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Influence of solvent selection and extraction temperature on yield and composition of lipids extracted from spent coffee grounds

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ABSTRACT

Spent coffee grounds (SCG) are a potentially sustainable source of C16-C18 triglycerides. This study investigates known solvent extraction technologies with a wide range of solvents for lipid extraction from SCGs, and determines the effect of solvent selection and process temperature on the extraction efficiency and composition of the obtained oil. A correlation between increasing solvent boiling point, and therefore process temperature, and improved oil extraction efficiency was observed in Soxhlet extractions with a wide range of solvents. Experiments at elevated temperatures (up to 200 °C) were performed through Accelerated Solvent Extraction (ASE) and temperature increase initially improved the oil extraction efficiency when non-polar solvents were used, before decreasing it at higher temperatures. Utilization of ethanol resulted in the highest oil extraction ratio by ASE (at 165 °C), suggesting that temperature increase is more beneficial to the extraction efficiency of polar solvents. In addition, analysis of the oils was carried out to evaluate the composition of the oils extracted from SCGs using different solvents and extraction parameters. The Nuclear Magnetic Resonance (NMR) results were in agreement with the values obtained from the titrimetric determination of the free fatty acid content (FFA) of the oils in terms of the comparative trends, and also tentatively suggest that some differences in the composition of the extracted oils might be related to the type of extraction solvent used.

1. Introduction

Coffee is a crop cultivated in 80 countries and one of the most popular beverages worldwide (Campos-Vega et al., 2015; Murthy and Madhava Naidu, 2012). According to International Coffee Association, (2016), 9.1 million tonnes of coffee were produced globally between October 2015 and September 2016 with a 1.8% increase in global coffee production compared to 2014/15. There are ~80 coffee species, however, only two are economically significant, *Coffea arabica* and *Coffea canephora* (Robusta) (Murthy and Madhava Naidu, 2012). Specifically, of the total worldwide coffee production in 2015, Arabica and Robusta varieties accounted for ~5.3 and ~3.8 million tonnes representing 58.2% and 41.8% of the overall respectively (International Coffee Association, 2016). Worldwide coffee consumption between October 2015 and September 2016 was 9.3 million tonnes, with the deficit between production and consumption covered by stocks accumulated in previous years, while an average annual growth rate of 1.9% has been observed in global coffee consumption since 2012/13 (International Coffee Association, 2016).

Spent coffee grounds (SCG) are the residues obtained during coffee brewing and represent the main coffee industry residual material (Campos-Vega et al., 2015). On average, 650 kg of roasted coffee are generated from one ton of green coffee and approximately 2 kg of wet SCGs are obtained for each kilogram of soluble coffee produced (Murthy and Madhava Naidu, 2012). Consequently, a significant amount of SCGs is generated annually and a waste management plan consistent with existing regulations is required. SCGs are used for various purposes such as composting, sugar production, mushroom growth and bioenergy production (Campos-Vega et al., 2015). However, much recent attention has been given to the potential use of SCGs oil as a biodiesel feedstock (Kondamudi et al., 2008; Oliveira et al., 2008).

Coffee seeds contain lipids stored in the endosperm tissue as energy reserve for germination and post-germination growth (Crisafulli et al., 2014). Coffee oil is mainly comprised of triglycerides and small amounts of diglycerides, monoglycerides and FFAs with the glyceride

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Abbreviations: SCG, Spent coffee ground; ASE, accelerated solvent extraction; NMR, nuclear magnetic resonance; FFA, free fatty acid

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portion accounting for 80–95%, while the rest of the oil consists of terpenes, sterols and tocopherols (Jenkins et al., 2014). Previous studies that investigated the extraction of lipids from SCGs through the Soxhlet method reported oil yields ranging from 7 to 30.4% w/w on a dry weight basis, with most researchers reporting values between 11 and 20% w/w (Al-Hamamre et al., 2012; Caetano et al., 2012; Deligiannis et al., 2011; Efthymiopoulos et al., 2017; Haile, 2014; Jenkins et al., 2014; Pichai and Krit, 2015).

Other researchers have used solvent extraction variations for extraction of SCG oil including microwave-assisted extraction with extraction ratios reported to range between 77.25 and 82.63% w/w of the total available oil (Ahangari and Sargolzaei, 2013), and ultrasound-assisted extraction with extraction ratios of 83–98% w/w of the total available oil (Abdullah and Bulent Koc, 2013; Ahangari and Sargolzaei, 2013; Rocha et al., 2014). Supercritical fluid extraction has also been used previously used for oil extraction from SCGs with extraction ratios ranging from 82.6 to 98.1% w/w (Ahangari and Sargolzaei, 2013; Akgün et al., 2014; Couto et al., 2009). In all the studies where an oil extraction ratio is stated, a Soxhlet method was utilised to determine reference oil content.

