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EFFECT OF ECOFRIENDLY BIO-BASED SOLVENTS ON OIL EXTRACTION FROM GREEN COFFEE BEAN AND ITS INDUSTRIAL PRESS CAKE

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Abstract - Oil recovery, retention index, and thermodynamic parameters of green coffee beans (GCB) and its press cake (PC) extraction using bio-based solvents were investigated. The extraction parameters investigated were temperature (35 to 55 °C), type of material (coffee beans and press cake), and type of solvent (ethanol, acetone, and ethyl acetate), at a fixed solvent to solid mass ratio (5:1) (w/w). The fatty acid profile of the ethanolic extract was assessed for both GCB and PC, and compared to the oil obtained from the mechanical pressing. It was observed that higher temperatures affected positively the extraction yields, especially when acetone and ethanol were employed, allowing a recovery up to 90% and 56.7% for GCB and PC, respectively. The solution retained in the raffinate phase from the GCB extraction was greater than that for the PC. For all operational levels, the ΔH and ΔS were positive. ΔG decreased with increasing temperature. Palmitic and linoleic acids were predominant in all types of oil. The oil obtained by pressing showed higher content of linoleic acid (45.32%), while the solvent-extracted oil from GCB had more palmitic acid (34.79%), and the PC oil presented intermediate levels of all the methyl esters.

Keywords: *Coffea arabica*; Alternative solvents; Thermodynamic; Food waste; Fatty acids.

INTRODUCTION

Recently, another operation has been introduced to the coffee industry, oil expression, which generates a great amount of residues. The green coffee oil expression operation, carried out with the aid of a screw press or expeller, is not efficient enough to completely remove oil from matrices with low oil content (< 20%) (Koubaa et al., 2016), such as green coffee beans (Farah, 2012). Besides leaving a residual oil in the meal (or press cake), a great amount of bioactive compounds may also be found in this residue, because most of the phenolic compounds are of hydrophilic nature (Oliveira et al., 2019a; 2019b). According to Affonso et al. (2016), coffee bean press cake is a residual biomass from the coffee bean oil extraction process, claimed to be rich in bioactive compounds of interest for human health, the food industry, and cosmetics. There is considerable emphasis on the recovery of plant biomass originating from the food industry in order to target it to other industries (Laufenberg et al., 2003), adding value and reducing environmental damage. In this sense, the large volume of beans produced in Brazil (63,400,000 x 60 kg bags) (USDA, 2019) gives rise to certain amounts of biomass with an important potential for the development of other products, such as, energetic beverages, food supplements, and cosmetics. An alternative to optimize the mechanical extraction process could be allying this method with solvent extraction, aiming at

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the exhaustion of the compounds of interest remaining in the residue, or even use the solvent extraction as the only step, as it is mostly used for soybean extraction. The extraction process aims at providing a maximum yield of substances of the highest quality. Literature about the most effective methods and the solvents to extract soluble compounds is abundant, but is to some extent contradictory (Contini et al., 2008). Considering the structure of the matrices and their physicochemical properties, it would be impossible to propose a universal extraction protocol. Different solvent systems have been used for the extraction of solids from plant material and the extraction yield is influenced by the solvent nature and the extraction method. According to Akowuah et al. (2005), depending on the solvent used for extracting desirable compounds, extracts obtained from the same material may vary widely with respect to their concentration and composition. Further, the solvent choice involves environmental, health, and safety (EHS) issues, which have led to the search of alternative solvents to hexane, which is inflammable and very toxic (Lusas et al., 1994; Wakelyn and Wan, 2005; Jérôme and Luque, 2017). Different types of solvents have been suggested as potential substitutes for hexane in order to overcome its shortcommings, such as ethanol (alcohol) (Hron, Koltun and Graci, 1982; Rittner, 1992), acetone (ketone) (Wan and Wakelyn, 1997), and ethyl acetate (ester) (Freeman et al.,1943; Madaus et al., 1983), which can all be considered as bio-based (derived from feestock and have the potential to replace fossil fuel based solvents and which are inherently renewable produced from biomass sources and so called, biorenewable) solvents (Pena-Pereira and Tobiszewski, 2017). The importance of finding a wide variety of solvents with different functionality is a major point, as solvent applications can vary significantly (Jessop, 2011; Pena-Pereira and Tobiszewski, 2017). Ethanol (Hron et al., 1982), as well as acetone (Weizmann fermentation process) (Weizmann and Hamlyn, 1920; Austin, 1998; Wintgens, 2008) and ethyl acetate (Freeman et al., 1943) can be obtained from bioprocesses and, thus, be considered bio-based and biorenewable solvents. Ethanol is a valuable alternative to be studied, because, although flammable, it is recognized as non-toxic and presents greater industrial safety (Hron et al., 1982; Rittner, 1992; FDA, CDER and CBER, 2017) compared to hexane. Further, it is highly available, especially, in Brazil and the United States, which are the largest producers of this solvent worldwide. Acetone can replace ethanol in the extraction, be easily concentrated by rectification, can reduce energy consumption up to 25% by the use of recirculation techniques, phosphatides and gums are insoluble in it remaining with the meal and can remove antinutritional factors, such as aflatoxins and gossypol as well as ethanol (Hron et al., 1982). Ethyl acetate has been widely studied as a potential solvent to extract oil (Freeman, Pack and McKinney, 1943; Madaus, Gorler and Molls, 1983) as it is rated as a moderate fire hazard, noncarcinogen, and low health hazard (Arendt and Langley, 1995; Langley and Finelt, 1997). Besides the type of solvent, temperature, solid-liquid ratio, particle size, and agitation are important parameters for the extraction of solids from food or plant matrices. There are several studies on the extraction behavior of different plant materials, such as coffee bean (Oliveira et al., 2018), soy bean (Dagostin et al., 2015; Cheng et al., 2018), neem seed (Adewoye and Ogunleye, 2012), aniseed (Scopel et al., 2016), avocado (Krumreich et al., 2018), pongam seeds (Kumar et al., 2018), pequi and murici seeds (Araújo et al., 2018), and walnuts (Chen et al., 2018). These studies were conducted with aqueous or organic solvent extraction including the parameters afore mentioned. It is generally reported that the extraction rate increases with increasing temperature and liquid/solid ratio, and decreasing particle size; however, these parameters shall be extensively studied, since high temperatures may favor the extraction yield of solids and disfavor the recovery of phenolic compounds and antioxidants (Torun *et al.*, 2015). Earlier works reported the extraction efficiency of different coffee species by using different extraction methods, such as, conventional (n-hexane, water, anhydrous and hydrous ethanol, methanol and their mixtures) (Bravo et al., 2013; Najdanovic-Visak et al., 2017; Somnuk et al., 2017), pressurized liquid (water, ethanol, and methanol) (Belandria et al., 2016; Oliveira et al., 2018), ultrasound assisted (ethanol) (Al-Dhabi et al., 2017), supercritical CO_2 (De Marco et al. 2018; Getachew et al., 2018), and microwave extraction (petroleum ether) (Tsukui et al., 2014). However, there is no reported study on the organic solvent extraction behavior of total soluble solids from green coffee beans and its press cake *in order to state the feasibility of mechanical oil extraction*. Therefore, the present study was carried out in order to determine the recovery yield of total soluble solids from green coffee beans and its press cake extracted by organic ecofriendly solvents, including ethanol, at different temperatures, to study and establish useful and relevant thermodynamic parameters for the process, and also, to assess the fatty acid profile of the ethanolic extracts.

