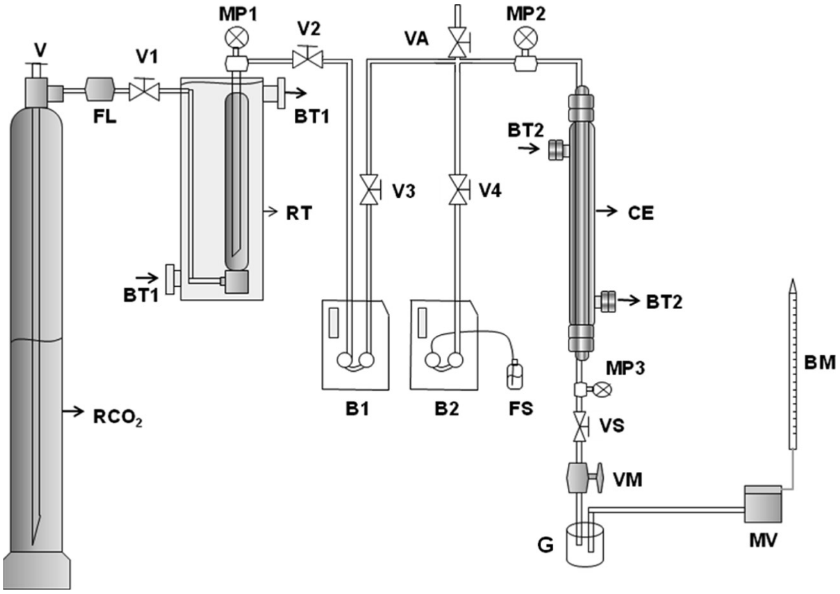

Figure 1. Experimental unit.

The experiments were conducted at 323 K, with an operational pressure of 25 MPa, constant solvent flow of 1.7×10^{-5} kg/s, and total extraction time of 5 h. Two experimental conditions were considered:

i) Condition 1: only CO_2 was used as extractive solvent.
ii) Condition 2: CO_2 + ethanol at 5% (v/v).

The other fixed conditions were particle size and bed density (mass of particles per unit of column volume). These experimental conditions were selected based on previous studies by Galvão (2009), who pointed to the pressure of 25 MPa and temperature of 323 K as being optimized conditions for the recovery of linseed oil within the investigated range of operating conditions. The fractions of extracted oil were collected in 25 mL glass vials (G) at previously established intervals, determined gravimetrically, combined in a single vial, and stored at 278 K in a refrigerator for subsequent analysis. For the extractions performed with the addition of cosolvent, the determination of the oil mass obtained was carried out after the cosolvent removal (using a rotary evaporator under vacuum at 313 K). Extraction curves (process yield versus extraction time) were plotted from these data.

Extract Analysis

The extracts were prepared to obtain fatty acid methyl esters (FAME) and underwent subsequent chromatographic analyses.

Obtaining Fatty Acid Methyl Esters (FAME)

The oil samples obtained were esterified according to the Association of Official Analytical Chemists AOAC 963-22 (2000) method and injected into the chromatograph.

Gas Chromatography

Analyses were performed by capillary gas chromatography (CGC) on an Agilent 6850 Series GC system. An Agilent DB-23 capillary column (50% cyanopropyl-methylpolysiloxane, 60 m × 0.25 mm × 0.25 μm) was used. The chromatographic conditions were the following: (1) temperature gradient: initial temperature was 383 K for 5 min, and heat was increased by 278 K/min up to 488 K, remaining at this temperature for 24 min; (2) vaporizer temperature: 523 K; (3) detector temperature: 553 K; and (4) carrier gas: He with flow rate of 1 mL/min. The identification of fatty acids in the samples was compared to the spectra of fatty acid patterns determined under the same conditions.

Modeling of Overall Extraction Curves

Mathematical models available in the literature were used in the modeling of extraction curves of the linseed oil. The software Mass Transfer, described by Kitzberger et al. (2009), in Delphi 7.0, was used for all the models.

