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Pressurized Liquid Extraction of Oil from Soybean Seeds†

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†This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: [10.1002/cjce.22992]

Received 15 February 2017; Revised 12 April 2017; Accepted 17 April 2017
The Canadian Journal of Chemical Engineering
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DOI 10.1002/cjce.22992

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Abstract: The aim of this study was to investigate the extraction of soybean oil using ethanol under pressurized conditions. The effects of pressure (10 and 20 MPa), temperature (30 to 90 °C) and solvent flow (1 and 3 mL/min) were evaluated applying different extraction times. In addition, the thermodynamics parameters of the process were determined. It was observed that the pressure exerted no influence on the extraction kinetics, while an increase in temperature promoted better yields. The use of the highest solvent flow increased the initial extraction rate, but did not influence the yield under equilibrium conditions. Based on the thermodynamic parameters, the extraction was classified as endothermic (44.11 kJ/mol), irreversible (143.52 J/mol K) and partially spontaneous (0.60 to -8.01 kJ/mol), and an increase in the temperature favoured this spontaneity. Extraction using the classical Soxhlet method was evaluated for comparison purposes using ethanol and *n*-hexane as solvents and ethanol showed a better extraction efficiency. The maximum yield obtained with pressurized liquid extraction (PLE) was 24.42 %, which represents ~94 % of the yield obtained by classical extraction. Linoleic and oleic acids were the main fatty acids identified in the soybean oil, representing ~76 % of the fatty acids composition, which was not influenced by the extraction method or the temperature used in the PLE. This article is protected by copyright. All rights reserved

Keywords: Ethanol; thermodynamic parameters; extraction kinetics.

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INTRODUCTION

According to the US Department of Agriculture,[1] the world soybean production in the 2015/2016 harvest reached 320 206 tons, being Brazil the second largest producer and exporter in the world, reaching a production of 100 000 tons and exporting 59 500 thousand tons.

Currently, the largest soybean markets in Brazil are the food industry (human and animal feed) and export sector (grain and oil), and soybean also provides a raw material for biodiesel production. According to ABIOVE,[2] the Brazilian production of soybean oil was equivalent to 8050 tons in July 2016, supplying a domestic consumption of 6500 tons. According to data from the Brazilian National Agency of Petroleum, Natural Gas and Biofuels,[3] soybean oil is widely used for the production of biodiesel and represents 75.17 % of the raw material for the national production of this biofuel.

In the case of vegetable oils, extraction is usually carried out using an organic solvent or mechanical pressing.[4] In solvent extraction, n-hexane is the solvent most commonly used in industry, since this petroleum distillate offers high stability and low levels of corrosion and it allows a high yield of oil to be removed from the vegetable matrix.[5] Extraction by mechanical pressing is easy to operate, adaptable to several oilseeds and promotes rapid extraction without harming the environment.[6] However, the efficiency is lower in comparison with processes in which solvents are used.

The traditional extraction methods mentioned above have limitations. Mechanical pressing is limited in terms of its applicability, especially the low oil extraction yield.[4] The solvent n-hexane is highly flammable and has a high toxicity, being considered an air pollutant and a health hazard.[7] The disadvantages of *n*-hexane have encouraged researchers to study the efficiency of other solvents. In this regard, the solvents most commonly cited are

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water, with or without enzyme addition,[8] supercritical carbon dioxide,[9] subcritical propane,[10] and short chain alcohols, particularly ethanol.[5,11–14]

In Brazil, ethanol is obtained from sugarcane, which allows the development of advantageous energy technologies which are not harmful to the environment. Brazil is the largest producer of sugarcane and its derivatives in the world and in the 2015/2016 harvest around 670 million tons of sugarcane and 30.5 million litres of ethanol were produced.[15] The use of ethanol as an extraction solvent is mainly due to the fact that it is produced on a large scale in Brazil, and it is renewable and non-toxic.[16,17] In addition, ethanol is considered a GRAS (generally recognized as safe) solvent recommended for use in the food and pharmaceutical industry.[18]

Several extraction techniques have been studied to obtain vegetable oils using environmentally acceptable solvents, including pressurized liquid extraction (PLE).[18,19] Pressurized liquids have the advantage of increasing the solubility of the oil in the solvent and improving the mass transfer properties, such as the diffusion rate. Also, PLE requires a shorter extraction time and consumes a smaller volume of solvent and it is therefore considered a process intensification method.[19]