MATERIALS AND METHODS

Sampling

The samples of Arabica green coffee beans were harvested (year 2018) in the cherry state in the municipality of Guaxupé (Minas Gerais) (latitude: 21°18′19″ S, longitude: 46°42′46″ W, elevation above sea level: 858 m) located in the Southeast region of Brazil. Both beans and press cake were a contribution from Cooperativa dos Cafeicultores de Guaxupé (Cooxupé, Guaxupé, Brazil). After mechanically

screw pressing the beans for the extraction of the oil (100 kg h^{-1}; Ecirtec, MPE-500 AC, Bauru, Brazil) the green coffee press cake was obtained. The cake was packed in polyethylene bags, with silica pouches, and frozen for further analyses. Both materials (beans and press cake) were ground (IKA, A11, Wilmington, US) and sifted (No. 20 < mesh < No. 80) (Bertel, VP-01, Caieiras, Brazil) (Sluiter et al., 2008). After sifting, the powders were dried (40 °C) in a vacuum oven (16.8 kPa) (Tecnal, TE-395, Piracicaba, Brazil) (approximately 20 days for green coffee beans and 7 days for the cake), and further used in the extraction process. The chemical characterization of the material is available in the work of Oliveira et al. (2019c).

Solvent extraction

The solvent extraction of soluble solids from green coffee and its press cake was carried out in batches using ethanol (boiling point = 78 °C, 99% purity), acetone (boiling point = 56 °C, 99% purity), and ethyl acetate (boiling point = 78 °C, 99% purity), at a constant liquid-solid ratio (5:1 w/w). Each experiment was carried out at least thrice on different days. The samples were placed in Falcon tubes (50 mL) and the solvents added in the convenient proportion. The tubes were then placed in a stirring Dubnoff Orbital water bath (220 rpm; Novatecnica, NT 230, Piracicaba, Brazil) at a constant temperature (according to each experiment) (Table 1) for 4 h (period determined in preliminary tests as enough to reach the equilibrium). A mild temperature range (35 - 55 °C) was chosen with the purpose of not degrading possible bioactive compounds present in the extracts to be analyzed in further studies.

After the extraction time had elapsed, an aliquot of the supernatant phase (extract phase; EP) (~ 2 mL) was removed from each tube, with the aid of pre-weighed microsyringes. The sample of EP withdrawn with the aid of the syringe (m_{EP}) was placed in a Petri dish, which was also previously weighed. Ethanol was used to wash out the syringe (after the EP disposal) into the Petri dish in order to remove any solids that may have become adhered to the syringe wall. The Petri dish containing the EP + ethanol was oven dried at 100 °C for at least 2 h in order to evaporate the solvent. Then, the Petri dish was weighed again and the soluble or extractable solids sample mass determined.

Table 1. Planning of the solid-liquid extraction of soluble solids from green coffee beans and its press cake.

Experiment	Ethanol	Acetone	Ethyl Acetate	Temperature (°C)
1	-	+	-	35
2	-	-	+	35
3	+	-	-	35
4	-	+	-	39
5	-	-	+	39
6	+	-	-	39
7	-	+	-	45
8	-	-	+	45
9	+	-	-	45
10	-	+	-	51
11	-	-	+	51
12	+	-	-	51
13	-	+	-	55
14	-	-	+	55
15	+	-	-	55

(-): Absence of solvent; (+): Presence of solvent.

The remaining content of the tube was subjected to centrifugation (3500 rpm/ 1 min) (Excelsa II - 206 BL, FANEM, São Paulo, Brazil) after the removal of EP. Then, the remaining liquid was properly discarded and a sample of the raffinate phase (RP) (remaining solid in the tube) was withdrawn and immediately weighed (m_{RP}) into a pre-weighed Petri dish, which was subjected to drying (100 °C/ 2 h) in order to remove the solvent. The samples (Petri dishes containing samples of RP) without solvent were cooled down in desiccators and weighed, allowing the calculation of the solvent mass fraction retained in the RP. The initial soluble solids content of raw materials (beans and cake) was determined using a Soxhlet type apparatus (OXY-901, ISB, Bom Princípio, Brazil) with ethanol.

Determination of soluble solids yield

The EP and RP were determined in terms of the mass fractions of the components of interest (soluble or extractable solids, solvent, and insoluble solids) for all extraction experiments performed. The mass fraction of the components in EP was determined using the data obtained from the samples taken with the microsyringe. The withdrawn EP sample (m_{EP}) mass was calculated using the mass difference of the syringe with extract and the empty syringe. The solvent mass in the EP sample was calculated from the mass difference of the Petri dish containing the extract sample after the solvent evaporation and the empty Petri dish. The mass fraction of soluble solids ($w_{1,EP}$) and the mass fraction of the solvent ($w_{2,EP}$) in the EP, insoluble solids free ($w_{3,EP} = 0$), were calculated according to Eqs. 1 and 2, respectively.

$$w_{1,EP} = \frac{m_{EP} - m_{EPF}}{m_{EP}} \quad (1)$$

$$w_{2,EP} = 1 - w_{1,EP} \quad (2)$$

where m_{EP} is the sample mass of EP and m_{EPF} is the final sample mass of EP after solvent removal (drying).

The mass fraction of the solvent in RP ($w_{2,RP}$) was calculated from the difference of weights found before and after drying RP sample (Eq. 3).

$$w_{2,RP} = \frac{m_{RP} - m_{RPF}}{m_{RP}} \quad (3)$$

where m_{RP} is the sample mass of RP and m_{RPF} is the final sample mass of RP after solvent removal.

