Extraction of palm oil using propane, ethanol and its mixtures as compressed solvent

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- Carotenoid content

A B S T R A C T

This work is aimed to investigate the extraction of palm oil using pressurized ethanol and propane as solvents. The effects of temperature (293–333 K), pressure (from 10 to 20 MPa), solvent flow rate (from 1 to 5 mL/min), and composition of the solvent mixture were evaluated on the oil extraction yield, and chemical profile of the extracted oils. The experiments were conducted in a 100 mL extractor coupled to a HPLC pump for ethanol and a syringe pump for the propane displacement. Global yields up to 75 wt% were obtained in the experiments. The kinetic profiles of the extractions were described by the Sovová’s model, which presented good agreement with the experimental observations. The palm oils extracted with distinct solvents were characterized regarding their density and viscosity in a temperature range from 293 to 343 K, its chemical profile determined by GC/MS, and carotenoid content.

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1. Introduction

The continuous decrease in fossil fuel reserves and the enhancement of the pollution in big cities have motivated the search for renewable sources of energy in industrial and academic centers [1–3]. The use of biofuels as sustainable energy is promising and a viable alternative to substitute fossil fuels [4–6]. Among the several vegetable oils that can be used in the biofuels production, the palm oil has been considered of great potential due to the high oil productivity of this plant [7,8]. Also, palm oil presents a very high content of carotenoids, which are preeminent nutraceutical compounds used in pharmaceutical and food industries [9–11].

Most part of studies related to biodiesel production is not focused on the obtaining the vegetable oil. Techniques like solid–liquid extraction and mechanical compression are often used for the vegetable oil extraction and, as a consequence, a series of purification/separation processes are required for assess oil with adequate characteristics for the biofuel production [12,13]. A potential technique for oil extraction from vegetable sources is the super/near critical fluids extraction, in which the thermodynamic properties of the solvent are sensible to changes in the process variables like temperature and pressure [14–16]. This aspect permits that the solvent density can be manipulated easier than that of the common organic solvents used in the vegetable oil extraction (n-hexane for example). The tunable properties characteristic of super/near critical fluids helps the development of compact and efficient extraction processes.

The carbon dioxide is certainly the most common compressed (supercritical or near critical) fluid employed for oil extraction from vegetable matrices. For instance carbon dioxide was already used as solvent for palm oil extraction [17,18]. On the other hand, the carbon dioxide is a poor solvent for triglycerides [19,20]. As a consequence, extraction yields and extraction rates for vegetable oil extraction using carbon dioxide as solvent are generally low [21]. Keeping the attractive properties of carbon dioxide that permits the prompt separation of oil and solvent, some light hydrocarbons, like propane, also presents good solvency for triglycerides, resulting in fast kinetics extractions, higher yields and reduced amount of solvent for the complete extraction [21–24].

An important aspect that can dictate the solvent selected for vegetable oil extraction is the focus of the oil use. In the biodiesel production the use of alcohols as solvents can be highlighted, as these solvents are also reactants in the process. Some works are available in the literature regarding the use of alcohols for vegetable oils extraction [25–27]. Although small chain alcohols are
not excellent solvents for triglycerides at ambient conditions, it
could be used as a compressed solvent where yields are improved
[28–30] or alcohols could also be added as a second solvent along
with a better solvent for vegetable oils [21].

The current work presents an investigation of the palm oil
extraction from palm fibers using pure ethanol, pure propane and
its mixtures as solvent. The effects of extraction process variables,
as pressure, temperature, and mixture solvent concentration on
the extraction kinetics, extraction yield and apparent solubilities were
evaluated. The Sovová mathematical model [31] was used for the
description of the kinetic extraction curves. The characteristics of
the extracted oil regarding its physico-chemical properties (density,
viscosity) and chemical profile (GC/MS), and the influence of the
solvent and extraction method on the carotenoid content in the
oils were also provided.