A notable advantage of PLE relates to the process variables, such as the use of temperatures (from low to high) and pressures above atmospheric conditions. The temperature applied in PLE influences the viscosity of the solvent and decreases the solute-solvent surface tension, allowing greater penetration of the solvent into the vegetable matrix.[20,21] The pressure combined with the temperature is critical to maintaining the solvent in the liquid state. The use of pressure facilitates the extraction from samples in which the analyte is retained in the pore of the matrix, since the pressure forces the solvent to penetrate areas of the matrix that would not normally be reached by the solvent using atmospheric conditions.[22]

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In this context, the objective of this study was to evaluate the efficiency of pressurized liquid extraction (PLE) to obtain soybean oil using ethanol as a solvent. The effects of the process variables (pressure, temperature and solvent flow rate) on the yield were evaluated, and the extraction kinetics and thermodynamic parameters were determined. Extraction by the classical Soxhlet method, using ethanol and *n*-hexane, was also carried out and the results compared with those obtained in the PLE.

MATERIALS AND METHODS

Preparation of Sample

The soybean seeds BMX RR (Transgenic), obtained in the Pranchita region, Paraná State, Brazil, had a moisture content of 0.0878 ±0.000 07 g/g (8.78 ±0.07 wt%). The material was ground in a knife mill (Willy, MSSL-031) at a speed of 5000 rpm and the granulometric classification was then carried out using Tyler sieves (Bertel, series 1.0) and a mechanical agitator (Marconi, MA 750). The particles retained on the 20-mesh sieve with an average diameter of 0.72 mm were used in the experiments.

Classical Extraction

The classical extraction was carried out in Soxhlet equipment (Logen Scientific), using ethanol (Panreac, 99.9 %) and *n*-hexane (Anidrol, 98.5 %) as solvents. The extraction was performed using a sample to solvent ratio of 1:30 (g/mL) and 480 min of extraction and the temperature was kept constant above the solvent reflux temperature (78.4 °C for ethanol and 69.1 °C for *n*-hexane) in all runs using an electric heating plate (Logen). The extraction flask was attached to the condenser coupled to a refrigerated bath (Marconi, MA 184), operating at 10 °C. After the extraction time the solvent remaining in the flask was evaporated to constant weight and the yield was calculated according to Equation (1).

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$$Yield \quad (\%) \quad = \frac{w_o}{w_a} x100 \tag{1}$$

where w_o (g) is the mass of extract obtained and w_a (g) is the initial mass of soybean fed into the extractor.

Pressurized Liquid Extraction (PLE)

The PLE experiments were conducted using ethanol (Panreac, 99.9 %) as the solvent in a laboratory unit operated in semi-continuous mode, made of 316 stainless steel, according to the scheme shown in Figure 1.

Figure 1

The experimental apparatus consisted of a reservoir containing the solvent, which was fed into the extractor by high pressure pump for liquids (Waters, 515). The solvent passed through the preheating zone (internal diameter of 1.58 mm and length of 5 m), to ensure that it entered in the extractor (internal diameter of 9.525 mm and length of 0.3 m) at the test temperature, which was monitored by a thermocouple (Salvi Casa Grande). Synthetic steel filters (Phenomenex, 2 μm pores, diameter of 6.35 mm and thickness of 0.79) were fixed at the ends of the extractor. The system was heated in a heating bath (Nova Ética, 314/8). The samples were collected after passing through a cooling system (consisting of a metallic container of 1.5 L and serpentine with an external diameter of 1/8" and length of 1 m, submerged in water at a temperature of 10 °C) connected to a thermostated bath (Tecnal, TE 184). The system pressure was monitored by a pressure indicator (Record) and controlled by a needle valve (Autoclave Engineers, 10V2071) and pressure reduction valve (SWAGELOK, KPB120A415P20000).

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The experimental procedure adopted was to feed the extractor with the seeds (~6 g), heat the system for 20 min and then fill the extractor with the solvent. The system was then pressurized by controlling the needle and pressure reducing valves. After the test pressure was reached, the static extraction period (10 min) began, with the system kept closed. After this time, the dynamic extraction was started, maintaining the solvent flow rate fixed. Samples with predetermined mass were collected after different extraction times (up to 240 min) in glass flasks. The excess solvent was evaporated to constant weight and the yield calculated according to Equation (1).