The mass of the system (solvent and material) (m_{system}), and the mass fraction of each component in the system are known variables. The remaining variables - mass of EP (m_{EP}), mass of RP (m_{RP}), soluble solids mass fraction in RP ($w_{1,RP}$), and insoluble solids mass fraction in RP ($w_{3,RP}$) - were determined through a global mass balance (Eq. 4). The mass balance for each component of the system (*i*) is presented in Eq. 5.

$$m_{system} = m_{EP} + m_{RP} = m_2 + m_s \tag{4}$$

where m_{system} is the mass of the global system, m_{EP} is the mass of EP, m_{RP} is the mass of the raffinate phase, m_2 is the solvent mass used in the extraction process, and m_s is the mass of sample used in the experiment (green coffee beans or press cake).

$$w_{i,system} m_{system} = w_{i,EP} m_{EP} + w_{i,RP} m_{RP} \tag{5}$$

where *i* = 1 (soluble solids) or 2 (solvent) or 3 (insoluble solids).

The parameter w_i is defined by Eq. 6, where m_i is the mass of a given component (*i*) in the EP or RP (m_P).

$$w_i = \frac{m_i}{m_P} \tag{6}$$

The soluble solids mass transfer (Γ_1) in the extraction process was calculated through Eq. 7, where m_s is the mass of sample (beans or cake) used in the extraction process, and $w_{1,s}$ is the mass fraction of soluble solids in the sample before the extraction process (Soxhlet extraction using ethanol as the solvent, which was chosen based on previous studies (Oliveira et al., 2019).

$$\Gamma_1 (\%) = 100 \left(\frac{w_{1,EP} m_{EP}}{w_{1,s} m_s} \right) \tag{7}$$

The retention index (RI) corresponds to the mass of adhered solution per soluble solids mass from RP, and it was calculated using Eq. 8.

$$RI = \frac{w_{1,RP} m_{RP} + w_{2,RP} m_{RP}}{w_{3,RP} m_{RP}} = \frac{m_{1,RP} + m_{2,RP}}{m_{3,RP}} \tag{8}$$

Thermodynamic study

Enthalpy (ΔH), entropy (ΔS), and Gibb's free energy (ΔG) variations are important thermodynamic parameters in order to study the spontaneity of the extraction process involving different systems. Thermodynamic parameters of the solid-liquid extraction process of green coffee beans and its press cake were assessed for each solvent using Eqs. 9 - 11. By knowing K_e at different temperatures, ΔH and ΔS parameters were calculated by a linear fit to the Van't Hoff equation (Eq. 10). Plotting ln K_e against 1/T gives -ΔH/R as slope and ΔS/R as intercept, from where ΔH, ΔS and ΔG were determined. K_e is the distribution coefficient for the solid-liquid system (Eq. 9), $m_{1,EP}$ (kg) is the soluble solids mass in the EP, $m_{1,RP}$ (kg) is the soluble solids mass in the RP, R (=8.3145 J/mol K) is the universal constant of gases, and T (K) is the extraction temperature.

$$K_e = \frac{m_{1,EP}}{m_{1,RP}} \tag{9}$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

$$\Delta G = \Delta H - T \cdot \Delta S \tag{11}$$

Statistical analysis

A completely randomized design (CRD) was applied in order to plan a factorial experiment with three replicates. Type of material (M), type of solvent (S), and temperature (T) were the independent variables studied as a factorial 2x3x5 (M×S×T) (Eq. 12). The ANOVA was carried out for the effect of each variable, and their interactions were evaluated. Scott Knotts's test was further applied to compare the means of the response variables (yield or RI) or their interactions, when significant ($p < 0.05$). All the analyses were performed using the software RStudio version 3.2.0 (R Core Team, 2015).

$$Y_{ijkz} = \mu + M_i + S_j + T_k + (MS)_{ij} + (MT)_{ik} + (TS)_{kj} + (MST)_{ijk} + e_{ijkz} \tag{12}$$

where Y_{ijkz} is the observed value for the response variable under study with respect to the *z*-th repetition of the combination of the *i*, *j*, *k* levels of the factors M, S, T, respectively; μ is the average of all experimental units of the response variable; $(MS)_{ij}$, $(MT)_{ik}$, $(TS)_{kj}$, $(MST)_{ijk}$ are the effects of the interactions of the factors under study; e_{ijkz} is the error associated with the observed value Y_{ijkz}: *i* = 1,2, *j* =1,2,3, *k* =1...5.

Fatty acid profile

The fatty acid profile was assessed for the ethanolic extracts obtained at 55 °C. The fatty acids of oils were converted in their methyl esters (FAMEs) before gas chromatographic (GC) analyses according to the modified methodology proposed by Orsavova et al., (2015). Quantitative determination of FAMEs was conducted using a gas chromatograph (Shimadzu Corporation, GC-2010, Tokyo, Japan) with a flame

ionization detector (FID) and SP-2560 capillary column (100 m × 0.25 mm × 0.2 μm) (Sigma-Aldrich Co. LLC) with a stationary phase (poly(biscyanopropylsiloxane); high polarity; non-bonded). The injection volume was 1 μL, the temperature of the injection port and detector was 260 °C with the split ratio of 1:20, and nitrogen was used as a carrier gas. Temperature programming was 140 °C/5 min, and a rate of 4 ºC/min until 240 ºC/ 30 min. Identification of FAMEs was performed by comparing their retention times with those of reference standards (mixture FAME Mix, SUPELCO, which included 37 FAMEs). For quantification of FAMEs, methyl-undecanoate (Sigma Aldrich Chemical Co., St. Louis, USA) was used as the internal standard. The results for fatty acids were expressed as percentages of total FAMEs.

RESULTS AND DISCUSSION

Soluble solids recovery (Γ_1)

Factorial assays allow for savings in time and resources, but mainly, they enable broader conclusions about the factors, including the study of the interaction among them, and greater precision for the estimates of the main effects of the factors (Linder-Olsson et al., 2001). Also, the degree of freedom associated with the residue is high when compared to simple experiments on the same factors, which contributes to decrease the residual variance, increasing the precision of the experiment (Walker, 1940). The results of the ANOVA, considering the sources of variation, such as material (M), solvent (S), and temperature (T) employed in the extraction process, are presented in Table 2.

In this part of the analysis, the ANOVA initially compares the model (all known sources of variation) randomly, and then compares each of the effects of the model (Table 2). The most important point to be evaluated in the ANOVA is the chance of an effect being due to randomization ($P_r > F$). In Table 2, the probabilities were very close to zero, that is, there was a chance near 0% of the effect of a given source of variation being due to randomization. Considering the significance level of 5%, which was used in this study, in order to assess the significance of a given effect, it is sufficient to verify that the value found for $P_r > F$ is less than 0.05.