2. Materials and methods

2.1. Materials and sampling preparation

Samples of palm coconut of Dura variety where kindly donated
by the company “Empresa Baiana de Desenvolvimento Agrícola
(EBDA)”. The palm nuts were withdrawn from the cluster seeds,
clean and pulped manually. The palm fibers were dried in a circu-
ulating air oven (Nova Ética, 400/4N) at 333 K by 18 h. Drying time
and temperature were selected from preliminary studies, where
the sample moisture was periodically measured by potentiometric
titration (Metrohm – Titrand 836) using the Karl Fisher reactant.
The solvent used during the Karl Fisher analysis was a mixture of
dry methanol and chloroform (20%, v/v). After drying, samples were
communited in a knife mill, and classified in a system of Tyler series
of sieves, selecting particle size between 8 and 24 mesh, which
is a common particle size employed in high pressure extractions.
The moisture of all samples was checked again by Karl Fisher titra-
tion, and final value was always lower than 1.5%. Samples were
stored under nitrogen atmosphere, protected from light and under
refrigeration until the extractions.

The derivatizing solution boron trifluoride–methanol
(BF3/methanol – Sigma Aldrich) was employed for GC analy-
sis of the fatty acid compounds. Propane (99.9%) was obtained
from White Martins (Brazil). Ethanol (Merk, 99.9%) was used as
received. All solvents used in this study were analytical grade.
The standard esters, ethyl palmitate, ethyl stearate, ethyl oleate, ethyl
linoleate, ethyl linolenate and ethyl arachidate (all ≥ 99%) were
obtained from Sigma–Aldrich Chemical Co.

2.2. Sample extraction

The extractions of the vegetable oil from the palm fiber were
accomplished in a semi-batch laboratory scaly unit developed for
extraction with compressed solvents (gas, liquid or mixture of
both). Basically, the unit consists of a syringe pump (ISCO model
500D) for the compressed fluid (propane) displacement, and a HPLC
pump (Series III) for the compressed liquid (ethanol) displace-
ment. These pumps were connected to a jacketed extractor of total
volume around of 100 mL (2.52 cm i.d. and 20 cm of length). The
syringe pump operates at constant pressure mode, and the HPLC
pump at constant flow rate mode. In this sense, for the extrac-
tions with pure propane as solvent, just the syringe pump was
used. For the extractions with pure ethanol as solvent, only the
HPLC pump was used. For mixtures of solvents, both pumps oper-
ated together, and the flow rate of each pump were calculated
based on the desired composition of the solvent mixture. At the
end of the extractor, a couple of needle valves were used to control
the total solvent flow. Two independent thermostatic baths, both
with precision better than 1 K, were used to the control of syringe
pump vessel and extraction temperatures. The pressure was con-
trolled by the syringe pump in all experiments were propane was
the solvent (as pure solvent or in a mixture with ethanol). For the
experiments with pure ethanol as solvent, the system pressure was
controlled by the needle valves at the end of the extractor. For all
experimental runs, a zero volume pressure transducer (Huba Con-
trol, pressure transmitter type 691), with a precision better than
0.01 MPa, was employed to the system pressure measurement.

Fig. 1 presents a schematic diagram of the apparatus used in the
extractions.

Around 25 g of the palm fiber were charged into the extraction
vessel to form a bed supported by two 300 mesh wire dishes placed
at the ends of the extraction vessel. The temperature control was
turned on and the system was pressurized up the extraction pres-
sure. Before the extraction, the system was kept at the experimental
condition for 30 min for stabilization. After that, both pumps were
turned on, and the sample valve was open for sampling collection
in intervals of time.

The experiments were conducted up to the achievement of the
zero rate extraction, i.e., when no more extract was possible to be
withdrawn from the palm fiber. For the experiments using ethanol
(as pure solvent or in mixture with propane), the solvent was
removed from the extract solution by gentle evaporation (tem-
perature lower than 323 K at ambient pressure) in an oven up to
constant weight of the sample. All experimental conditions were
performed at least in duplicate in order to establish the uncertainty
of the results. Global liquid yields were obtained with uncertainties
always lower than 1.5%.