The wide range of oil yields obtained in previous studies can be attributed to the different blends of coffee varieties used in the samples, the origin of coffee (cultivation, climate, time of picking) and the upstream processing (wet or dry processing and roasting) (Al-Hamamre et al., 2012; Jenkins et al., 2014; Oliveira et al., 2008). The different methods of coffee brewing generally do not significantly affect the lipid content of SCGs (Campos-Vega et al., 2015). Other parameters that affect the oil extraction efficiency of solvent extraction are related to the extraction procedure including moisture content, particle size, coffee to solvent ratio, type of solvent, extraction method and extraction duration (Al-Hamamre et al., 2012; Caetano et al., 2012; Efthymiopoulos et al., 2017; Pichai and Krit, 2015). With the exception of supercritical fluid extraction where lipids are removed by a supercritical fluid (e.g. CO_2), all the methods use organic solvents for lipid extraction.

The effect of solvent selection on the SCG oil extraction efficiency is a research objective that has been addressed by very few studies, with only Al-Hamamre et al. (2012) and Caetano et al. (2012) examining more than 3 different solvents. In particular, Caetano et al. (2012) performed Soxhlet experiments with hexane, heptane, octane, ethanol, isopropanol and mixtures of hexane and isopropanol ranging from 50:50 vol/vol to 80:20 vol/vol for durations of 2.5–9 h and found that the greatest oil yield was obtained with octane (26.5% w/w) and the lowest with hexane and ethanol (16% w/w). Al-Hamamre et al. (2012) used pentane, hexane, toluene, chloroform, acetone, isopropanol and ethanol in Soxhlet extractions for durations of 15–70 min and found that hexane resulted in the highest oil yield (15.28% w/w) and chloroform in the lowest (8.6% w/w).

Generally, non-polar solvents are better suited to oil extraction than polar ones, because the low presence or complete absence of charges allows penetration into the low polar matrix of SCGs (Al-Hamamre et al., 2012; Pujol et al., 2013). Polar solvents like alcohols are known to extract higher amounts of FFAs and undesired products such as proteins, carbohydrates, Maillard reaction products, phosphatides and other compounds (Al-Hamamre et al., 2012; Johnson and Lusas, 1983; Kondamudi et al., 2008).

The FFA content of oil is a major quality factor when considering transesterification to produce biodiesel, as high amounts of FFAs increase oil acidity, susceptibility to oxidation, speed up degradation and inhibit alkaline catalyzed transesterification (Al-Hamamre et al., 2012; Predojević, 2008). In general, FFA levels between ~3% and ~20% relative to oil weight are common in previous studies using hexane as the solvent (Al-Hamamre et al., 2012; Efthymiopoulos et al., 2017; Go et al., 2016; Haile, 2014; Kwon et al., 2013; Vardon et al., 2013), however values as low as 0.31% w/w (Deligiannis et al., 2011) and as high as 59% w/w (Caetano et al., 2012) have been reported, suggesting a significant variation in the composition of oil extracted from different sources with different extraction parameters. The composition of the extracted oil is an important parameter for its subsequent utilization either as a biodiesel feedstock or in the food and cosmetic industry and a number of authors have reported the use of ^{1}H NMR spectroscopy for the analysis of the composition of lipids and fats containing complex lipid mixtures (Guillén and Ruiz, 2001; Nieva-Echevarría et al., 2014; Satyarthi et al., 2009; Skiera et al., 2014), while it has also been used for the broad analysis of oils extracted from coffee grounds and SCGs (D'Amelio et al., 2013; Jenkins et al., 2014).

The effect of process temperature on the solvent extraction of oil from SCG has not been previously investigated, and only Ahangari and Sargolzaei, (2013) have extracted SCG oil through microwave-assisted solvent extraction with hexane and petroleum benzene at elevated temperatures by applying irradiation levels of 200 W and 800 W, though without specifying the achieved temperature. Generally, an increase in temperature improves the solubility of lipids, as high temperature can disrupt the cohesive and adhesive interactions between oil molecules and oil-matrix molecules respectively, thus increasing the diffusion rate of the lipids (Johnson and Lusas, 1983; Richter et al., 1996).

Previous studies that investigated the effect of extraction temperature (40 °C to 100 °C) on the accelerated solvent extraction of lipids from sources like rice bran (Jalilvand et al., 2013), pistachio seed (Sheibani and Ghaziaskar, 2008) and corn kernels and oats (Moreau et al., 2003) observed that increase of process temperature resulted in improved oil extraction efficiency. Increase of the extraction temperature decreases the strength of solvent intermolecular forces and thus its viscosity allowing better penetration into the matrix particles, and decreases surface tension allowing the solvent to better coat the feedstock and therefore increase rates of lipids extraction (Camel, 2001; Kaufmann and Christen, 2002; Richter et al., 1996). A decrease in surface tension also leads to easier formation of cavities and lipid molecules are more quickly dissolved in the solvent (Richter et al., 1996).