Considering the response variable Γ_1, the ANOVA came out significant ($p < 0.05$) for all effects (main effects and interactions). In this case, only the ternary interaction (M×S×T) was analyzed. This case occurs when the null hypothesis for the interaction between the factors is rejected. This result implies that the effects of the factors act in a dependent way. In this case, the comparisons between the levels of one factor take into account the level of the other factor, since the significant result for the interaction indicates that the effects are dependent on the levels of each factor. Since the results of each effect were dependent on the other two effects, Scott Knott's test was only performed for the significant ternary interaction, which was analyzed through the unfolding of the interactions in each combination of levels (Table 3). Considering the solvent effect on each level of temperature and material (Table 3), it was possible to observe that the Γ_1 (%) for green coffee beans was higher when acetone was used as the extractor solvent at all temperatures analyzed. The solvent ethyl acetate was only more efficient than ethanol to extract soluble solids at 55 °C. At 39, 45, and 50.9 °C there was no significant difference among these two solvents' performance, showing that either one could be used in order to achieve a similar result and also that their polarity difference did not influence the extraction recovery of soluble solids.

However, it could influence the extract composition, which was not evaluated in this study. In opting for one, rather than the other, the solvent ethanol might be a good choice, since it is highly available (which lowers its cost) in many countries, especially in Brazil and in the United States, also due to its non-polluting and favorable to handling features. A wide range of literature has indicated that, in general, ethanol allows a better quality meal recovery and results in a greater extraction of sugars, free fatty acids, pigments, waxes, and peroxides (Beckel et al., 1948; Hron and Koltun,

Table 2. ANOVA table ($p < 0.05$) for the soluble solids mass transfer (Γ_1) and retention index (RI) of the solid-liquid extraction process of green coffee beans and its press cake using different solvents and temperatures.

Source	Γ_1				RI				$P_r > F$	
	DF	SS	MS	F_c	DF	SS	MS	F_c	Γ_1	RI
Material (M)	1	2.52	2.52	531.03	1	6.34	6.34	19.36	< 0.01*	< 0.01*
Solvent (S)	2	1.42	0.71	150.38	2	0.14	0.07	1763.4	< 0.01*	< 0.01*
Temperature (T)	4	5.49	1.37	289.48	4	0.08	0.02	< 0.01	< 0.01*	< 0.01*
M*S	2	0.18	0.1	19.32	2	0.24	0.12	32.77	< 0.01*	< 0.01*
S*T	8	0.57	0.07	15.14	8	0.26	0.03	8.98	< 0.01*	< 0.01*
M*T	4	0.27	0.07	14.04	4	0.26	0.07	18.4	< 0.01*	< 0.01*
M*S*T	8	0.32	0.04	8.39	8	0.13	0.02	< 0.01	< 0.01*	< 0.01*
Residue	60	0.28	0.005		60	0.22	0.004			
Total	89	11.07	0.12		89	7.67	0.09			

*Significant at $p < 0.05$. DF: degree of freedom; SS: sum of squares; MS: medium square; F_c: caluculated F; P_r: p-value.

Table 3. Soluble solids mass transfer (%Γ_1) of the solid-liquid extraction process of green coffee beans and its cake using different solvents and temperatures.

Solvent	Coffee Beans				
	35 °C	39 °C	45 °C	51 °C	55 °C
Acetone	$42.96\pm1.07^{a,D,\alpha}$	$52.28\pm0.98^{a,C,\alpha}$	$54.12\pm6.72^{a,C,\alpha}$	$82.46\pm7.47^{a,B,\alpha}$	$90.04\pm3.7^{a,A,\alpha}$
Ethyl Acetate	$23.78\pm1.23^{c,E,\alpha}$	$37.86\pm2.46^{b,D,\alpha}$	$43.7\pm1.81^{b,C,\alpha}$	$60.0\pm2.06^{b,B,\alpha}$	$65.68\pm5.41^{b,A,\alpha}$
Ethanol	$34.58\pm3.39^{b,C,\alpha}$	$36.79\pm2.64^{b,C,\alpha}$	$41.62\pm2.19^{b,B,\alpha}$	$63.39\pm1.78^{b,A,\alpha}$	$42.18\pm0.85^{c,B,\alpha}$
	Press Cake				
Acetone	$27.92\pm0.89^{a,C,\beta}$	$37.56\pm1.94^{a,B,\beta}$	$38.28\pm3.58^{a,B,\beta}$	$39.29\pm0.2^{b,B,\beta}$	$56.66\pm2.77^{a,A,\beta}$
Ethyl Acetate	$22.68\pm3.88^{a,D,\alpha}$	$31.84\pm2.02^{b,C,\beta}$	$34.26\pm3.13^{a,B,\beta}$	$35.27\pm2.46^{b,B,\beta}$	$47.42\pm3.66^{b,A,\beta}$
Ethanol	$24.63\pm1.67^{a,B,\beta}$	$26.56\pm1.81^{c,B,\beta}$	$29.64\pm0.89^{b,B,\beta}$	$44.33\pm1.39^{a,A,\beta}$	$46.54\pm2.21^{b,A,\alpha}$

Mean ± standard deviation (n = 3). Different lowercase letters in the same column, for each solvent level, indicate significant difference among the treatments by the Scott Knott's test ($p < 0.05$) (Solvent unfolding within each temperature and material levels). Different uppercase letters on the same line, for each temperature level, indicate a significant difference among the treatments by the Scott Knott's test ($p < 0.05$) (Temperature unfolding within each material and solvent levels). Different Greek letters in the same column, for each material level, indicate a significant difference between the treatments by the Scott Knott's test ($p < 0.05$) (Material unfolding within each temperature and solvent levels).