Initially, experiments were carried out to evaluate the effect of the pressure, at 10 and 20 MPa, maintaining the temperature and solvent flow fixed at 70 °C and 1 mL/min, respectively. Subsequently, experiments were performed at temperatures of 30, 50, 70, and 90 °C at 10 MPa with a solvent flow of 1 mL/min. The effect of the solvent flow (1 and 3 mL min^{-1}) was evaluated using temperatures of 70 and 90 °C at 10 MPa. In all conditions evaluated, ethanol was under subcritical conditions.

Thermodynamic Parameters

Equation (2) was used to calculate the distribution coefficient of the solid-liquid system:[23]

$$K = \frac{q_\infty}{q_s} = \frac{q_\infty}{q_0 - q_\infty} \quad (2)$$

where q_∞ is the saturation yield, q_s is the amount of oil remaining in the seeds and q_0 is the total amount of oil present in the seeds (g of oil per g of seeds). The value of q_0 was based on the yield obtained in the classical extraction using ethanol as the solvent.

The thermodynamic properties were calculated from the linear adjustment of ln K and 1/T, based on the Van't Hoff equation (Equation (3)).

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$$\ln K = -\frac{\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (3)$$

where K is the distribution coefficient, ΔH° is the standard enthalpy change (J/mol), ΔS° is the standard entropy variation (J/mol K), R is the universal gas constant (8.314 J/ mol K) and T is the temperature (K).

The standard Gibbs free energy (J mol^{-1}) was calculated according to Equation (4).

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \quad (4)$$

where ΔH° is the variation in the standard enthalpy (J/mol), ΔS° is the variation in the standard entropy (J/mol K) and T is the temperature (K).

The thermodynamic parameters of the process (enthalpy, entropy, and Gibbs free energy) were calculated using Microsoft® Excel 2010 software.

Fatty Acids Composition

To determine the fatty acids composition, a gas chromatograph (GC–MS QP2010 SE, Shimadzu) coupled to a mass spectrophotometer was used. The samples were derivatized with BF3-methanol (Sigma-Aldrich) following the method described in AOCS Ce 2-66[24] and analyzed using the following chromatographic conditions: initial temperature of the column 70 °C increasing to 180 °C at a rate of 10 °C/min and then to 240 °C at a rate of 4 °C/min, which was held for 4 min. A Shimadzu Rtx-Wax capillary column (30 m x 0.32 mm x 0.25 µm) was used, with the injection of 1 µL in 1:20 split mode. The analysis was performed with the injector and detector both at 250 ºC. The components present in the samples were identified through a comparison with a FAME (fatty acid methyl esters) mixture (Supelco) and quantified using methyl heptadecanoate (Sigma-Aldrich, > 99 % purity) as the internal standard.

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Analysis of Data

All assays and analysis were performed in duplicate and the data collected were subjected to ANOVA using Excel® 2010 software and the Tukey test (with a 95 % confidence interval), to evaluate differences between the results.

RESULTS AND DISCUSSION

Classical Extraction

Table 1 shows the yields obtained from classical extraction (Soxhlet) using ethanol and *n*-hexane as solvents.

It can be observed in Table 1 that ethanol provided a higher yield when compared to *n*-hexane ($p < 0.05$). This result is due to the capacity of ethanol to remove other solutes besides lipids.[13] According to reports in the literature, during extraction with ethanol, in addition to lipids, phosphatides, polyphenols, pigments and soluble sugars are extracted.[12,25] Baümler et al.[12] studied the composition of the material extracted from sunflower seeds by Soxhlet extraction and verified the presence of sugars in the extracts obtained using ethanol as the solvent.

The results obtained with the use of ethanol corroborate with the studies of Terigar et al.,[26] Toda et al.,[5] and Dagostin et al.[13] who reported yields of 18.9, 25.6, and 25.58 %, respectively, for Soxhlet extraction using this solvent.