This paper presents results of experimental investigations into effect of solvent extraction conditions on oil extraction efficiency and composition of oils extracted from SCGs, with a comprehensive range of polar and non-polar extraction solvents investigated along with varying process temperatures. In this paper, the FFA content of the extracted SCG oil samples was determined by titration, with NMR analysis undertaken in order to make a preliminary assessment of changes in extracted oil composition when different solvents were used.

2. Materials and experimental methods

The SCG samples used were provided by bio-bean Ltd. and local coffee shops. Multiple SCG batches were used due to supply issues, and these resulted in different oil yields after Soxhlet extraction. *N*-Hexane was chosen as the baseline solvent based on previous studies which considered different solvents and found *n*-hexane to be amongst the most effective in extracting oils from SCGs (Al-Hamamre et al., 2012; Haile, 2014; Kondamudi et al., 2008), while the samples were dried prior to oil extraction at a temperature of 100 °C for 5.5 h. Information regarding the origin and upstream processing of the samples used was not available, however, it was known that three samples had been utilised for instant coffee production and will be referred to throughout as ICG1, ICG2 and ICG3, where ICG stands for instant coffee grounds, and the rest were products of the retail market used in espresso machines and will be referred to as RCG1 and RCG2, where RCG stands for retail coffee grounds. Table 1 shows the average baseline oil yields on a dry weight basis obtained after three repeats utilising *n*-hexane as the extraction solvent.

When oil extraction ratios obtained from different SCG batches are compared in the Results section, it is the extracted oil yield relative to oil yield achieved by Soxhlet with *n*-hexane (Table 1) which is presented.

Table 1
Average oil yields extracted from various SCG samples with *n*-hexane.

SCG sample	% Average oil yield (w/w)
ICG1	24.26 ± 1.62
ICG2	25.16 ± 1.09
ICG3	24.78 ± 0.61
RCG1	16.32 ± 0.19
RCG2	14.80 ± 0.85

2.1. Solvent extraction through Soxhlet method

Oil extraction from dry ICG1 and RCG1 samples was conducted with a Soxhlet extractor and extractions of 8 h were performed with approximately 22.5 g of dry SCGs at a SCG-to-solvent ratio of 1:9 w/v. The average cycle time was 15 min, while the temperature was adjusted depending on the solvent used to maintain this constant cycle frequency, while three experimental repeats were performed with each solvent.

2.2. Solvent extraction at elevated temperature – ASE

Solvent extraction at conditions of elevated temperature was performed in an ASE 150 (Thermo Fisher Scientific) with the ICG1, ICG2, ICG3 and RCG2 samples and various extractions solvents. ASE shares the same principles of operation with Soxhlet, however, in ASE the solvents are used near their supercritical region and have better extraction and mass transfer properties, thus leading to fast extractions (20–25 min) (Camel, 2001). The high pressure applied (70–140 bar) increases the boiling point of solvents and allows them to remain liquid at elevated temperatures (100–200 °C). In general, extraction temperature has been observed as more influential than pressure in determining yields (Camel, 2001), and ASE does not attempt to maintain a specified pressure during a cycle.

Initially, the stainless steel extraction cell (66 mL capacity) contained approximately 23 g of dry SCGs and was loaded into the ASE oven, preheated to the desired temperature. The cell was then filled with solvent and pressurized by a high-pressure pump (70 mL/min). A static extraction (without continuous solvent flow) was then performed, followed by pressure release and rinsing of extracted lipids and “used” solvent into a collection vial through a filter inserted at the bottom of the extraction cell. This was accomplished by a second volume of solvent which fills the cell and initiates the second static period. All the extraction experiments were performed for 3 static cycles of 5 min, a setting that was found in preliminary experiments to be the most efficient. The coffee to solvent ratio is automatically determined by the instrument and ranged from 1:5.8 to 1:6.6 w/v. Following completion of the final static cycle, the cell is purged with compressed nitrogen gas to remove the residual solvent, extracted lipids and final solvent volume.

2.3. Oil yield and extraction ratio calculation

In both the extraction methods described (Sections 2.1 and 2.2), the oil remains dissolved in the solvent and further processing is required to remove residual solvent. Rotary evaporation was used to remove excess solvent, and any remaining solvent traces were removed by thermal drying at 100 °C for 2 h. The achieved oil yields were calculated as per Eq. (1).

$$\%\ oil\ \ yield = \frac{W_1}{W_2} \times 100 \tag{1}$$

Where W_1 is the weight of the oil and W_2 the weight of the dry SCG sample. The oil extraction ratios obtained were calculated based on Eq. (2):

$$\%\ oil\ \ extraction\ \ ratio = \frac{\%\ (\frac{W}{W})oil\ \ extracted}{\%\ (\frac{W}{W})average\ \ oil\ \ yield} \times 100 \tag{2}$$

Where the% (w/w) oil extracted corresponds to the amount of oil extracted relative to SCG dry weight, and the denominator to the hexane-extracted oil yield of the specific SCG batch used in each case (Table 1).