1984; Rittner, 1992; Gandhi et al., 2003). From these results, another fact that could be stated is that, in spite of acetone being only slightly less polar than ethanol, it showed far better performance in the extraction process, which could possibly be due to the chemical composition of the vegetable matrix analyzed. The solvent effect on the extraction of soluble solids from the press cake showed a different behavior from that presented for the beans. In that case, acetone performed better only at 39 and 55 °C, and at 45 °C it showed the same efficiency as ethyl acetate. Ethanol was the greatest solvent in recovering the soluble solids from the cake at 51 °C; showing that at higher temperatures ethanol should be used, and at lower temperatures, acetone should be the best choice. Regarding the temperature effect on each level of solvent and material (Table 2), overall, the greatest Γ_1 (%) for green coffee beans was obtained at the two highest temperatures studied. Acetone presented the best results, showing that the temperature may exert great influence on the extraction processes, as observed also for the ethyl acetate results, where the higher yields were obtained at the highest temperatures. The elevation of temperature from 35 to 51 °C promoted an increase of 91 and 83% in the results obtained with acetone and ethanol, respectively. On the other hand, acetone performed similarly at 39 and 45 °C, meaning that the lowest temperature could be used in order to save energetic costs in the process. This energetic cost saving could also be observed when ethanol was applied at 35 and 39 °C, where no differences in the results were observed. The temperature effect on the extraction of soluble solids from the press cake presented results as expected, because the most reasonable recovery yields were obtained at 55 °C. Ethyl acetate results were similar at 45 and 51 °C, indicating that the process could be carried out at 45 °C without harming the process efficiency. The same trend was observed for acetone and ethanol results, where in the case of acetone it is suggested to perform the process at 39 °C, rather than at 45 or 51 °C; regarding the ethanol results, it is cost saving to carry out the process at 35 °C, rather than at 39 or 45 °C. As expected, the temperature effect on the recovery yield was greater for the green coffee beans, which present higher content of extractable solids compared to its press cake. This fact could be also confirmed when analyzing the effect of the materials on each level of solvent and temperature (Table 3), where the Γ_1 (%) was significantly higher for the beans rather than for the cake at all temperatures and most of the solvents (excluding ethanol, that showed similar results for both materials at 55 °C, and ethyl acetate, at 35 °C). When a low solvent to solid ratio is used, as in this study (5:1 w/w), the extraction may be limited by the saturation of the solutes that are soluble in the solvent, and, generally, by raising the temperature up to a point, there is an increase of the solutes solubility in the solvent and consequent increase in the yield of the extraction process. The solubility of the oil or extractable solids in the solvent may be related to the temperature, matrix composition, and also to the type of extraction process, being important criteria for the process, since with an increase in temperature the solubility increases and, consequently, there is an improvement in the extraction efficiency (Takeuchi et al., 2009; Azmir et al., 2013; Varzakas and Tzia, 2015). Another interesting behavior observed was the lowering of the recovery of soluble solids from green beans when the temperature was raised from 51 to 55 °C and the extraction was carried out with ethanol, which could be explained, according to Dibert et al. (1989), by the fact that, for a given mass ratio, when there is no adsorption of the solute to the solid matrix, the extraction yields at equilibrium do not depend on the temperature of the system. These authors studied the equilibrium data of the green coffee oil extraction using hexane (20 h; 30, 40, and 50 °C), and also reported this trend when raising the temperature from 40 to 50 °C at the same mass ratio applied in this study. They also observed that the equilibrium concentration yield decreased with increasing liquid to solid mass ratio.

The results indicated the feasibility of solid-liquid extraction in order to extract the solids from either the

beans or the cake. The solid-liquid extraction could be employed as a single-process, or combined with the mechanical pressing, in order to optimize this process in terms of recovery efficiency. As reported in a previous study of this research group (Oliveira et al., 2019c), the oil content of the beans and cake, respectively, were 8.6 and 6.3 %, showing the inefficiency of the pressing process in order to extract the oil (< 30%) from the beans, and consequently, reaffirming the advantages of employing the solvent extraction.

Retention Index (RI)

The retention index (RI) is an important extraction parameter to be analyzed, since it measures the solution adhered to the insoluble solids. This variable substantially impacts the extractors design, as it influences the number of stages of the process and also the solvent recovering stage - the higher the RI, the higher is the operational cost (Rodrigues et al., 2010). The RI is directly related to the solution viscosity, particle size, and to the physicochemical affinity between the solution and the oily matrix (Wlsniak et al., 1987). Regarding this response variable (RI), the ANOVA (Table 2) was significant for the triple interaction (M×S×T), as well as for Γ_1. Considering only the interaction amongst material, solvent, and temperature, since the linear factors should not be discussed if the interactions were significant, the results for RI are presented in Table 4, where it is possible to evaluate the behavior of the RI for the unfolding of each independent variable analyzed into the other variables.

Table 4. Retention index (RI) of the solid-liquid extraction process of green coffee beans and its press cake.

Temperature (°C)	RI		
	Acetone	Ethyl Acetate	Ethanol
		Coffee Beans	
35	$1.12\pm0.02^{b,A,\beta}$	$1.20\pm0.24^{b,A,\beta}$	$1.36\pm0.05^{a,A,\alpha}$
39	$1.03\pm0.08^{b,A,\beta}$	$1.31\pm0.01^{a,A,\beta}$	$1.10\pm0.07^{b,A,\delta}$
45	$1.38\pm0.26^{a,A,\alpha}$	$1.39\pm0.18^{a,A,\alpha}$	$1.26\pm0.01^{b,A,\beta}$
51	$1.05\pm0.02^{b,A,\beta}$	$1.42\pm0.16^{a,A,\alpha}$	$1.04\pm0.06^{b,A,\delta}$
55	$1.01\pm0.03^{c,A,\beta}$	$1.33\pm0.03^{a,A,\beta}$	$1.19\pm0.01^{b,A,\gamma}$
		Press Cake	
35	$0.70\pm0.06^{b,B,\alpha}$	$0.65\pm0.02^{b,B,\beta}$	$0.83\pm0.03^{a,B,\alpha}$
39	$0.70\pm0.01^{a,B,\alpha}$	$0.60\pm0.04^{a,B,\beta}$	$0.66\pm0.0^{a,B,\gamma}$
45	$0.60\pm0.03^{a,B,\beta}$	$0.63\pm0.01^{a,B,\beta}$	$0.59\pm0.0^{a,B,\gamma}$
51	$0.75\pm0.01^{a,B,\alpha}$	$0.75\pm0.01^{a,B,\alpha}$	$0.77\pm0.02^{a,B,\beta}$
55	$0.64\pm0.01^{a,B,\beta}$	$0.65\pm0.03^{a,B,\beta}$	$0.70\pm0.02^{a,B,\beta}$

Mean ± standard deviation (n = 3).
Different lowercase letters in the same row, for each solvent level, indicate significant difference among the treatments by the Scott Knott's test ($p < 0.05$) (Solvent unfolding within each temperature and material levels).
Different uppercase letters in the same column, for each material level, indicate a significant difference among the treatments by the Scott Knott's test ($p < 0.05$) (Material unfolding within each temperature and solvent levels).
Different Greek letters in the same column, for each temperature level, indicate a significant difference between the treatments by the Scott Knott's test ($p < 0.05$) (Temperature unfolding within each material and solvent levels).