The models applied to the extraction curves were:

- Esquível et al. (1999). This is an empirical model, whose equation (Equation (1)) is able to represent the typical shape of an extraction curve expressing extract mass or yield versus time. Since this model is totally empirical, its unique adjustable parameter, b, does not have physical interpretation.

$$m(t) = X_0 \; F\left(\frac{t}{b+t}\right) \tag{1}$$

  where $m(t)$ = extract mass (kg), X_0 = extract global yield (kg extract/kg feed), F = raw material feed (kg), t = time (min), and b = model parameter (min).
- Crank (1975) model. This model was presented by Reverchon (1997) and considers the solid particle as spheres. The governing mass transfer mechanism is intraparticle diffusion, therefore D, the effective solute diffusion coefficient in the particle, is the only model parameter. Equation (2) expresses the modeled extraction curve:

$$m(t) = X_0 \; F\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty} \exp\left(\frac{-n^2\pi^2 Dt}{r^2}\right)\right] \tag{2}$$

  where D = effective diffusion coefficient of the solute into the particle (m^2/min) and r = particle radius (m).
- Simple single plate (SSP) model discussed by Gaspar et al. (2003). As well as Crank's model, this approach considers intraparticle diffusivity to be the controlling mechanism of SFE. The difference is that now the solid particle is taken as a flat plate instead of a sphere. Thus, the effective diffusion coefficient within the solid matrix is again the model parameter, as can be observed in Equation (3). It is important to notice that both Crank's and Gaspar's models are based on Fick's second law of diffusion.

$$m(t) = X_0 \; F\left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2\pi^2 Dt}{\delta^2}\right)\right] \tag{3}$$

  where δ = particle thickness (m).

- Martínez et al. (2003) model. This model was originally conceived to consider the SFE extracts as mixtures of multiple compounds, to deal with the fact that each solute can have its own interactions with the solvent and then be extracted at different times. The model is based on the mass balance in the extraction bed, where the interfacial mass transfer term is a function of each solute. The model parameters t_{mi} and b_i are, respectively, the instant at which the extraction rate reaches its maximum value and a parameter related to the extraction rate. In the present work we assume the extract as a single pseudo compound, in a way that only one value of b and t_m should be found. Therefore, the model has two parameters, as shown in

$$m(t) = \frac{X_0\ F}{\exp(bt_m)}\left\{\frac{1+\exp(bt_{mi})}{1\ +\ \exp[b_i(t_{mi}-t)]}-1\right\} \tag{4}$$

  where b = extraction rate parameter (min^{-1}) and t_m = maximum extraction rate time (min).

Manufacturing Cost

According to Albuquerque and Meirelles (2012), COM provides analysis of data that can be compared with the costs of conventional extraction processes, creating new rationales for the development of SFE industries. According to Turton et al. (1998) and Albuquerque and Meirelles (2012), COM is influenced by direct costs, which are directly dependent on the production rate of raw materials, solvent lost during the process, demand for steam and cooling water required for the evaporator and condenser, electricity, and operational labor; fixed costs, which involve expenses for equipment, installation, depreciation, taxes and insurance, etc.; and general expenses, which consists in administrative costs, sales expenses, and research and development, among others.

The costs estimate of the SFE process for the production of linseed oil was made using the TECANALYSIS software, which is based on the methodology of Turton et al. (1998), and presented by Rosa and Meireles (2005), where production or manufacturing cost (COM) is calculated as a function of the following factors: fixed capital investment, costs of raw materials, operators, utilities, and waste treatment. More information about each cost factor can be obtained in Turton et al. (1998).

The expression for the calculation of manufacturing cost is given by Equation (5), as also presented by Comim et al. (2010):

$$COM = 0.304\,FCI + 2.73\,COL + 1.23\,(CUT + CRM + CWT) \tag{5}$$

where COM is the manufacturing cost corresponding to one year of operation; FCI is the capital investment, represented by equipment cost; COL is the cost of operational labor; CUT is the utility cost, consisting of energy cost of flash distillation, condenser, pump, and heat exchange operations; CRM is the raw material cost, consisting of CO_2, transport, and solid matrix costs; and CWT is the waste treatment cost.

The economical viability of SFE for linseed oil was evaluated by comparison with the commercial value of similar oil (in terms of characteristics).

Statistical Analysis

The results are presented as mean ± standard deviation. Variations found in the experimental trials were assessed using analysis of variance (ANOVA) and Tukey's test. Student's *t*-test for duplicate samples was used to compare the means obtained, where a significance level of $p < 0.05$ was set for all the calculations. EXCEL and INSTAT were the software programs used for testing.