Pressurized Liquid Extraction

Figure 2 shows the extraction kinetics data obtained at 70 °C with a flow rate of 1 mL/min at pressures of 10 and 20 MPa. The data reported in this figure verify that the

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increase in pressure had no influence on the yield ($p > 0.05$), and at 240 min yields of 22.49 and 22.32 % were obtained at 10 and 20 MPa, respectively. This effect is observed because the ethanol is well below its critical temperature, so that the pressure exerts little effect on the solvent properties.[27]

This is consistent with the results obtained by Conte et al.[14] in the extraction of safflower seed oil using ethanol under pressurized conditions. The authors reported yields of 12.21 % and 11.21 % at 10 and 20 MPa, respectively. Sheibani and Ghaziaskar[28] reported that the yield of pistachio oil extraction was only slightly influenced by an increase in pressure from 10 to 15 MPa. Debien et al.[29] carried out the pressurized liquid extraction of Brazilian ginseng oil at 90 °C, using ethanol at 10 and 20 MPa, and obtained yields of 3.13 % and 3.63 %, respectively. Freitas et al.[20] reported the extraction of grape seed oil by PLE at 10.34 MPa and affirmed that this pressure is sufficient to maintain the solvent, *n*-hexane, in the liquid state.

Considering the energy consumption and that there was no significant difference ($p > 0.05$) between the yields at the pressures evaluated, a pressure of 10 MPa was selected for the subsequent steps. Figure 3 shows the results of these experiments at temperatures of 30 to 90 °C, maintaining a fixed flow rate of 1 mL/min.

Based on the data shown in Figure 3, it is possible to verify that the oil diffuses faster in the initial extraction stage and after around 50 min the diffusion occurs slowly, with a tendency to reach equilibrium. An increase in temperature favoured higher oil yields ($p < 0.05$) and yields of 12.35, 16.9, 22.49, and 24.42 % were obtained at temperatures of 30, 50, 70, and 90 °C, respectively.

The results showed that the highest extraction temperature (90 °C) promoted the

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highest yield. The advantage of PLE in relation to the classical extraction procedure, conducted at atmospheric pressure, is that the pressurized solvents used in PLE remain in the liquid state above their boiling points, allowing the use of high temperatures in the extraction.[22,30] High temperatures improve the extraction efficiency by increasing and accelerating the mass transfer and diffusion rate.[31] According to Freitas et al.,[20] this occurs because the high temperature affects the solute-matrix interactions, weakening the hydrogen bonds and promoting an increase in the solubility of the compounds of the vegetal matrix in the solvent, and also favours solvent transport due to a decrease in the viscosity.

Colivet et al.[32] performed the extraction of oil from watermelon seeds using ethanol under pressurized conditions (10.34 MPa) and obtained yields of 24.69 and 37.21 % at 40 and 80 °C, respectively. Dunford and Zhang[30] performed the extraction of wheat germ oil under pressurized conditions (10.34 MPa) in order to investigate the effect of temperature (45 to 90 °C) and obtained yields of > 10.5 % at 90 °C. In addition, Dagostin et al.[13] reported higher yields of flaky soybean oil with increasing temperature; however, the extraction was conducted at low pressure with temperatures of 25 to 55 °C.

The best yields for PLE were obtained for the higher temperatures and thus these temperatures were selected to evaluate the influence of the solvent flow. Figure 4 shows the extraction kinetics obtained at 10 MPa as a function of temperature (70 and 90 °C) at solvent flow rates of 1 and 3 mL/min.

It can be observed in Figure 4 that an increase in the flow rate influenced the initial rate of extraction, however, it did not influence the yield at equilibrium ($p > 0.05$). Based on the extraction kinetics at 70 °C, shown in Figure 4a, it is possible to verify that during the first 5 min of extraction yields of 2.57 and 5.98 % were obtained, respectively, for the solvent flows of 1 and 3 mL/min. A similar trend was observed at 90 °C, an increase in the initial rate of extraction being achieved with a faster solvent flow.

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According to Pitipanapong et al.,[33] this occurs because the higher amount of solvent introduced into the extractor increases the solute-solvent contact surface. For a flow rate of 1 mL/min, the extraction rate is lower due to greater solvent penetration into the particles of the vegetable matrix, because the solvent stays for a longer time in contact with the solid, demonstrating the effect of internal diffusion. Conte et al.[14] conducted the extraction of safflower oil at 30 °C under pressurized conditions and obtained yields of 9.29 % and 17.62 % at 10 MPa and 10.27 % and 16.58 % at 20 MPa, using solvent flow rates of 1 and 3 mL/min, respectively.