It was observed that, for all solvents and temperatures there was a significant difference among the results for the adhered solution mainly for the green coffee beans, with the highest values obtained for this material. Although both materials had a similar composition, the heat treatment and the pressing of the material influenced the retention of the solution, which is interesting, because it indicates that, with application of pre-treatments, there is an improvement in the efficiency of the process.

The higher RI for coffee beans extraction was observed when ethyl acetate was employed as the solvent, at most temperature levels, except at 35 °C, in which the solvent ethanol presented higher RI. Regarding the press cake, only at 35 °C was there a significant difference amongst the solvents; the solvent ethanol presented higher RI at 35 °C. On the other hand, the other solvents showed that they were not distinguishable for this variable.

By unfolding the interaction of each solvent level within each material and temperature levels of the beans extraction, ethyl acetate and acetone showed the best results (lower RI) at the extreme (the lowest and the highest) temperature levels; ethanol, however, followed the expected trend, where the lowest content of solution adhered to the raffinate was verified at the highest temperatures. This same behavior of the solvent ethanol was observed for the press cake; acetone showed the lowest values of RI at 45 and 55 °C.

This leads to the conclusion that the highest temperature employed in the extraction process (55 °C) was more efficient to extract the soluble solids from the green coffee materials, since it presented the lowest RI; however, it is important to state that the RI is not the only parameter affecting the yield of the process. Although it was expected that the lowest temperatures would present greater RI values, as occurred in the case of ethanol for both the press cake and coffee beans, since at low temperatures the lowest yields were obtained, it could also be due to the low solubility of the solids in the solvent. The increase in temperature provides a decrease in the viscosity of the solution (Amarante et al., 2014), allowing the decrease of the amount of adhered solution in the inert matrix. This is due to the fact that RI is an important variable due to its direct impact on the solvent content used in the extraction process, amount of extract obtained, losses of solution in the raffinate stream (Wlsniak et al., 1987), and recovering costs regarding the solvent loss in the raffinate phase.

According to Rittner (1992), polar alcohols have high affinity for the solid matrix, tending to become more adhered to it, and consequently increase the RI. However, this could not be corroborated by the results for coffee beans, since the greater RI values were

obtained to the solvent ethyl acetate, which was the least polar solvent studied.

Araújo et al. (2018) reported the dependence of the RI on the temperature and solvent type for the soluble solids extraction process of pequi and murici seeds. When using ethanol as the solvent, the authors observed that the increase in temperature promoted an increase in RI, whereas when isopropanol was used the RI reduced when the temperature was raised from 35 to 45 °C; as the concentration of ethanol in the solvent increased, the variation of the RI response variable occurred.

Thermodynamic study

In order to perform the thermodynamic study of the soluble solids extraction from green coffee beans and its press cake with different alternative solvents, the distribution coefficients (K_e) were experimentally determined (Table 5). The thermodynamic parameters (ΔH, ΔS, and ΔG) for the extraction of soluble solids were obtained from the values of K_e at different temperatures. ΔH and ΔS values were obtained from the linear and angular coefficients of the linear regressions of the experimental data through Eq. 10 ($R^2 > 90\%$) (Figure 1) and ΔG values were obtained using Eq. 11.

The values of the thermodynamic parameters are shown in Table 5.

In the thermodynamic study, the enthalpy (ΔH) and entropy (ΔS) variation values were positive. The Gibb's energy variation (ΔG) decreased with increasing temperature. The positive ΔH values indicate the

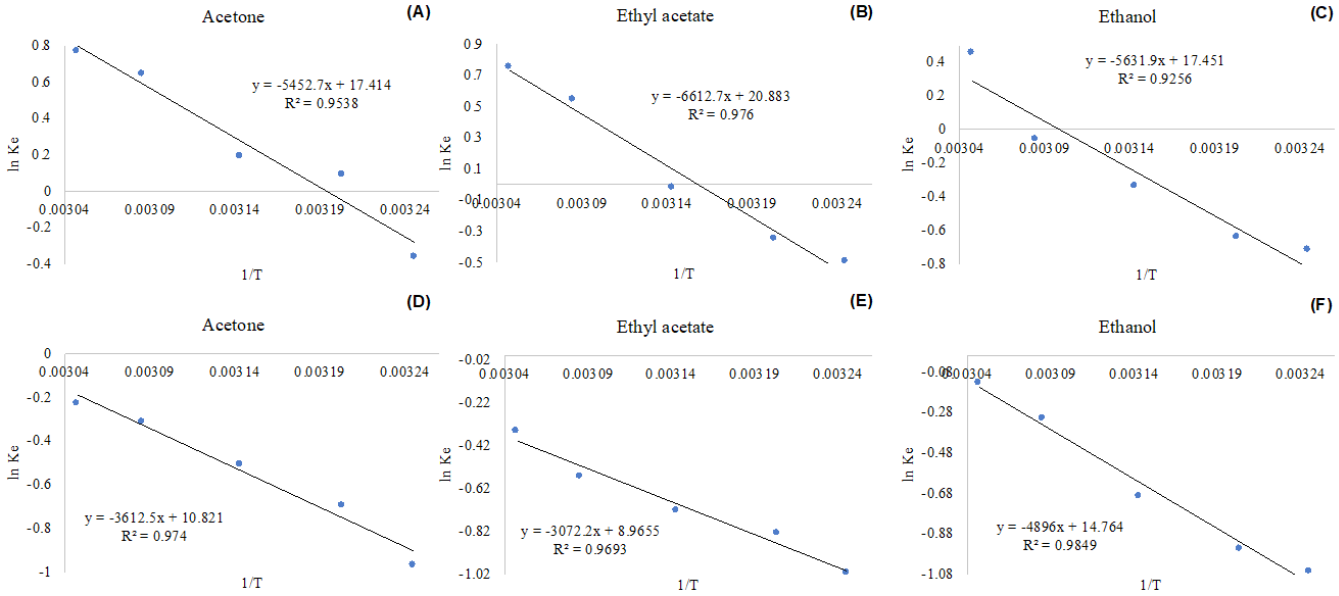

Figure 1. Plot of ln K_e versus 1/T (K^{-1}) for green coffee beans (A, B, and C) and press cake (D, E, and F).

Table 5. Thermodynamic parameters of the solid-liquid extraction of soluble solids from green coffee beans and its press cake using alternative solvents.