2.4. Determination of FFA content through titration

The acid value and FFA content of the oil samples extracted with various solvents were determined through the method of titration with phenolphthalein as the indicator (Kardash and Tur, 2005). In order to improve the accuracy of the method, which depends on identifying the exact point of color change, and therefore the validity of the obtained results, a pH meter (Hannah, HI991001) with accuracy of ± 0.02 was used to detect the equivalence point. The standard deviation of the obtained FFA weight percentages was found to be 0.87 as calculated from a total of 40 experimental repeats.

2.5. NMR analysis

A range of oils extracted from the SCGs were selected for analysis by ^{1}H NMR; these were the oils obtained from Soxhlet extraction, and oils extracted by ASE using ethanol and *n*-hexane at various temperatures. For NMR analysis, the oil samples were diluted into chloroform-d ($CDCl_3$), typically 0.025 mL of oil into 1 mL of $CDCl_3$. The samples were transferred into 0.5 mm NMR tubes.

NMR spectroscopic analysis of oil samples was carried out at 298 K using a Bruker Advance III 600 spectrometer, operating at 600.13 MHz, and equipped with a cryoprobe. The acquisition parameters were as follows: spectral width 12335 Hz, relaxation delay 1 s, acquisition time 4 s, 32 scans, flip angle of 30° deg. A 0.3 Hz line broadening was applied prior to Fourier transform, and the spectra were referenced to residual $CHCl_3$ in the solvent at (d, 7.26 ppm). Data was processed manually using Bruker TOPSPIN—NMR software (version 3.5.6). The method of evaluating NMR spectra to give the apparent ratios of the various lipid components was adapted from that of Nieva-Echevarría et al. (2014). Estimations of component mass percentage were made using an assumed molecular weight for all lipid chains, corresponding to that of palmitic acid which is broadly representative of lipids found in oil from SCG (Jenkins et al., 2014). Further information on the method and spectra is supplied in the Supporting information.

The spectra obtained from NMR analysis of the SCG oils were broadly similar in their apparent composition; and were similar to those reported by other researchers (Döhlert et al., 2016; Jenkins et al., 2014). An example spectrum which highlights some of the main spectral peaks and assignments is given in Fig. 1.

Using the spectral peaks particular to FFAs, triglycerides, 1-monoglycerides, 1,2-diglycerides, and 1,3-diglycerides, estimations were made of the molar ratios of these various constituent components of the oils, using the peak areas. The COO$\underline{\mathbf{H}}$ peak could provide a unique signal in the ^{1}H spectrum for FFAs, however, fast proton exchange processes with water in $CDCl_3$ result in the broadening of the signal arising from the carboxylic acid group (COO$\underline{\mathbf{H}}$) at around 12 ppm, such that is not apparent in the spectrum. Skiera et al. (2014) investigated the FFA content in pharmaceutical lipids using NMR spectroscopy. Their method involved the addition of small amounts of deuterated dimethyl sulfoxide (DMSO-*d6*) to the fatty oils in $CDCl_3$, which slowed the proton transfer sufficiently to allow the detection of the COO$\underline{\mathbf{H}}$ signal. Addition of DMSO-*d6* was also trailed in the present work; however, addition of DMSO-*d6* at various levels resulted in the visible precipitation of some of the oil. Instead, a method was adopted that used the signal arising from the acyl group (COOH-C$\underline{\mathbf{H}}_2$-) of the FFA, which is distinguishable from the ester functional group in glycerides.