The highest yield obtained in the PLE (24.42 %) was lower ($p < 0.05$) than that obtained by the classical method (26.05 %). The sample:solvent ratio may have been a factor influencing yield. In the PLE a sample:solvent ratio of ~2:1 (w/v) used was whereas the classical method required a ratio of 1:30 (w/v), besides that during extraction by the classical method, the solvent remains in contact with a solid matrix for a longer time, resulting in extraction of higher oil content. However, it should be noted that the classic method presented an increase of only 7 % in the yield. Saxena et al.[11] studied the extraction of cottonseed oil using ethanol and *n*-hexane as solvents and observed that an increase in the solid:liquid (m/v) ratio from 1:5 to 1:15 promoted an increase in the yield for the two solvents evaluated. According to Goula,[34] a higher amount of solvent in the solid-liquid system promotes a greater concentration difference, favouring the mass transfer process.

According to the data obtained for the extraction kinetics, the highest yield obtained under equilibrium conditions was 24.42 % at 90 °C and 10 MPa. Toda et al.[5] studied the kinetics of soybean oil extraction at low pressure using ethanol and obtained a yield of 20.06 % at 60 °C.

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Thermodynamic Analysis

The thermodynamic parameters were determined from the equilibrium yield and the amount of oil remaining in the meal after extraction. The distribution coefficients at different temperatures were calculated using Equation (2). Table 2 shows the equilibrium yield and the amount of oil remaining in the meal after the extraction process, as well as the respective distribution coefficients for each temperature evaluated in the PLE.

It can be seen in Table 2 that the distribution coefficient increased when the temperature ranged from 30 to 90 °C. Figure 5 shows the linear correlation between ln K and 1/T, which presented a coefficient of determination (r^2) of 0.97, indicating that the model satisfactorily describes the experimental values.

It was possible to estimate the standard enthalpy change (ΔH°) and the standard entropy variation (ΔS°) from Equation (4), by means of the angular and linear coefficients given in Equation (5).

$$\ln K = -5{,}305.3 \frac{1}{T} + 17.262 \quad (5)$$

Based on the results obtained for ΔH° and ΔS°, the Gibbs free energy variation (ΔG°) was determined, and this parameter was calculated using Equation (3). Table 3 shows the thermodynamic parameters for the extraction of soybean oil.

As observed in Table 3, based on the slope of the line, the value for the enthalpy variation (ΔH°) was 44.11 kJ/mol. The positive sign of the enthalpy (ΔH°>0) indicated that the process is endothermic and requires more energy during extraction.[35] The intercept of the line allowed the calculation of the change in the entropy (ΔS°>0), which was found to be 143.52 J/mol K. Positive entropy indicates that the endothermic process shows randomness and irreversibility.[36]

The negative value for the Gibbs free energy variation (ΔG°<0) indicates a decrease in

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free energy and therefore the process of extracting soybean oil at temperatures of 50 to 90 °C was spontaneous,[23] with values of 0.60 to -8.01 kJ/mol. The spontaneity of the soybean oil extraction was favoured by an increase in the extraction temperature, since the Gibbs free energy was more negative at the higher temperatures.

Maziane and Kadi[37] performed the calculation of the thermodynamic parameters for the extraction of olive bran oil in the temperature range of 20 to 50 °C and obtained ΔG° values ranging from -4.47 at -6.25 kJ/mol. Dagostin et al.[13] obtained a ΔH° value of 95.01 kJ/mol and ΔS° of 320.02 J/mol, with ΔG° ranging from -0.41 to -11.61 kJ/mol in the temperature range of 25 to 55 °C, for the extraction of soybean oil from flakes using ethanol.

Fatty Acids Composition

The samples obtained by PLE and classical extraction were analyzed in terms of the fatty acids composition and the results are shown in Table 4. Samples obtained at 70 and 90 °C, using flow rate of 3 mL/min and 20 MPa, in the PLE were selected in order to evaluate an influence of temperature.

It can be seen from the data reported in Table 4 that the fatty acids composition was not affected by the extraction method used or by the temperature applied in the PLE ($p > 0.05$). Freitas et al.,[20] Jesus et al.,[27] and Trentini et al.[38] reported that the PLE process conditions have little influence on the fatty acids composition of grape, palm, and macauba pulp oils.