Solvent	Temperature (°C)	Coffee Beans				Press Cake			
		Ke	ΔH (kJ/ mol)	ΔS (J/(mol K))	ΔG (J/ mol)	*Ke*	ΔH (kJ/ mol)	ΔS (J/(mol K))	ΔG (J/ mol)
Acetone	35	0.69±0.11	45.34	144.8	720.06	0.38±.02	27.9	83.45	2186.36
	39	1.1±0.04			138.01	0.56±0.05			1850.9
	45	1.34±0.38			-727.83	0.6±0.09			1351.86
	51	2.16±1.19			-1593.67	0.73±0.15			852.83
	55	1.9±0.06			-2175.72	0.8±0.06			517.36
Ethyl acetate	35	0.61±0.06	54.98	173.63	1475.6	0.36±0.07	25.54	74.54	2573.03
	39	0.71±0.11			777.6	0.44±0.04			2273.36
	45	0.98±0.35			-260.75	0.49±0.07			1827.6
	51	2.12±1.08			-1299.08	0.57±0.06			1381.82
	55	1.73±0.66			-1997.1	0.7±0.13			1082.15
Ethanol	35	0.49±0.09	46.83	145.1	2114.16	0.34±0.03	40.61	122.15	2971.81
	39	0.53±0.11			1530.87	0.39±0.03			2480.8
	45	0.71±0.06			663.2	0.42±0.02			1750.35
	51	1.57±0.29			-204.5	0.73±0.04			1019.92
	55	0.94±0.37			-787.8	0.87±0.08			528.9

endothermic nature of the process, which requires energy to occur. The positive values of ΔS indicate an increase in the degree of molecular disorder during the process for the solids-oil-solvent system (the randomness of the process). This effect was expected because the oil was transferred from a solid phase (beans or cake) to a liquid one (solvent) (Nwabanne, 2012; Amarante et al., 2014). The extraction process involves the mixing of at least two different substances, which leads to the increase of their disorder (Johnson and Lusas, 1983). The same trend was also observed by other authors for the extraction of oil from several plant matrices, regardless of the type of solvent used (Liauw et al., 2008; Meziane and Kadi, 2008; Kostić et al., 2013; Sulaiman et al., 2013; Amarante et al., 2014). Regarding the ΔS, positive for all treatments, the extraction of soluble solids for green coffee beans was higher. In this study, ΔS, related to the increase of the system disorder in the extraction process, was influenced by the type of solvent (acetone, ethyl acetate, and ethanol), besides the type of material (beans or press cake). For the coffee beans, ΔS was lower for acetone and higher for ethyl acetate. For the cake, the behavior was different, with the highest ΔS for ethanol extraction and the lowest values for ethyl acetate extraction. The process is controlled by the ΔS, being favored by the temperature increase, significantly influencing the recovery of soluble solids and making the process more spontaneous, with low (< 0) ΔG values (Araújo et al., 2018). The spontaneity of the process (ΔG < 0) was observed only for coffee beans at higher ranges of temperature (> 45 °C).

The lowest ΔG was obtained for the solvent acetone employed in the green coffee beans extraction, which may explain the good yields obtained with this solvent. These results could also be related to the fact that the extract shows better solubility in acetone. On the other hand, ΔG values for the press cake extraction process decreased with temperature increase, but were found to be positive at the highest temperature evaluated (55 °C), indicating that at lower temperatures the process is not spontaneous. The positive ΔG values observed for the press cake show that the separation process did not occur completely, and that higher temperatures (> 60 °C for acetone and ethanol and > 70 °C) should be employed in order to favor the extraction of target compounds (soluble solids) and to make the process more spontaneous. Since the effect of the temperature is to enhance the influence of a positive ΔS, the process will be spontaneous at temperatures above $T = \Delta H/\Delta S$, which may also explain the lower yield obtained for this material (Doan et al., 2019).

According to Cooney et al. (2009) and Rodrigues et al. (2010), the most effective solvents in oil extraction are those with low water content, because they cause greater variations of ΔS and, consequently, result in negative ΔG. Thus, moisture content in a solvent is not favorable in the extraction of oils. In this way, the drying of the raw material is an important factor in the yield of the process, because its moisture migrates to the extract phase, decreasing the solubilizing power of the solvent (Aquino et al., 2009). Also, in processes where ΔH > 0 at higher temperatures, ΔS becomes dominant and, consequently, the oil dissolution process becomes more spontaneous.

In the literature, the thermodynamic parameters are reported for several systems using ethanol as solvent, generally comparing with the results obtained with hexane, and other alternative solvents considered less toxic. Liauw et al. (2008) studied the process of neem oil extraction with ethanol, using the same solvent:seed mass ratio and temperature range as in this study, although different particle sizes were applied. They obtained ΔH in the range of 75-115 kJ/mol, and ΔS values from 263 to 392 J/(mol K). ΔH and ΔS results for hexane were lower than those obtained with ethanol, and it was a system where ethanol extraction exhibited lower values of ΔG than the hexane extraction process. Meziane and Kadi (2008) studied the process of olive oil extraction (oil content of 11.07%) with ethanol (96%), and temperature range of 20 - 50 °C. The authors observed ΔH values of 12.91 kJ/mol, ΔS of 59.33 J/ (mol K), and ΔG < 0. Similar parameters were obtained by Amarante et al. (2014) in the process of extracting castor oil (oil content of 14.78%) using ethanol, and temperature range of 20 - 55 °C (ΔH = 12.27 kJ/mol, ΔS = 57.41 J/(mol K), ΔG < 0). Sulaiman et al. (2013), studying the oil extraction process from coconut residues using hexane and petroleum ether, obtained positive values for ΔH and ΔS, and a negative ΔG.

Evaluating all parameters analyzed (extraction yield, RI, and thermodynamic parameters), it was possible to observe that acetone was more efficient in the extraction of soluble solids from green coffee beans and its press cake. This shows that applying alternative solvents is possible, and allows the achievement of satisfactory yields, which can be improved with further studies. The negative value for ΔG for the soluble solids extraction from green coffee beans at higher temperatures showed that the process was feasible and spontaneous and that the extraction increased with increasing temperature as ΔG became more negative. The value of the thermodynamic parameters indicated that the extraction was endothermic and the process was irreversible.

Fatty acid profile

The fatty acid profile was assessed for the ethanolic extracts (Table 6) obtained at 55 °C.

Fatty acids composition of vegetable oils is formed by a mixture of saturated (SFAs) and unsaturated

Table 6. Fatty acid profile of ethanolic extracts of green coffee beans and its press cake compared to the green coffee oil obtined from mechanical pressing (GCOMP).