The experiments were conducted evaluating the influence of
temperature (293–333 K), pressure (10–20 MPa), solvent total liq-
uid flow rate (1–5 mL/min), and ethanol/solvent proportion (0,
25, 50, 75 and 100 v/v%). Ndiaye and co-workers [32] investi-
gate the phase behavior of propane and vegetable oils, and the
results indicated that the system is completely miscible in pres-
sures higher than 4–5 MPa. For PLE extraction (pressurized liquid
extraction) technique, typical pressures around 10 MPa are fre-
quently used [30]. In this work, we choose to investigate pressures
in levels where it was guaranteed the homogeneity of the mix-
tures.

 Soxhlet extraction was performed to compare the liquid yield
and chemical profile of the oil with the ones from high pressure
compressed solvent extraction. 3 g of the sample and 150 mL of
n-hexane (VETEC, analytical grade) were placed inside a Soxhlet
equipment for 6 h, according procedure described in the literature
[18].
2.3. Extraction modeling

The Sosnová model [29] was used to describe the palm oil extraction using propane, ethanol and its mixtures as solvent. According to Sosnová model, the oil in the solid matrix (O) can be separated in two parts: in the region near to the particle surface (P), and inside the pores or internal part of the solid matrix, where the solvent access is more difficult (K), as presented in Eq. (1).

\[ q(t=0) = q_0 = \frac{v}{N} = qp + qk = \frac{\mu}{N} + \frac{k}{N} \]

(1)

where \( q \) is the concentration of the solute in the solid phase \( q \) is the concentration of the solute in the solid phase in solvent free basis (g oil/g solid), \( t \) is the extraction time, \( q_0 \) is the initial concentration of the solute in the solid phase in solvent free basis (g oil/g solid), \( N \) is the inert solid mass. The mass balance for the oil in a bed element result in Eqs. (2) and (3).

\[ \rho_{bed}(1 - e) \frac{\partial \mu}{\partial t} = J(q, C) \]

(2)

\[ \rho_f \varepsilon \frac{\partial C}{\partial t} + \rho_f \varepsilon \frac{\partial C}{\partial t} = J(q, C) \]

(3)

where \( e \) is the porosity of the bed; \( \rho_{bed} \) is the solid phase density; \( \rho_f \) is the fluid density; \( z \) is the axial direction; \( t \) is the extraction time; \( J \) is the interfacial mass transfer rate; \( C \) is the concentration of solute in the fluid phase in a solvent free basis (g oil/cm³).

The Sosnová model presents analytical solutions as described in Eqs. (4)–(6), that illustrate the distinct phases of the extraction: constant extraction rate due to the large amount of solute available (Eq. (4)); region where the mass transfers in the film and in the solid particle are important (Eq. (5) with \( t_{cer} < t < t_{fer} \)), and the region where the mass transfer in the solid is dominant (Eq. (6)).

\[ m_c = A[1 - \exp(-z)], \quad \text{for} \ t < t_{cer} \]

(4)

\[ m_c = m_0 q_0 \frac{\varepsilon - z}{\varepsilon} \exp(Z/(h_k - 1)), \quad \text{for} \ t_{cer} < t < t_{fer} \]

(5)

\[ m_c = m_0 q_0 \left\{ \frac{1}{r} \ln(1 + \exp(\gamma - 1)) \right\} \exp(\gamma \left( \frac{z}{\varepsilon} - \psi \right) (1 - r)), \quad \text{for} \ t > t_{fer} \]

(6)

where \( m_c \) is the mass of extract, \( r \) is the radial direction, and the \( Z \) and \( Y \) are estimated parameters, from which it can be obtained the mass transfer parameters for the extractions:

\[ K_c \alpha = \frac{2QF\mu_{bed}}{m_c} \]

(7)

\[ K_c \alpha = \frac{rQF(1 - e)C_0}{mS\mu v} \]

(8)

2.4. Oil characterization

The fatty acids present in the palm oil were converted into its methyl esters through derivatization with boron trifluoro methanol reactant (BF3/MeOH) according to the methodology described in the standard AOAC 969.33 (AOAC, 1997). The triglycerides profile was obtained using a Shimadzu 17A gas chromatograph coupled with a mass spectrometer detector (QP 2010 plus), equipped with an apolar (DB5) capillary column (30 m × 0.25 mm i.d.). The column temperature was initially maintained at 120 °C by 5 min, and then raised to 280 °C at a rate of 2 °C min⁻¹, staying at this temperature by 20 min. Helium at 1 mL/min was the carrier gas. The analyses were performed with the injector and detector at 280 °C and 300 °C, respectively, and the injection volume was 1.0 µL in 1:10 split mode. Mass spectra were scanned from m/z 40 to 650 Da, at a rate of 1.5 scans s⁻¹. Electron impact ionization energy was 70 eV. The identification of compounds presented in the palm oil was accomplished by comparison its spectrum with the Willey library spectra and by using authentic standards.