Linoleic and oleic acids were the main fatty acids identified, in agreement with results reported in the literature for soybean oil obtained from classical extraction,[39] ultrasound-assisted extraction[40,41] and supercritical extraction,[42] and for a commercial sample.[43]

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4. Conclusions

The potential of pressurized liquid extraction to obtain soybean oil, with ethanol as the solvent, was explored. The yield obtained during the extraction time was not influenced by an increase in pressure; however, it did increase as a function of temperature, with the highest yield obtained at 90 °C. A faster flow rate led to an increase in the initial extraction rate, but did not affect the equilibrium yield. The thermodynamic parameters indicate that the extraction process using pressurized ethanol is spontaneous, especially at higher temperatures. Classical extraction (Soxhlet) showed a maximum yield of 26 %, using ethanol, while PLE indicated a maximum yield of 24.42 %. The extracted soybean oil contained ~76 % of the linoleic and oleic acids.

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Table 1. Yield obtained from soybean seeds by classical extraction (Soxhlet).

Solvent	Yield (%)
Ethanol	26.05±0.7[a]
n-hexane	18.65±0.18[b]

Means followed by different letters indicates a significant difference ($p<0.05$)

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Table 2. Yield equilibrium, amount of oil that remained in the meal after extraction process and distribution coefficients.

T (°C)	q_∞ (g/100 g)	q_s (g/100 g)	K
30	12.35	13.69	0.90
50	16.86	9.19	1.84
70	22.49	3.56	6.32
90	24.42	1.62	15.05

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Table 3. Thermodynamic parameters for the extraction of soybean oil using ethanol under pressurized conditions.

T (°C)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)
30	44.11	143.52	0.60
50			-2.27
70			-5.14
90			-8.01

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Table 4. Fatty acids composition in soybean oil samples obtained by PLE and conventional extraction using ethanol as the solvent.

Fatty Acid[1]	Extraction method		
	Classical	**PLE - 70 ºC**	**PLE - 90 ºC**
C16:0 - palmitic	13.09±0.03[a]	13.34±0.10[a]	13.00±0.27[a]
C18:0 - stearic	4.37±0.05[a]	4.30±0.01[a]	4.12±0.16[a]
C18:1 - oleic	19.32±0.17[a]	18.17±0.29[a]	18.53±0.27[a]
C18:2 - linoleic	57.06±0.19[a]	57.97±0.14[a]	57.70±0.07[a]
C18:3 - linolenic	6.16±0.01[a]	6.23±0.05[a]	6.65±0.08[a]

[1]Results in g/100 g of oil. Means followed by the same letter (in each row) indicates no significant difference ($p>0.05$).

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List of Figure Captions

Figure 1. Experimental apparatus used in pressurized liquid extraction: (SR) solvent reservoir, (P) high pressure liquid pump, (CV) check valve, (HS) heating system (PH) pre-heating, (E) extractor (T) temperature indicator, (C) cooling system, (TA) thermostatic bath, (PI) pressure indicator, (NV) needle valve (PV) pressure reduction valve, and (S) sampling.

Figure 2. Kinetics of extraction using ethanol as the solvent under pressurized conditions at 70 °C and pressures of: ■ 10 MPa; ● 20 MPa.

Figure 3. Kinetics of extraction using ethanol as the solvent under pressurized conditions at 10 MPa and temperatures of: ■ 30 °C; ● 50 °C; ▲ 70 °C; ▼ 90 °C. Means followed by different letters indicate a significant difference ($p<0.05$).

Figure 4. Kinetics of extraction using ethanol as the solvent under pressurized conditions at 10 MPa with a solvent flow of ■ 1 mL/min and ● 3 mL/min for: (a) 70 °C and (b) 90 °C.

Figure 5. Linear fitting between ln K and 1/T.