Results and Discussion

Raw Material Characterization

Table I summarizes the characteristics of the samples used in the SFE experiments.

The sample of natural linseed had a moisture content of $7.6 \pm 0.1\%$. According to the literature, the SFE technique allows the use of raw materials with moisture content of up to 12% (Snyder et al., 1984). Accordingly, it was decided to work with natural linseed instead of submitting it to the drying process. This procedure was chosen in order to avoid thermal degradation of the oil contained in the seeds, given that it is rich in polyunsaturated fatty acids and thus highly susceptible to oxidation (Giroux et al., 2010).

SFE Experiments

Table II shows the yield obtained for the linseed oil extraction process under each experimental condition assessed. The yield of the SFE process was calculated from the ratio between the mass of linseed oil extracted (solvent free) and the mass of linseed introduced into the extraction column.

According to the results, the process yield increased considerably with the addition of cosolvent, indicating that the use of 5% (v/v) ethanol significantly favored recovery of the oil contained in the seeds. This fact is likely the result of intermolecular interactions between cosolvent (ethanol) and the components of the solid matrix (lipids present in the seed).

In studies conducted by Güçlü-Üstündağ and Temelli (2005), the addition of ethanol as cosolvent to the SC-CO_2 process promoted an increase in the solubility of a number of fatty acids, mainly due to H-bonding interactions. According to Temelli (2009), the association of polar cosolvents to the vegetable oil extraction process generally causes an increase in solubility, as a result of an increase in density of the SC-CO_2 + cosolvent mixture or intermolecular interactions between the cosolvent and a particular solute.

Lipid Composition

Table III shows the composition of fatty acids (FA) in the linseed oil obtained for each extraction condition investigated. Palmitic (C16:0), stearic (C18:0), oleic (C18:1),

Table I. Characterization of the linseed samples used in the supercritical assays

Mean particle diameter (m)	Moisture content (%)	Bed density (kg/m^3)
0.42×10^{-3}	7.6 ± 0.1	953 ± 2

Table II. Influence of the addition of cosolvent on the yield of the linseed oil extraction process

Experimental condition	P (MPa)	T (K)	% Cosolvent (v/v)	Yield (%)
1	25	323	0	8.6 ± 0.6
2	25	323	5	28.8 ± 1.4

linoleic (C18:2), and α-linolenic (C18:3) were the main fatty acids found in the brown linseed extracts.

Table III shows no significant differences ($p > 0.05$) between the fatty acid profile of the samples, that is, the samples obtained with the use of ethanol cosolvent (condition 2) exhibited no significant difference ($p > 0.05$) compared to the samples obtained with the use of CO_2 pure (condition 1). This result indicates that the addition of 5% (v/v) ethanol cosolvent did not influence the fatty acid composition of linseed oil. Although the use of ethanol promoted greater oil recovery, resulting in better extraction yields, it was not selective for any particular fatty acid.

Overall Extraction Curves (OEC) and Modeling

The OEC (process yield versus extraction time) for both conditions used are shown in Figure 2.

The experimental time for the assays was fixed at 300 min. As shown in Figure 2, the extraction curves practically coincided at the start of the process, diverging only after 60 min of extraction. For condition 1, the end of the constant extraction rate (CER) region occurred after 120 min of extraction, whereas for condition 2, the linear portion extends to 300 min. Figure 2 shows the increased extraction rate resulting from the addition of the ethanol cosolvent to the linseed oil extraction process. At the end of extraction, 0.09 and 0.29 $g_{oil}/g_{raw\ material}$ were obtained for extractions 1 and 2, respectively, that is, the addition of ethanol caused a significant increase of approximately 335% in linseed oil recovery.

In kinetic evaluation, the curve modeling for linseed extract was performed using the following models: Crank diffusion model (Crank, 1975), Esquível's model (Esquível et al., 1999), and the models of Gaspar et al. (2003) and Martínez et al. (2003).

The values found for the adjusted parameters of each model and the mean square error (MSE) are shown in Table IV.