Density analyses of the palm oil fiber were conducted in a densimeter (Anton Paar, DMA 4500) using the principle of the oscillatory tube, in the range from 293 to 343 K. The rheological characterization was performed in a controlled tension reometer (Anton Paar, Physica MCR 301) using the plate–plate geometry. Share rates from 50 to 1000 s⁻¹ were used to assess the viscosity of palm oil from 293 to 333 K.

The beta-carotene content in the extracted oils was determined in an UV spectrophotometer (Itachi U1800) using measurements at 450.5 nm. Solutions of a standard beta-carotene (Sigma–Aldrich) were prepared in n-hexane to obtain the calibration curve. Samples of oils extracted were prepared in n-hexane and the total beta-carotene was determined in each sample at 450.5 nm, as recommended in some previous works in the literature [11,17,33].

3. Results and discussion

3.1. Extraction yield and solubility

Table 1 presents the experimental conditions and results obtained for the liquid yield extractions of the vegetable oil from palm fiber using compressed propane, ethanol and its mixtures as solvent. The Soxhlet extraction provided yield of oil of 61.3%. It can be observed that the propane is an excellent solvent for extraction of the palm oil fiber, as higher yields were obtained when compared to the Soxhlet extraction. The extractions using propane, ethanol or its mixtures as solvent are, in fact, a dynamic PLE (pressurized liquid extraction) process. As pointed out by Herrera et al. [29], the dynamic PLE mode could improve the extraction rate by allowing a better contact between the matrix and fresh solvent pumped in a continuous way through the extraction cell, which can explain the slightly better extraction using compressed propane compared to hexane.

The solubility’s obtained in the propane extraction were higher than those from the ethanol extractions. Also, the propane solubility’s values are in agreement with those reported in the literature for vegetable oil extraction [22,23]. In should be important to mention that for the case of pure propane, the vegetable oil is totally miscible in the experimental range of temperature and pressure investigated [32]. In this sense, the solubility reported in Table 1 represents an apparent solubility that is a consequence of the free oil soluble in the amount of solvent loaded into the extractor.

Ethanol is a poorer solvent when compared with propane or higher alkanes for triglycerides extraction, but yields higher than 50% were achieved using ethanol, indicating that this pressurized solvent was able to extract the vegetable oil. Also, the mixture ethanol/propane as solvent in all proportions tested provided high yields in the extraction. These results are potential attractive when is considered an extraction process focused on the biodiesel production where the solvent of the extraction can be directly applied as a reactant for the transesterification reaction.

Fig. 2 presents the extraction kinetic curves using pure propane as solvent. It can be observed from Fig. 2A that in the experimental flow rate range investigated the curves are very similar, indicating that the extraction is taken place on process conditions where temperature and pressure have a secondary effect on the amount of oil soluble on the solvent. This fact can be confirmed by the similar apparent solubility’s obtained at distinct flow rate extractions (experimental conditions 1–3 in Table 1). Fig. 2B denotes that temperature (from 293 to 333 K) and pressure (from 10 to 20 MPa) also exert a weak effect on the extraction yield. This find be
Table 1  
Experimental conditions and extraction yields [100 mass of extract/mass of raw material] for the extraction of palm oil fiber.