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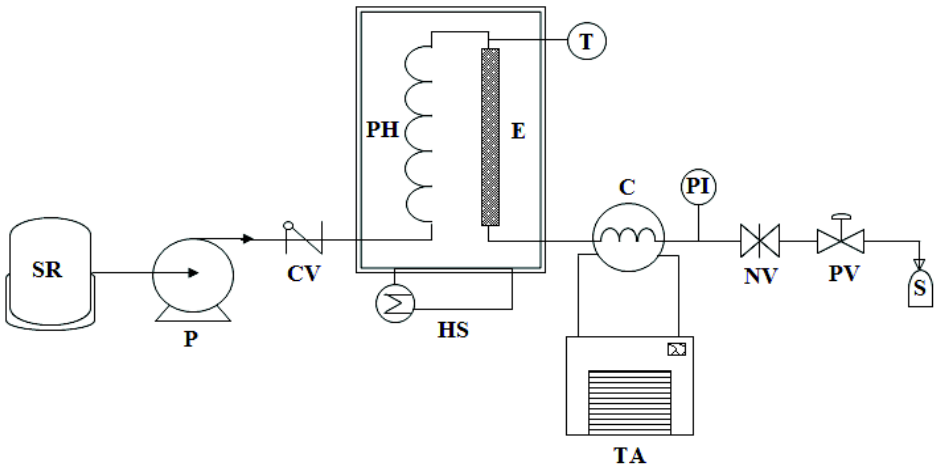

Figure 1

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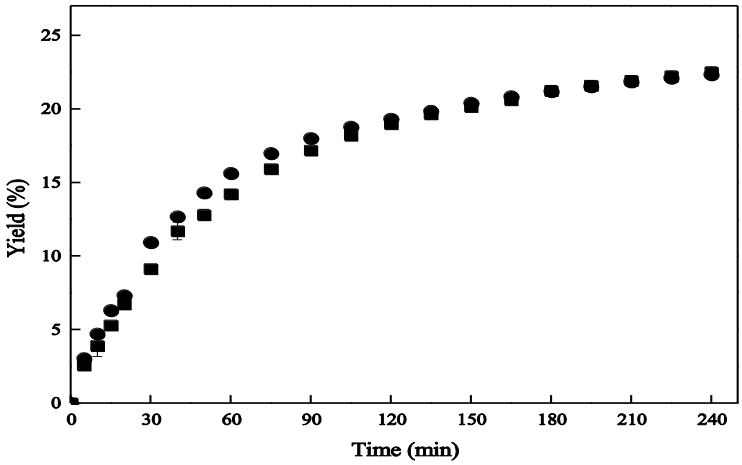

Figure 2

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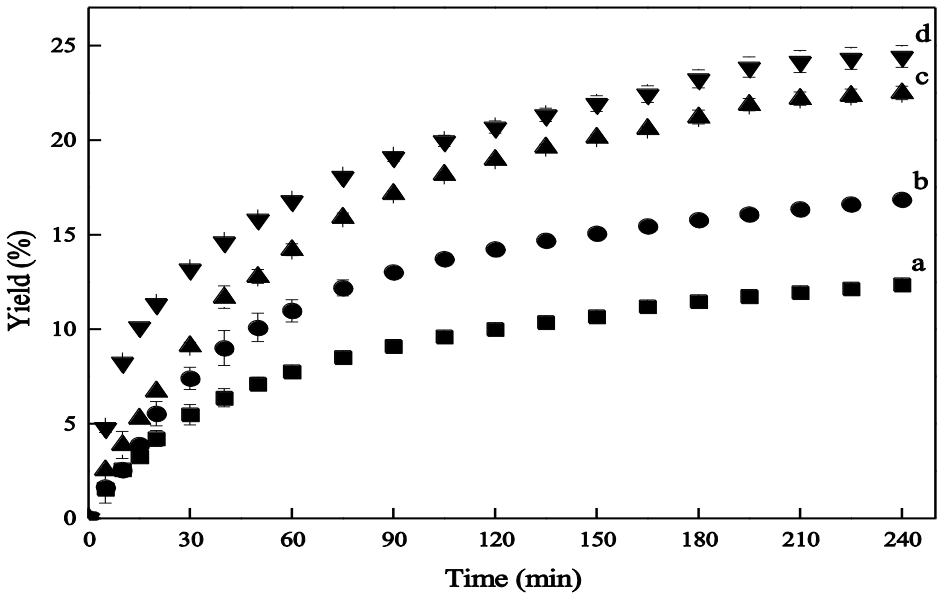