Table III. FA composition (GC area % of total FA) of brown linseed oil obtained by SFE

	Fatty acid composition (%)					
Experimental conditions	C16:0	C18:0	C18:1	C18:2	C18:3	Nd
1[a]	6.51	5.19	21.96	13.86	51.49	0.99
2[b]	6.34	5.24	22.46	12.79	52.71	0.46

[a] Only CO_2 was used as extractive solvent.

[b] CO_2 + ethanol at 5% (v/v).

nd = not determined.

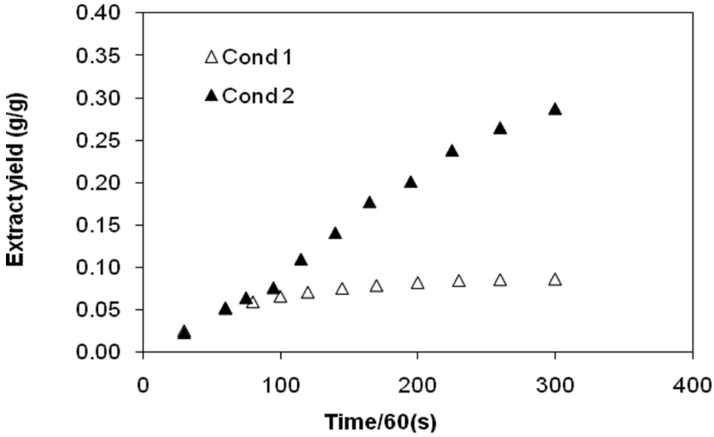

Figure 2. Experimental extraction curves of linseed at 25 MPa, 323 K, and 1.7×10^{-5} kg/s. (Δ) Condition 1: only CO_2; (▲) condition 2: CO_2 + ethanol at 5% (v/v).

In general, the Martínez et al. (2003) model and the simple single plate (SSP) model discussed by Gaspar et al. (2003) adjusted best to the experimental data and obtained the lowest MSE.

The SSP model is a diffusive model that assumes the shape of the plate for the particle. This model supplies a good fit to the experimental linseed oil extraction data over the entire length of the curve in the assays where the cosolvent was not used. In the cases where the cosolvent was used in the extraction process, the shape of the extraction curves was quite different. For these assays, only the Martínez et al. (2003) model managed to represent the tendency of the curves. This indicates that the presence of a cosolvent alters the mass transfer mechanisms of the process, reducing the importance of diffusion in the solid matrix.

The Martínez et al. (2003) model has two parameters to calculate (b_i and t_{mi}), in contrast to the other models used here, which have only one parameter to calculate. The existence of an extra parameter in the Martínez et al. (2003) model resulted in lower mean square errors in predicting experimental linseed oil extraction data.

Figures 3 and 4 show the kinetic extraction curves calculated for each model tested, along with the experimental data. Figure 3 shows the model fit for the experiment conducted without the cosolvent at 25 MPa and 323 K (condition 1). The models describe the curve behavior well, with good representation of the experimental data, mainly for the SSP model, whose mean square error was 0.019.

Figure 4 shows the model fit for the experiment carried out at 25 MPa and 323 K in the presence of 5% ethanol (v/v) cosolvent (condition 2). For this case, only the Martínez et al. (2003) model fit the experimental data well, obtaining a mean square error of 0.463. The remaining models did not reflect the tendency of the curve, showing very high deviations.

Economic Evaluation

The SFE conditions used for cost evaluation were 25 MPa/323 K (extraction condition 1), since it was the condition that resulted in the best recovery of linseed oil without the addition of cosolvents. Such a choice was based on the impossibility

Table IV. Parameters of the models fitted to the experimental curves obtained in the SFE tests for linseed oil/CO_2 and linseed oil/CO_2/5% ethanol (v/v)

			Crank (1975)		SSP (Gaspar et al., 2003)		Esquível et al. (1999)		Martínez et al. (2003)		
P (MPa)	T (°C)	Cosolvent (%)	$D \times 10^9$ (m^2/min)	MSE	$Dm \times 10^9$ (m^2/min)	MSE	b (min)	MSE	$bi \times 10^3$ (min^{-1})	tmi (min)	MSE
25	50	0	3.55	0.171	4.71	0.019	36.68	0.342	14.42	−319.30	0.281
25	50	5	1.01	47.250	1.61	37.287	136.67	32.457	15.90	132.24	0.463