<table>
<thead>
<tr>
<th>Run</th>
<th>Flow rate (mL/min)</th>
<th>T(K)</th>
<th>P(MPa)</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>Apparent solubility (g/mL/solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>313</td>
<td>10</td>
<td>100% Propane</td>
<td>70.6</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>313</td>
<td>15</td>
<td>100% Propane</td>
<td>69.7</td>
<td>1.14</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>313</td>
<td>10</td>
<td>100% Propane</td>
<td>69.5</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>293</td>
<td>10</td>
<td>100% Propane</td>
<td>72.8</td>
<td>1.01</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>293</td>
<td>20</td>
<td>100% Propane</td>
<td>73.9</td>
<td>1.01</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>313</td>
<td>15</td>
<td>100% Propane</td>
<td>71.2</td>
<td>1.25</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>313</td>
<td>10</td>
<td>100% Propane</td>
<td>71.1</td>
<td>1.27</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>333</td>
<td>20</td>
<td>100% Propane</td>
<td>72.6</td>
<td>1.40</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>313</td>
<td>10</td>
<td>100% Ethanol</td>
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<td>10</td>
<td>3</td>
<td>313</td>
<td>10</td>
<td>100% Ethanol</td>
<td>70.6</td>
<td>0.35</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>313</td>
<td>10</td>
<td>100% Ethanol</td>
<td>69.5</td>
<td>0.34</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>293</td>
<td>10</td>
<td>25% Ethanol/75% propane</td>
<td>53.3</td>
<td>0.15</td>
</tr>
<tr>
<td>13</td>
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<td>10</td>
<td>25% Ethanol/75% propane</td>
<td>64.6</td>
<td>0.33</td>
</tr>
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<td>68.0</td>
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<td>10</td>
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<td>73.1</td>
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<td>3</td>
<td>313</td>
<td>10</td>
<td>25% Ethanol/75% propane</td>
<td>75.2</td>
<td>0.62</td>
</tr>
<tr>
<td>17</td>
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<td>10</td>
<td>25% Ethanol/75% propane</td>
<td>74.5</td>
<td>0.74</td>
</tr>
<tr>
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<td>293</td>
<td>10</td>
<td>25% Ethanol/75% propane</td>
<td>75.1</td>
<td>0.34</td>
</tr>
<tr>
<td>19</td>
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<td>15</td>
<td>50% Ethanol/50% propane</td>
<td>75.3</td>
<td>0.42</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>333</td>
<td>15</td>
<td>50% Ethanol/50% propane</td>
<td>75.7</td>
<td>0.66</td>
</tr>
<tr>
<td>21</td>
<td>3</td>
<td>293</td>
<td>15</td>
<td>50% Ethanol/50% propane</td>
<td>66.1</td>
<td>0.25</td>
</tr>
<tr>
<td>22</td>
<td>3</td>
<td>313</td>
<td>15</td>
<td>50% Ethanol/50% propane</td>
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<td>3</td>
<td>333</td>
<td>15</td>
<td>50% Ethanol/50% propane</td>
<td>67.8</td>
<td>0.63</td>
</tr>
<tr>
<td>24</td>
<td>Soxhlet with n-hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

Fig. 2. Extraction of oil from palm fiber using compressed propane as solvent. (A) Influence of solvent flow rate (313 K and 10 MPa). (B) Influence of temperature and pressure on the extraction kinetic curves (3 mL/min).

related to the fact that compressed propane is a very good solvent for triglycerides [32,34,35]. It should be emphasized that propane was in a compressed liquid state for all experimental conditions investigated in this work. In this sense, its density variation was not very pronounced with pressure and temperatures in the range investigated.

Although pressure and temperature presented a weak effect on the extraction yield (measured at the time when no more oil could be extracted from the palm fiber), the effects of temperature and pressure were both positive on the apparent solubility’s (initial linear step of the extraction) of the palm oil extracted with propane. Results presented in experimental runs 3–8 in Table 1 indicated that pressure showed a positive effect just at 333 K, i.e., nearer to the critical temperature of propane than at 293 K. In this sense, the enhancement in pressure produced a more pronounced effect on solvent density at 333 K, and a consequent improvement in the propane solvent power. The enhancement in temperature also resulted in a higher amount of vegetable oil solvated in the solvent, as the increase in temperature leads to the enhancement of solute vapor pressure and better solvation properties for the solvent. As previously commented, the effects of temperature and pressure could be related to the oil and solvent physical properties, as oil and solvent present complete solubility under the operating conditions investigated.