Due to the complex composition of the oils analyzed in this work

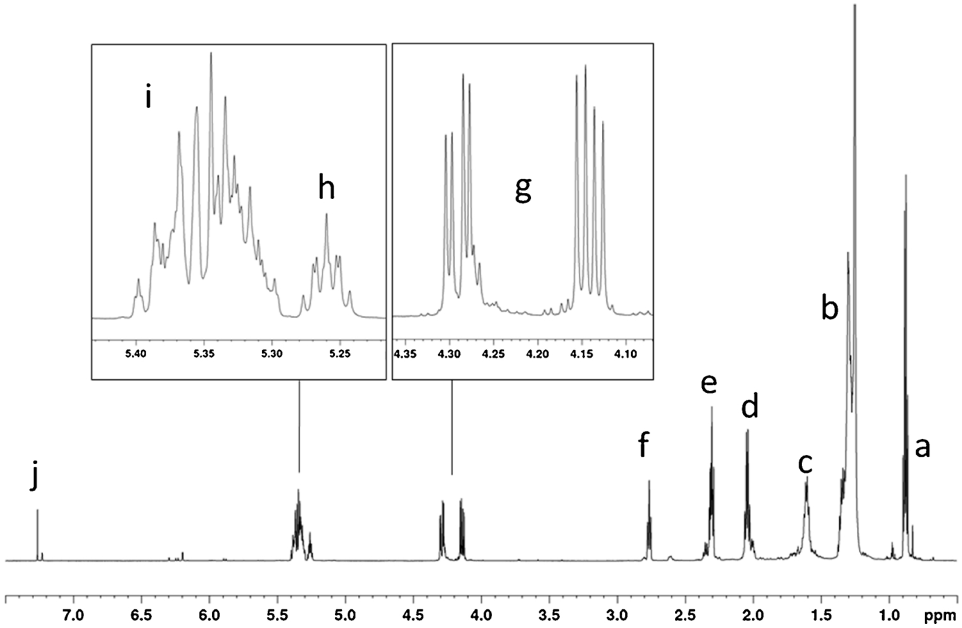

Fig. 1. Example ^{1}H NMR spectrum highlighting some main spectral peaks and their assignments. Spectrum shown is of the oil extracted from SCGs using ASE with hexane solvent at 125 °C. (a) $-C\underline{\mathbf{H}}_3$, (b) $-(C\underline{\mathbf{H}}_2)_{n-}$, (c) $-OCOCH_{2-}C\underline{\mathbf{H}}_{2-}$, (d) $-C\underline{\mathbf{H}}_2-CH=CH-$, (e) $-OCO-C\underline{\mathbf{H}}_{2-}$, (f) $=HC-C\underline{\mathbf{H}}_{2-}CH=$, (g) $R'OC\underline{\mathbf{H}}_{2-}CH(OR')-C\underline{\mathbf{H}}_2OR''$, (h) $R'OCH_{2-}C\underline{\mathbf{H}}(OR')-CH_2OR''$, (i) $-C\underline{\mathbf{H}}=C\underline{\mathbf{H}-}$, (j) residual solvent $C\underline{\mathbf{H}}Cl_3$.

(including mono-, di and triglycerides), previously reported methods (e.g. (Satyarthi et al., 2009; Skiera et al., 2014, 2012)) needed to be adapted to take account of each of these components. Part of the method used in this paper relied on making an assumption of the average molecular masses of each component. Small variations in the actual molecular compositions, and overlapping spectral peaks, therefore lead to error in the NMR method. A detailed appraisal of the absolute accuracy of the quantitative results obtained by the NMR analysis is beyond the scope of this paper, and is left to future work.

2.6. Solvents used and their characteristics

A wide range of solvents was used to examine solvent property effects on lipid extraction efficiency and lipid composition. Table 2 shows the different solvents used, along with their chemical formula, molecular weight, boiling point, dielectric constant and dipole moment, where, solvents with a dielectric constant of less than 15 are considered to be non-polar.

The utilization of both polar and non-polar solvents allowed for the evaluation of the effect of solvent polarity on the oil extraction efficiency, while the range in solvent boiling point resulting in different process temperatures, useful in understanding the effect of temperature. Furthermore, the use of solvents of homologous series (alkanes, alcohols) with increasing carbon chain lengths allowed for the determination of the effect of solvent molecular weight on lipid extraction efficiency. It can be seen in Table 2 that all of the alkanes are non-polar, while all of the alcohols are polar with the exception of hexanol, which is considered to be mostly non-polar because of the dominance of the long non-polar hydrocarbon chain over the polar $-OH$ moiety, but with some polar properties due to its high dipole moment, while pentanol is slightly polar (Tayar et al., 1991). Dichloromethane is a slightly polar solvent that solvates positively charged species via its negative dipole (although it has a dielectric constant lower than 15), while toluene is non-polar.

3. Results and discussion

3.1. Effect of solvent selection on oil extraction efficiency – Soxhlet

Fig. 2(a) shows the oil extraction ratio obtained against the polarity of the solvent used, expressed by its dielectric constant. Fig. 2(b) shows the oil extraction ratios achieved with different solvents versus the solvent boiling point. The standard deviation for each point in Fig. 2(a) and (b) is 3.25.

Fig. 2(a) shows that the oil extraction ratio obtained with non-polar solvents ranges from 76.74 to 123.88%, with pentane extracting the

Table 2
Chemical formulas and properties of the solvents used in the experimental part of this study.

Solvent	Chemical Formula	Molecular weight (g/mol)	Boiling point (°C)	Dielectric constant	Dipole Moment (D)	Polarity
Alkanes						
Pentane	C_5H_{12}	72.15	36	1.84	0	Non-polar
Iso-hexane	C_6H_{14}	86.17	60	1.89	0.02	Non polar
Hexane	C_6H_{14}	86.17	69	1.88	0	Non-polar
Heptane	C_7H_{16}	100.2	98	1.924	0	Non-polar
Octane	C_8H_{18}	114.23	126	1.95	0	Non-polar
Alcohols						
Ethanol	C_2H_6O	46.07	79	24.26	1.69	Polar
Propanol	C_3H_8O	60.1	97.15	20.45	1.64	Polar
Butanol	$C_4H_{10}O$	74.12	116–118	17.8	1.74	Polar
Pentanol	$C_5H_{12}O$	88.15	138	13.9	1.91	Slightly polar
Hexanol	$C_6H_{14}O$	102.17	157	13.3	1.74	Non-polar
Others						
Dichloromethane	CH_2Cl_2	92.14	40	9.1	1.5	Slightly polar
Toluene	C_7H_8	84.93	111	2.38	0.36	Non-polar