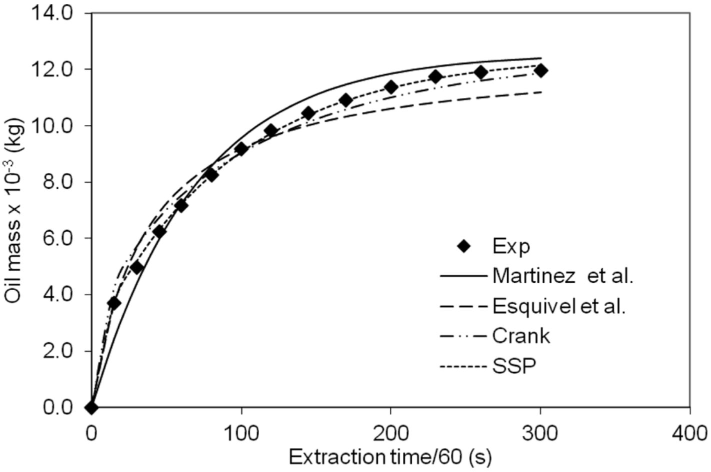

Figure 3. Comparison between the experimental data and the fits of different models for the extraction curve: oil mass vs. extraction time P = 25 MPa, T = 323 K, and cosolvent percentage = 0%.

of estimating the costs for solvent removal of the product, since the software used, TECANALYSIS, does not offer this option.

The SFE data used to estimate the COM values are presented in Table V.

For the calculation of COM, the parameters of assays performed in the 0.145 L experimental extractor were extrapolated to an industrial-scale supercritical extraction unit containing two 500 L columns operating alternatively, simulating a continuous process. Fixed capital investment (FCI) involves expenses for equipment. The cost of this industrial-scale unit is in of the order US$1,150,000 (Albuquerque and Meireles, 2012), considering an annual depreciation rate of 10%. A total annual

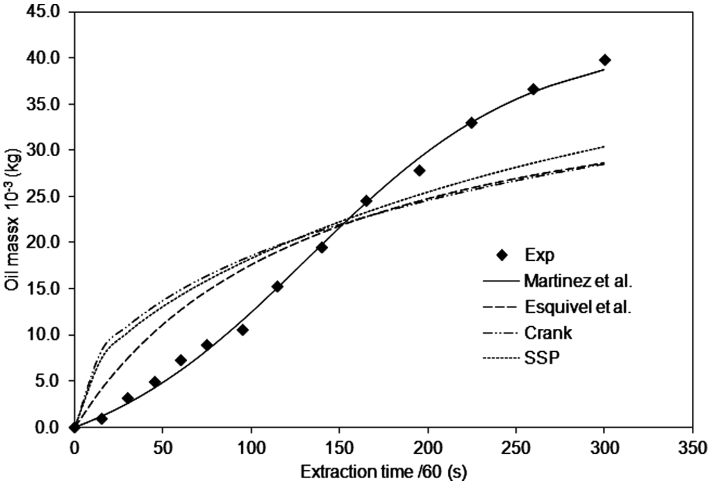

Figure 4. Comparison between the experimental data and the fits of different models for the extraction curve: oil mass vs. extraction time. P = 25 MPa, T = 323 K, and cosolvent percentage = 5%.

Table V. SFE data used for determination of COM for linseed oil: parameters considered for cost estimation

Process parameter	SFE (Condition 1)	Reference
Initial investment (equipment)	Unit with 0.5 m^3 (US$1,150.000 in Chinese market price)	Albuquerque and Meireles (2012)
Time of annual operation	24 h/day during 330 days/year	Albuquerque and Meireles (2012)
Operational labor cost	6.00 US$/h	Albuquerque and Meireles (2012)
Raw material cost	465 US$/ton	Sidra (2012)
Transportation cost	zero (was considered that the industry SFE is located next to a flaxseed meal processing industry)	—
Initial moisture	7.6% (w/w)	—
Final moisture	final moisture = initial moisture	—
Milling and drying cost	30 US$/ton $_{\text{(raw material)}}$	Mezzomo et al. (2011)
CO_2 cost and lost	0.15 US$/kg, 2%	Albuquerque and Meireles (2012)
Electricity, water refrigeration, and saturated steam costs	0.107 US$/Mcal, 0.0837 US$/Mcal, 0.0133 US$/Mcal	CPFL (2011); Rosa and Meireles (2005); Comim et al. (2010)
Depreciation	10.0%/year	Comim et al. (2010)
Separation pressure	4 MPa (considering that in this condition all extract liquid)	Rosa and Meireles (2005); Comim et al. (2010)
SFE pressure	25 MPa	—
SFE temperature	323 K	—
Cosolvent	no	—
CO_2 flow rate (ton/h)	0.17	—
Batch density (kg/m^3)	953	—
Wastewater treatment	zero (the raw material remaining after extraction can be used in animal feed)	—