Fig. 3 presents the extractions kinetic curves using pure ethanol as solvent. It can be observed from Fig. 3A that the flow rate of ethanol from 1 to 5 mL/min did not exert influence on the extraction kinetics or in the apparent solubility’s (experimental runs 9–11 in Table 1). As the ethanol is far below from its critical temperature, the pressure has a small effect on the solvency properties of the solvent [14,15,30]. In this sense the pressure was kept constant at 10 MPa for the extractions with pressurized liquid ethanol. Fig. 3B presents the kinetics of the oil extraction from palm fiber using pure ethanol as solvent at distinct temperatures, from where it can be seen that the extraction rate is improved with temperature. In the experimental range investigated, the change in temperature has a small effect on the density of pure ethanol, and so the
improvement in temperature has as direct result better extraction conditions: the viscosity of oil and solvent are decreased, the diffusion coefficient is enhanced, and the vapor pressure of the solute is increased with temperature [21–24,31]. The apparent solubility of palm oil in ethanol also showed an enhancement with temperature (see experimental runs 12–14 in Table 1). The improvement in these properties is particularly important for ethanol, as this alcohol is not an excellent solvent for the triglycerides, as in the case of hydrocarbon solvents [34,35].

Figs. 4 and 5 present the effects of temperature and concentration of the ethanol/propane solvent mixture on the yield of the extraction of the vegetable oil from palm fiber. It can be observed that the presence of propane increase the total yield of the process in all compositions investigated, as propane is a better solvent for the vegetable oils than ethanol. These results are also evidenced by the values of the apparent solubilities, where the composition of propane has a direct effect on the solubility value (Table 1). An inspection of these figures reveals that as the content of propane is decrease, the influence of temperature becomes more important on process.

3.2. Kinetic modeling

For the mathematical modeling of the extraction kinetics, the initial parameters were estimated according the procedure described in the literature [22,23]. Initial concentration of oil in the inert solid was kept constant, as well as the bed porosity (0.62); and bed density (0.58 g cm⁻³). Table 2 presents global results from the model fitting, and Fig. 6 depicts the performance of the model in describing the experimental information. It can be
Table 2
Sovová model results of fitting the kinetic of extraction of palm oil with compressed propane, ethanol and its mixtures as solvent.

<table>
<thead>
<tr>
<th>Run</th>
<th>Flow rate (mL/min)</th>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Solvent</th>
<th>$K_f$ (min⁻¹)</th>
<th>$K_a$ (min⁻¹)</th>
<th>$R^2$</th>
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<td>100% propane</td>
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<td>0.031</td>
<td>0.99</td>
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<td>0.030</td>
<td>0.98</td>
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<td>100% Ethanol</td>
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<td></td>
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<td>0.002</td>
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<tr>
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<td>15</td>
<td>293</td>
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<td>25/75% Ethanol/propane</td>
<td>0.0151</td>
<td>0.002</td>
<td>0.99</td>
</tr>
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<td>313</td>
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<td>25/75% Ethanol/propane</td>
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<td>0.018</td>
<td>0.97</td>
</tr>
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<td>25/75% Ethanol/propane</td>
<td>0.0150</td>
<td>0.020</td>
<td>0.98</td>
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<td>18</td>
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<td></td>
<td>0.0144</td>
<td>0.017</td>
<td>0.99</td>
</tr>
<tr>
<td>19</td>
<td>19</td>
<td>313</td>
<td>15</td>
<td>50/50% Ethanol/propane</td>
<td>0.0148</td>
<td>0.022</td>
<td>0.97</td>
</tr>
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<td>20</td>
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<td>0.0157</td>
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<td>0.0150</td>
<td>0.030</td>
<td>0.99</td>
</tr>
<tr>
<td>22</td>
<td>22</td>
<td>313</td>
<td></td>
<td>75/25% Ethanol/propane</td>
<td>0.0144</td>
<td>0.020</td>
<td>0.97</td>
</tr>
<tr>
<td>23</td>
<td>23</td>
<td>333</td>
<td></td>
<td></td>
<td>0.0140</td>
<td>0.022</td>
<td>0.98</td>
</tr>
</tbody>
</table>

noted that for all experimental condition the Sovová model was able to describe the extraction kinetics with a good agreement with the experimental data ($R^2 > 0.97$). The external mass transfer coefficient ($K_a$) was similar to both solvents. On the other hand, as a general trend the internal mass transfer coefficient ($K_f$) was higher when used propane than when using ethanol, as the transport properties of propane are more attractive than those of ethanol for vegetable oil extraction at the experimental conditions investigated.