Figure 3

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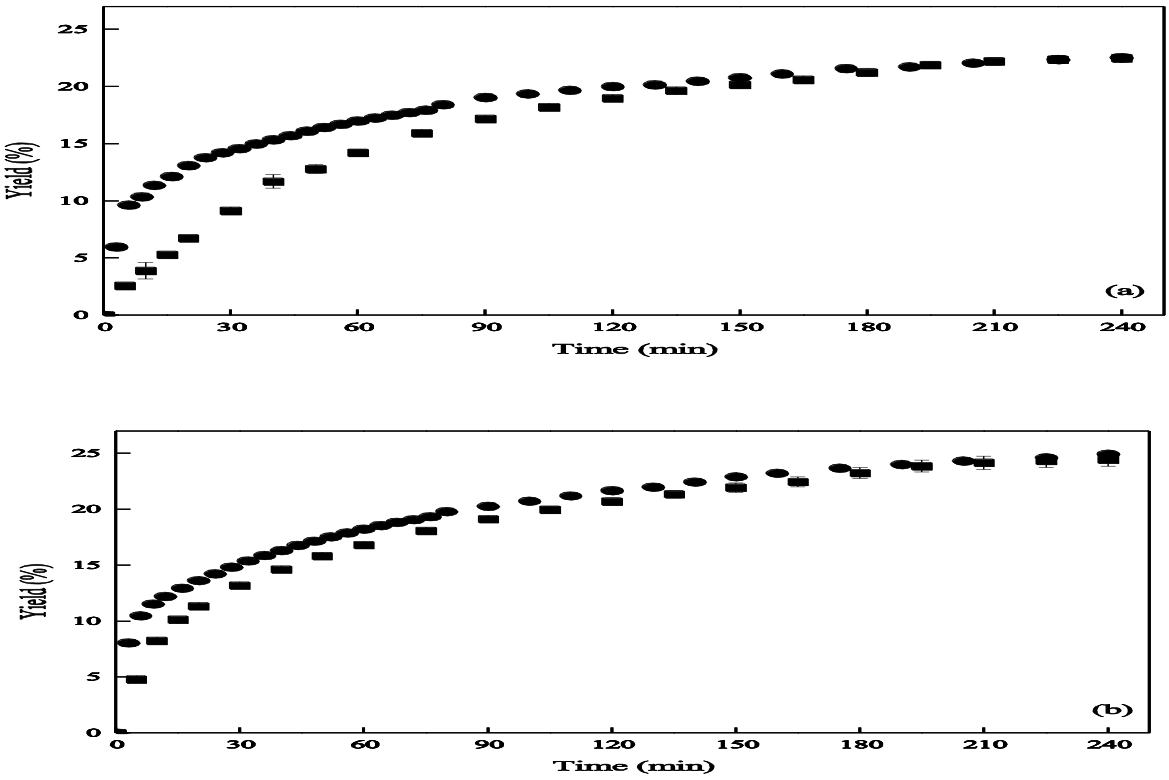

Figure 4

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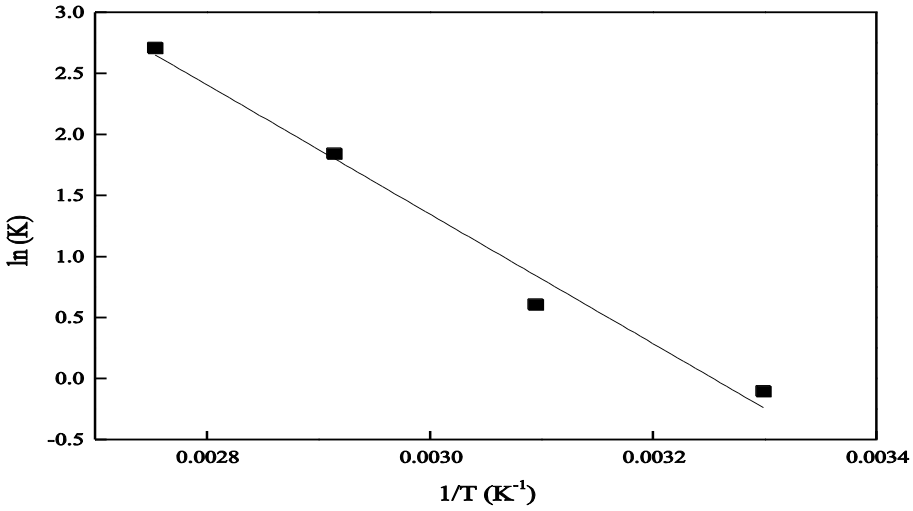

Figure 5

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