Fatty acid	IUPAC Fatty acid	Retention time	Coffee beans (%)	Press cake (%)	GCOMP (%)
Palmitic	C16:0	20.558	34.79	34.48	33.42
Trans-9-octadecenoic	C18:1 (trans)	23.914	7.53	7.71	7.61
Oleic (*Cis)*	C18:1	24.873	8.89	8.41	7.88
Linoleic	C18:2	26.333	42.28	43.66	45.32
Arachidic	C20:0	27.044	2.91	2.36	2.69
α-Linolenic	C18:3	27.995	1.23	1.51	1.52
Minority compounds	-	-	2.38	1.87	1.56

(UNFAs) fatty acids classified according to the number of unsaturated bonds as either monounsaturated (MUFAs) or polyunsaturated fatty acids (PUFAs). Nevertheless, each oil has a specific fatty acid distribution depending on the plant source (Orsavova et al., 2015). Orsavova et al. (2015) reported that the impact of fatty acids on human health could be assessed according to individual fatty acids because of their different influences on human health and risks of serious diseases. Saturated fatty acids with fewer than 12 carbon atoms, called short and medium chain saturated fatty acids (MCFAs), have not been found in the samples analyzed, which correlates with results in the literature (Folstar, 1976; Speer, Sehat and Montag, 1993; Speer and Kölling-Speer, 2006). Palmitic acid (C16:0) was found to be a predominant saturated fatty acid in the samples in the range of 33.4 to 34.8%, which is higher than the results presented by Speer et al. (1993) for both Robusta (27.2 - 32.1%) and Arabica (26.6 - 27.8%) green coffees. In fact, some studies have reported various impacts of saturated fatty acids on human health (Borlak and Welch, 1994; Williams, 2000; Lunn and Theobald, 2006).

There are many natural sources of monounsaturated fatty acids (MUFAs), such as red meat, whole fat milk products, nuts and fruits (*i.e*., olives and avocados). The investigated samples showed the highest proportion of MUFAs or PUFAs (polyunsaturated fatty acids) in their FAMEs composition. In general, MUFAs were distributed in the range from 7.53 to 8.89%. Oleic acid (C18:1) was found as the most abundant MUFA in all samples. Observed contents of oleic acid in the selected samples were significantly in accordance with reported values (Speer and Kölling-Speer, 2006; Wagemaker et al., 2011; Oliveira et al., 2014). It has been documented that MUFAs may reduce LDL cholesterol, while possibly increasing high-density lipoprotein (HDL) cholesterol (FAO and WHO, 2010). Oleic acid (C18:1, n-9) may lead to insulin resistance, contrary to PUFAs with protection against insulin resistance (FAO and WHO, 2010). The saturation index in red blood cell membranes is formed by the ratio of stearic (C18:0) to oleic acid (C18:1), and it is an appropriate biomarker for investigating the relation between the pattern of metabolism and breast cancer risk (Pala et al., 2001).

Primary sources of PUFAs, especially linoleic acid, are algae and marine phytoplankton, forming the main part of fish feed (Yongmanitchai and Ward, 1993; Mišurcová, 2011; Mišurcová et al., 2011; Ambrožová et al., 2014). Other sources are mostly nuts, seeds, and leafy vegetables (De Caterina and Basta, 2001). In the analyzed green coffee oil samples PUFAs were the predominant part of the fatty acid composition. Even though there were only minor variations among samples, the highest content was found for the oil obtained by mechanical pressing (GCOMP). The most abundant PUFA was linoleic acid in all analyzed samples, in the range from 42.3% (green beans oil) to 45.3% (GCOMP). Similar results have been reported for green coffee (Calzolari and Cerma, 1964; Carisano and Gariboldi, 1964; Hartman et al., 1968; Chassevent et al., 1974; van de Voort and Townsley, 1974).

Recent studies have clearly shown the important impact of PUFAs on human health in the prevention of, particularly, cardiovascular disease (DVD), coronary heart disease and cancer; inflammatory, thrombotic and autoimmune disease; hypertension; type two diabetes, renal diseases; and rheumatoid arthritis, ulcerative colitis, and Crohn's disease (De Caterina et al., 2000; Abedi and Sahari, 2014). The difference between the locations of the first double bond in the fatty acid carbon chain (n-3 and n-6 PUFAs) is the reason for significant differences in their biological functions that might be derived from the course of their interactions (Mišurcová et al., 2011). In the analyzed oils, n-3 PUFA represented by α-linolenic acid was found in the range of 1.23 -1.52%. The group of n-6 PUFAs was represented by linoleic acid, which was found to be the predominant PUFAs in the analyzed samples.

Speer et al. (1993) identified nine different fatty acids in green coffee oil (C16:0 ~27.8%; C18:0 ~6.3%; C18:1 ~8.2%; C18:2 ~54.3%; C18:3 ~2.6%; C20:0 ~2.8%; C20:1 ~0.3%; C22:0 ~0.6%; C24:0 ~0.4%), which were similar to those found in this work, only that C22:0 (docosanoic acid) and C24:0 (tetracosanoic acid) were considered as being minority compounds as they were found in low quantities.

Fatty acid profiles of green coffee oil obtained by extraction with ether (Calzolari and Cerma, 1964), petroleum ether (Carisano and Gariboldi, 1964), and hexane (Hartman et al., 1968; Chassevent et al., 1974;

van de Voort and Townsley, 1974) have been reported, and the results closely match those of this work, as palmitic and linoleic acids were also found to be the major fatty acids in the samples. This shows that the type of extraction (Table 6) may have a greater influence on the fatty acids profile than the solvent type.

CONCLUSIONS

The experimental results showed that the conditions during the extraction process had a significant influence on the extractability of total soluble solids from green coffee beans and from its press cake. The highest efficiency of soluble solids extraction at 55 °C and 4 h was achieved with acetone and ethyl acetate. The solution retained in the raffinate phase from the green coffee beans extraction process was greater than that for the green coffee press cake. On the other hand, in general, the soluble solids extraction yield was higher for the beans regarding each solvent used. The increase in temperature favored the extraction yield. For all operational levels, the ΔH and ΔS were positive, and ΔG decreased with increasing temperature, the process being independent of the solvent, endothermic, favored by the temperature increase. The process was spontaneous for green coffee beans at the highest temperature ranges. The thermodynamic study showed that the soluble solids extraction from green coffee beans and from its press cake is a process that requires more energy to be carried out, therefore the study of parameters such as temperature and type of solvent is very important in order to optimize such processes. Thus, the study indicated the feasibility of the solid-liquid extraction in order to extract the solids from coffee beans. Regarding the press cake, it would require higher temperature ranges in order for the process to be spontaneous. The solid-liquid extraction at higher temperatures could be employed as an alternative to the mechanical pressing process.

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