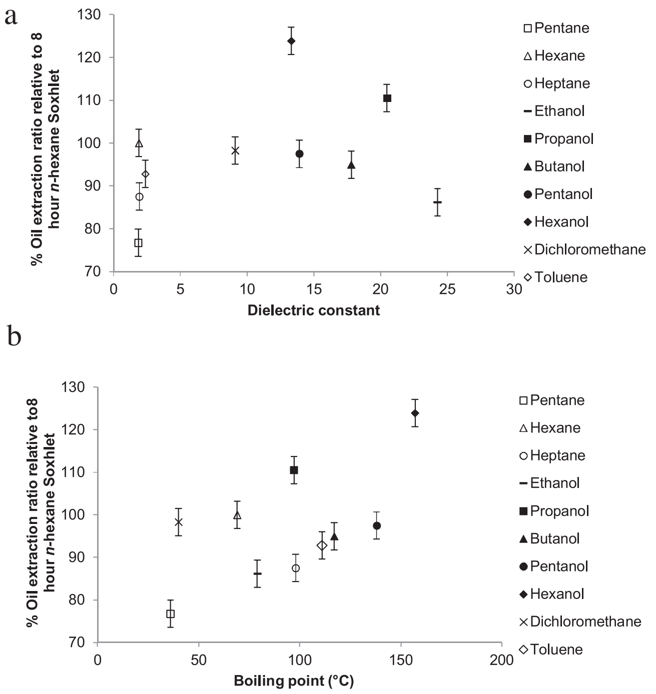

Fig. 2. (a) Oil extraction ratios obtained versus dielectric constant of the solvent used. (b): Oil extraction ratios obtained versus solvent boiling point.

lowest quantity of available lipids and hexanol the highest. The polar alcohols resulted in oil extraction ratios between 86.18 and 110.52% with ethanol extracting the lowest amount of oil and propanol the highest. A weak trend of decreasing oil extraction ratio with increasing alcohol dielectric constant can be observed in Fig. 2(a), especially if propanol is excluded.

Fig. 2(b) suggests that there might be a weak correlation between increasing solvent boiling point, and therefore temperature of the extraction, and higher oil extraction ratio. High temperatures (100–200 °C) are known to cause the loosening of the coffee cell wall structure and increase the solubility of components like arabinogalactans and mannans (Campos-Vega et al., 2015; Quinn, 1988). Therefore, it is suggested that the high extraction temperature achieved with solvents like hexanol decreased the selectivity of the process and resulted in the extraction of cell wall components and bound lipids (Campos-Vega et al., 2015; Zuorro and Lavecchia, 2012).

It is interesting to note that with regards to any possible effect of the solvent molecular weight on oil extraction ratio, while the highest extraction ratio was obtained by the solvent of highest molecular weight (hexanol), no clear relationship between molecular weight and solvent extraction efficiency was found. This suggests that the penetration of the solvent molecules into the SCGs was not limited by the solvent molecular weight and hence molecule size. This can be likely attributed to the high temperatures used in upstream coffee processing (drying after harvesting and roasting) that deform the structure of cell walls and change porosity, thus leading to the formation of large micropores and resulting in loss of selective permeability (Aguilera and Stanley, 1999; Borém et al., 2008; Quinn, 1988). The influence of molecular weight therefore appears to be indirect through its relation with the boiling point which dictates the temperature of Soxhlet extraction. It is likely therefore, that other physical properties that increase with molecular mass, such as surface tension and dynamic viscosity are also secondary in importance to the extraction.

Other studies have also examined the effect of different solvents on the extraction efficiency of SCG oil through the Soxhlet method, and these are shown in Table 3 along with the average oil yields achieved in this study. Only results from solvents that have also been used in the present research are shown, and actual oil yields from all studies are presented instead of extraction ratios for comparison purposes. The SCG-to-solvent ratios used by Al-Hamamre et al. (2012), Caetano et al. (2012) and Kondamudi et al. (2008) were 1:3 w/v, 1:20 w/v and 1:4.2 w/v respectively.

Table 3
Comparison between the% w/w dry weight oil yields achieved from the present study and other researchers.