operation time of 7920 h/year was considered, with working time of 24 h, 330 days/year. The cost of operational labor (COL) is related to the operators of the extraction units. Two operators per shift will be needed to work in an industrial unit containing two extraction columns, plus one CO_2 reservoir, one flash tank, one condenser, one heat exchanger, and one expansion valve (Ulrich, 1984; Pereira and Meireles, 2007). COL was estimated from the number of man-hours required to run each item of equipment of the supercritical extraction unit as 6.00 US$/h (Albuquerque and Meireles, 2012).

In this simulation, cost of raw materials (CRM) was mainly composed of the solid substance (seed) cost, second, by the pretreatment cost of the raw material, and finally by the CO_2 cost. In Brazil, the linseed cost is high because of small production, limited to the south of the country (Sidra, 2012).

The utilities cost (CUT) considers the energy use involved in the solvent cycle for steam, cold water, and electricity. The cost of electricity used was 0.107 US$/kWh (the price charged by the electric power company for industries in 2011 (CPFL, 2011). According to Comim et al. (2010), CUT is affected by three different factors: type of equipment, pressure, and temperature. The binary pressure and temperature affect the flash distillation costs, while the pressure affects the pump costs since it is the equipment responsible for creating and maintaining the pressure in the supercritical apparatus. In this simulation, CUT is mostly affected by the cost of CO_2 condensation after the separation vessel, despite operational conditions.

The solvent flow rate presented in Table V was calculated based on the assumption that conserving the Q/F ratio from small to large scale leads to similar extraction kinetics, and, thus, equal extraction curves. This was observed in SFE from other oily seeds (Martínez et al., 2007; Mezzomo et al., 2009), indicating that keeping constant Q/F is a valid scale-up criterion. Moreover, the model parameters are preserved from small to large scale when such criterion is adopted.

The influence of the extraction time on the specific COM, defined as the manufacturing cost divided by the total mass of produced extract, can be observed in Figure 5. In the calculation of the specific COM, the extraction yields for each extraction time presented in Figure 2 were used (only condition 1).

Extraction condition 1 (without cosolvent) shows an inflection at around 120 min of extraction, with increasing specific costs from this point on. Such behavior is attributed to the fact that the highest extraction rates were obtained during the constant extraction rate (CER) region of the extraction curve ($t_{CER} = 120$ min),

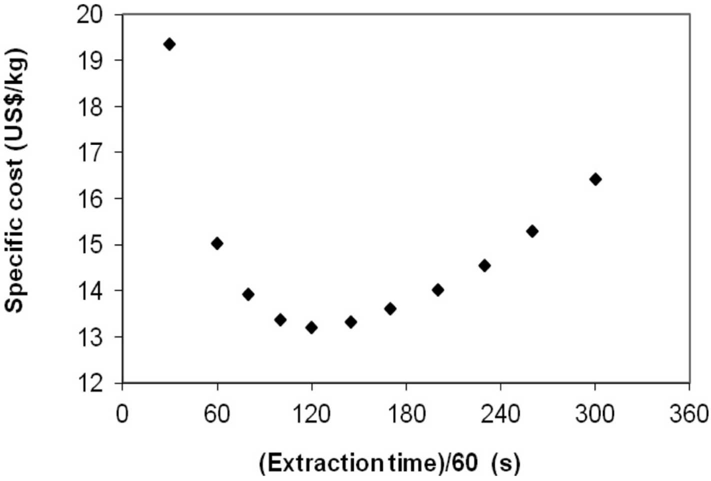

Figure 5. Influence of extraction time on the specific manufacturing cost of linseed oil; condition 1: only CO_2.