3.3. Oil characterization

The chromatographic profile of the palm oil extracted is presented in Table 3. It can be seen that the chemical profile is quite similar for all extracted palm oils, and comparing with literature [17] or a commercial palm oil. In fact these analyses provided the chemical triacylglycerols profile that is expected to be similar for vegetable oils independent the extraction technique or solvent [21–24]. On the other hand, another components like phospholipids, high molecular weight hydrocarbons, and wax, for example, could be distinctly extracted depending the extraction technique and solvent, which can influence other chemical properties of the oil.

Fig. 7 presents the results of density and viscosity analyses of oils extracted with compressed propane and ethanol, compared to the values from a commercial and the Soxhlet samples. For density, it can be noted this property presents a linear dependence with temperature, with value of $0.90 \pm 0.03 \text{g/cm}^3$. Also, it seems that the oil extracted with ethanol present a shift in density compared to the other two that are extracted with hydrocarbon solvents. This result suggests that polar components could also be extracted along with the triglycerides of the vegetable oil. The viscosity profile of the oils shows some distinct values at low temperatures, but the behavior is quite similar for temperatures higher than 303 K.

Visual inspection of oils indicated that the palm oils extracted with ethanol were more colorless than those from propane or Soxhlet extraction, suggesting a possible variation on the carotenoid content in the palm oil depending on the extraction method/solvent. Table 4 presents the results of the beta-carotene concentration in the oils extracted. It can be noted that beta-carotene concentration from 1.7 to 6.5 mg/g oil were observed
Table 3
Fatty acid profile of the palm oil extracted using compressed propane and ethanol as solvents.

<table>
<thead>
<tr>
<th>Run</th>
<th>Solvent</th>
<th>Lauric (mg/100g)</th>
<th>Myristic (mg/100g)</th>
<th>Palmitic (mg/100g)</th>
<th>Stearic (mg/100g)</th>
<th>Oleic (mg/100g)</th>
<th>Linoleic (mg/100g)</th>
<th>Linolenic (mg/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Propane</td>
<td>0.1</td>
<td>0.8</td>
<td>42.0</td>
<td>4.4</td>
<td>35.4</td>
<td>9.4</td>
<td>0.3</td>
</tr>
<tr>
<td>5</td>
<td>Propane</td>
<td>0.1</td>
<td>0.7</td>
<td>41.2</td>
<td>4.3</td>
<td>38.3</td>
<td>9.7</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>Propane</td>
<td>&lt;0.1</td>
<td>0.8</td>
<td>43.5</td>
<td>4.7</td>
<td>38.7</td>
<td>9.5</td>
<td>0.1</td>
</tr>
<tr>
<td>7</td>
<td>Propane</td>
<td>0.3</td>
<td>0.6</td>
<td>44.8</td>
<td>4.8</td>
<td>37.5</td>
<td>8.3</td>
<td>0.4</td>
</tr>
<tr>
<td>8</td>
<td>Propane</td>
<td>0.2</td>
<td>0.9</td>
<td>44.9</td>
<td>4.5</td>
<td>39.9</td>
<td>10.0</td>
<td>0.2</td>
</tr>
<tr>
<td>9</td>
<td>Propane</td>
<td>&lt;0.1</td>
<td>0.9</td>
<td>41.9</td>
<td>4.6</td>
<td>39.7</td>
<td>9.4</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>Propane</td>
<td>0.1</td>
<td>1.0</td>
<td>45.0</td>
<td>4.8</td>
<td>39.8</td>
<td>8.8</td>
<td>0.4</td>
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<tr>
<td>11</td>
<td>Propane</td>
<td>0.1</td>
<td>0.7</td>
<td>42.9</td>
<td>4.6</td>
<td>38.2</td>
<td>8.7</td>
<td>0.3</td>
</tr>
<tr>
<td>12</td>
<td>Propane</td>
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<td>0.9</td>
<td>40.9</td>
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<td>39.1</td>
<td>9.1</td>
<td>0.1</td>
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<tr>
<td>13</td>
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<td>0.7</td>
<td>42.3</td>
<td>4.7</td>
<td>35.5</td>
<td>9.4</td>
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<tr>
<td>Soxhlet</td>
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<td>0.9</td>
<td>46.0</td>
<td>5.0</td>
<td>38.1</td>
<td>9.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Literature [9]</td>
<td>0.2</td>
<td>1.1</td>
<td>44.0</td>
<td>4.5</td>
<td>39.2</td>
<td>10.1</td>
<td>0.4</td>
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</tr>
<tr>
<td>Commercial Sample</td>
<td>&lt;0.1</td>
<td>0.8</td>
<td>45.3</td>
<td>4.9</td>
<td>40.0</td>
<td>9.0</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