Solvent	Present study (ICG1)	Present study (RCG1)	Al-Hamamre et al. (2012)	Kondamudi et al. (2008)	Caetano et al. (2012)
Non-polar					
Pentane	18.61	–	15.18	–	–
Hexane	24.26	16.32	15.28	13.4	16
Heptane	–	14.49	–	–	18
Toluene	22.51	–	14.32	–	–
Polar					
Dichloromethane	23.83	–	–	15.2	–
Ethanol	20.90	–	12.92	–	16

In general, previous studies reported oil yields of a magnitude similar to RCG1 (Table 1), a fact that can likely be attributed to the source of coffee samples. Al-Hamamre et al. (2012) similarly to the present study achieved one of the lowest oil yields with ethanol and attributed it to the formation of complex formations between fatty acids and carbohydrate breakdown components that inhibit the extraction process. Kondamudi et al. (2008) found that use of dichloromethane resulted in a slightly higher oil yield than hexane with a possible explanation being the drying process, which was carried out at a temperature of 50 °C and may potentially have led to incomplete moisture removal. Therefore the slightly polar character of dichloromethane may have been responsible for the slight oil yield increase relative to that obtained with hexane, as polar solvents can improve the oil extraction efficiency from wet samples (Johnson and Lusas, 1983). Caetano et al. (2012) achieved a higher oil yield with heptane comparing to hexane and ethanol extractions, however, extractions with the various solvents were conducted for different and not specified durations.

3.2. Solvent extraction at elevated temperature – ASE

Ethanol (polar) and the non-polar solvents of the homologous series of alkanes (*n*-hexane and its branched-chain isomer iso-hexane *iso*-hexane, heptane and octane) were used in ASE experiments. Fig. 3 shows the average oil extraction ratios obtained at temperatures ranging from 60 °C to 200 °C.

It can be seen in Fig. 3, that when the extraction was performed with *n*-hexane at a temperature close to its boiling point (70 °C), an average oil extraction ratio of 63.5% was extracted. As the extraction temperature was increased, the oil extraction ratio increased up to a maximum of ~85.5% w/w at 145 °C, while a further temperature

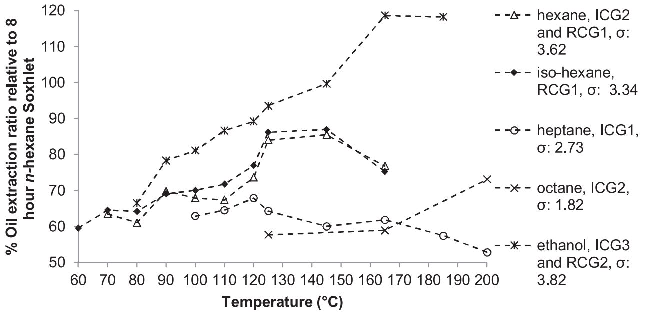

Fig. 3. Oil extraction ratios obtained using ASE at various temperatures with different solvents.

increase led to a slight decrease in oil extraction ratio. Iso-hexane resulted in oil extraction ratios very similar to those obtained with *n*-hexane (maximum of 87% at 145 °C), which can be attributed to the almost identical solvent properties.

When the extraction was conducted with heptane at a temperature close to its boiling point (100 °C), the obtained oil extraction ratio was ~63% w/w, while Soxhlet led to an extraction ratio of 87.5% w/w (Fig. 2(b)). An increase in temperature resulted in slight oil extraction ratio increase, with a maximum of 68% obtained at 120 °C, but further temperature increase led to lower extraction ratios. Octane extracted and extraction ratio of 57.7% at 125 °C which slightly increased at 165 °C and reached a maximum at 200 °C (73.1%). Experiments with octane at higher temperatures were not performed due to equipment limitations, so it is not known if an eventual decrease in oil extraction ratio with increasing temperature would have been observed, as was the case with other solvents (Fig. 3).

Fig. 3 suggests that there is an optimum temperature that promotes rapid lipid diffusion rates and results in high oil extraction ratios. However, the relatively high oil extraction ratios obtained at high temperatures (100–200 °C) may also have occurred due to the extraction of bound lipids and impurities from the solid matrix and ruptured cell walls respectively (Quinn, 1988; Zuorro and Lavecchia, 2012). The slight decrease of oil extraction ratio observed in most cases after a certain temperature is possibly related to reduced stability and degradation of the lipids (Campos-Vega et al., 2015; Novaes et al., 2015).

Fig. 3 also shows that when ethanol was used at a temperature similar to its boiling point (80 °C), an average oil extraction ratio of 66.5% w/w was obtained, while Soxhlet extraction resulted in an extraction ratio of 79.3% (Fig. 2(b)). The obtained oil extraction ratios increase as the temperature of the ASE process increases up to a maximum of 118.7% w/w at a temperature of 165 °C, while further temperature increase does not significantly affect the extraction efficiency of the process. The high oil extraction ratios obtained can be possibly attributed to the polar character of ethanol, which potentially leads to the extraction of compounds other than triglycerides (e.g. phosphatides, proteins, carbohydrates) (Al-Hamamre et al., 2012; Johnson and Lusas, 1983; Kondamudi et al., 2008), and to the concurrent high extraction temperature that reduces the selectivity of the process.

3.3. Determination of FFA content

Fig. 4 shows the weight percentage of each oil sample that corresponds to FFAs, against the polarity of the solvent used, as expressed through its dielectric constant. All the oil samples were extracted from the ICG1 sample.