Table VI. Percentage of each individual cost in the COM of linseed oil

Individual cost	% COM
FCI	19.87
CRM	65.90
COL	13.68
CUT	0.54
CWT	0
Cost of manufacturing (US$)	1,757,285.83
Mass of extract (kg)	133,029.30
Specific cost (US$/kg)	13.21

FCI = value of fraction of investment (US$/year); CRM = raw material cost (US$/year); COL = operational labor cost (US$/year); CUT = utilities cost (US$/year); CWT = waste treatment cost (US$/year); COM = manufacturing cost (US$/year).

that is, after 2 h the extraction rate starts to decrease (falling extraction rate (FER) stage of the extraction curve in Figure 2) and the mass of extract produced decreases, raising the specific cost of the product. Furthermore, if a very long extraction time is used, the impact of the raw material cost on the COM decreases (since the frequency of fresh raw material is reduced), but the investment, operational labor cost, and utility costs increase, raising the specific cost of the extract. In the case of the condition studied it is more beneficial to work with 2 h production cycles, which would result in a product with a specific cost of 13.21 US$/$\text{kg}_{\text{oil.}}$ According to these results, one way to reduce COM even more would be to increase the yield of the CER region and reduce its duration.

In Brazil, the linseed oil obtained by cold mechanical pressing is sold at 53.40 US$/kg (Naturalis, 2012). Thus, considering that the difference between the cost of manufacturing the oil by SFE and the market price is 40.18 US$/kg oil or 404%, the SFE process was considered feasible for manufacturing linseed oil.

Table VI shows the impact of each individual cost in the COM of linseed oil. The percentages were calculated only for the lowest specific cost observed.

Under the study conditions, the highest costs for the SFE process of linseed oil production were those involving raw materials and fixed capital investments. CRM accounted for 65.90% of the COM and FCI represented 19.87%, with 13.68% and 0.54% spent on COL and CUT such as energy, steam, water, etc. Cost of waste treatment (CWT) is disregarded, since it was considered that the solid waste generated (depleted linseed) can be used in the production of animal feed. As mentioned previously, linseed cost in Brazil is quite high due to small grain production. Consequently, this fact contributes to the raw material cost being the major component of the COM of linseed oil by the SFE process.

Conclusions

The SFE process of linseed oil production resulted in mean extraction yields of 8.6% (for extraction condition 1) and 28.8% (condition 2). These results indicate that the use of 5% (v/v) ethanol as cosolvent (extraction condition 2) considerably favored the recovery of oil contained in the seeds, likely resulting from an increase in oil solubility caused by a density rise in the $SC\text{-}CO_2$ + cosolvent mixture.

As to oil composition, the main fatty acids detected were α-linolenic (51.49% to 52.71%) and oleic (21.96% to 22.46%) acid, with no significant statistical difference ($p > 0.05$) between the samples.

With respect to economic assessment, the SFE process used in the manufacture of linseed oil was economically feasible, which resulted in a product with a specific cost of 13.21 $US\$/kg_{oil}$. Even though taxes, storage, and transportation costs must be added to the estimated price to derive the final cost of the linseed oil, it was considered that the product can be competitive in the market, given that the difference between extraction cost and market price of the oil was 40.18 $US\$/kg_{oil}$ or 404%. The most onerous costs for the process were those involving raw materials and fixed capital investment.

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Nomenclature

b	adjustable parameter of the empirical model, min
b_i	parameter related to the extraction rate in Martínez et al. (2003) model, min^{-1}
CER	constant extraction rate
COL	cost of operational labor, US$
COM	manufacturing cost corresponding to one year of operation, US$
Cond 1	condition 1
Cond 2	condition 2
CRM	raw material cost, US$
CUT	utility cost, US$
CWT	waste treatment cost, US$
D	solute diffusion coefficient in the particle, m^2/min
F	solid feed, kg
FCI	capital investment, US$
FER	falling extraction rate
MSE	mean square error
P	pressure, MPa
Q	solvent flow rate, kg/s
$SC\text{-}CO_2$	supercritical CO_2 extraction
SFE	supercritical fluid extraction
SSP	simple single plate
T	temperature, K
t_{mi}	instant at which the extraction rate reaches its maximum value, min
Yield	(kg of linseed oil extracted/kg of raw material used) × 100, %

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