* Runs labeled according Tables 1 and 2.

in the oils extracted. These values are in agreement with some carotenoid determinations in palm oils [11]. Table 4 reveals that the concentration of beta-carotene is strongly dependent on the type of the solvent. The concentration in the oils extracted by propane is about 300% higher than that observed in the oils extracted with pure ethanol. It should be noted that the total extraction yields are similar in some cases (compare for instance runs 1–8 with runs 10 and 11), but the concentration of carotenoids is totally different. Some works in the literature indicate that non-polar solvents (like propane and the hexane used in the Soxhlet extraction) are better solvents to extract the carotenes than polar solvents, such as ethanol [3,36,37]. This aspect suggests that ethanol can be also used as a selective solvent for vegetable oil, leaving the carotenoids in the solid residue for posterior extraction with a nonpolar solvent. This two-steps extraction/fractionation process is now under investigation in our laboratory and will be subject of a future communication.

The last column of Table 4 presents mean values of concentration of carotenoids for each solvent type. The Tukey-test was used for statistical comparison of the solvent effect and the result confirmed that ethanol and propane produces significantly different carotenoid concentration on the oils. Also, according to the Tukey test with 95% of confidence level, the mixture of both solvents in the range of 25–75 v/v% were not statistically significant for changing the beta-carotene content on the palm oil extracted, indicating a high affinity of the carotenoids with the hydrocarbon solvent.

Table 4
Beta-carotene concentration on the palm oil extracted with compressed solvents.

<table>
<thead>
<tr>
<th>Run</th>
<th>Flow rate (mL/min)</th>
<th>T(K)</th>
<th>P (MPa)</th>
<th>Solvent</th>
<th>Beta-carotene concentration (mg/10g oil)</th>
<th>Average concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>313</td>
<td>10</td>
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<tr>
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<td>2</td>
<td>313</td>
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<td>5.61</td>
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<td>4</td>
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<td>10</td>
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<td>5.41</td>
<td>5.50*</td>
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<td>5</td>
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<td>100% propane</td>
<td>5.16</td>
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<td>25% ethanol/75% propane</td>
<td>3.21</td>
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<td>6.43</td>
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* Distinct letters means that the values are significantly different at p < 0.01 (Tukey test).
content on the palm oil during the extraction of palm oil fiber using compressed carbon dioxide.

4. Conclusions

In this work, it was investigated the extraction of palm oil using ethanol, propane and its mixtures as compressed solvents. The results showed that yields around 70% were obtained in the extractions, indicating that both compressed liquid solvents are potential for palm oil extraction. The Sovová model was able to satisfactory model the kinetic extraction for both solvents and its mixtures. The chemical profile regarding the oil fatty acid distribution was quite similar independent on the extraction method or solvent employed. From the results, it can be concluded that liquid propane is a slightly better solvent than ethanol and that a mixture of both solvents could be an interesting route for extraction of vegetable oils to directly conduct to biofuel production. The β-carotene content was quite different depending on the solvent used: ethanol, propane or mixtures of both components, suggesting that ethanol can be used as solvent for a selective triglycerides extraction from palm oil fiber.

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References