Fig. 4 shows that the FFA content of the oil samples increased with increasing solvent polarity. This is in agreement with previous studies which suggest that polar solvents tend to extract higher amounts of FFAs (Al-Hamamre et al., 2012; Johnson and Lusas, 1983; Kondamudi et al., 2008). Other compounds of acidic character, such as phosphatidic acid and carbohydrate derived acids, may have been extracted due to the high polarity of some solvents (Harwood et al., 1998; Mercier et al., 1980). Furthermore, the high temperature applied when solvents with high boiling points were used may have resulted in thermal degradation of lipids, leading to the formation of FFAs. Therefore, the strong acidic character of some samples can be possibly attributed to the synergistic effect of solvent polarity and extraction temperature. Fig. 5 shows a comparison of the estimated FFA content obtained from the classic titrimetric method and an NMR method (Section 2.5).

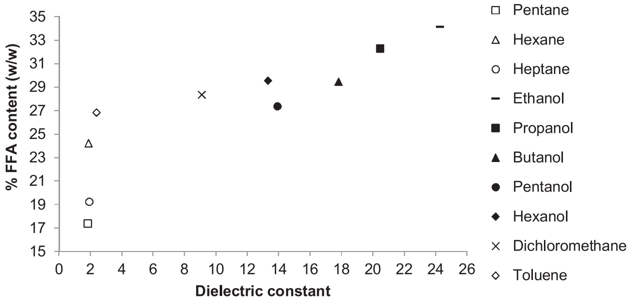

Fig. 4. % FFA content of oil samples extracted with various solvents, versus dielectric constant of the solvent.

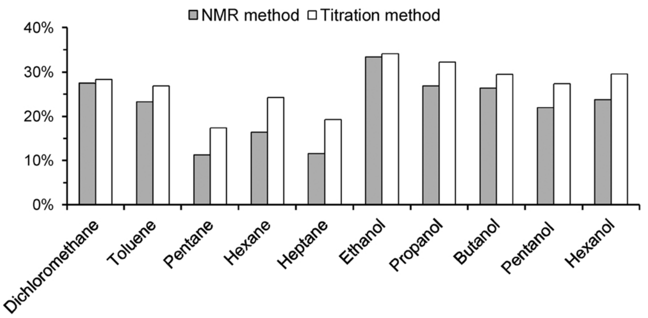

Fig. 5. Comparison of FFA content (% w/w) of oil samples extracted with various solvents determined through titration and NMR.

Fig. 5 shows that notwithstanding sources of error in both methods, comparison of the results obtained by NMR to the conventional titrimetric method suggests that both methods yield comparable results, though the NMR method appears to give a systematically lower estimation of FFA content. In order to evaluate the strength of the linear relationship between the FFA content values obtained by the two methods, the Pearson correlation coefficient (r) was determined, with the obtained value of 0.9680 indicating a strong linear relation between the two result sets. The 95% confidence intervals around the obtained r ranged between 0.8664 and 0.9926.

3.4. Compositional analysis of extracted oil – NMR

Table 4 shows the apparent molar ratios of the identified constituents of the oils (normalised to the triglyceride component), and the estimated percentage composition by mass obtained according to the method described in Section 2.5. It can be seen in Table 4 that based on the NMR analysis performed, triglycerides and FFAs were the main components of each oil, and that the proportions of these appear to vary between oils extracted with different solvents. The comparative level of mono- and diglycerides also varied, with the obtained spectra suggesting that higher levels of these were generally present in the oils extracted with the longer chained alcohols.

An unidentified triplet peak (at about 4.05 ppm) was apparent only in the spectra of the oils obtained from Soxhlet extraction using propanol, butanol, pentanol and hexanol. A two-dimensional COSY NMR experiment was carried out on the propanol sample, and the peak was seen to be coupled to $-\mathrm{OCO\text{-}C}\underline{\mathrm{H}}_2$- (i.e. peak C in Fig. 1). It is tentatively suggested that this peak could arise from alkyl esters present in the sample; alkyl esters could have been produced by esterification of FFAs or glycerides during the extraction process by reaction with the alcohol solvents. This observation could also possibly account for the higher levels of mono- and diglycerides identified in the oils from these solvents based on the obtained spectra. The unidentified peak was not observed in samples arising from ethanol, and had a smaller relative area for the short-chained alcohols. The potential presence of esters in some of the SCG oil samples is supported by previous studies which investigated single-step, or direct, transesterification of SCG oil, where extraction and transesterification were undertaken simultaneously (Calixto et al., 2011; Liu et al., 2017; Najdanovic-Visak et al., 2017; Park et al., 2016), with Calixto et al. (2011) reporting that increase of process temperature in the range of 200 and 330 °C had a beneficial effect on reaction yield when using supercritical methanol for direct

Table 4
Composition of oils obtained from Soxhlet extraction using different extraction solvents, using 1H NMR spectra. Estimations were made of the apparent molar ratios of the components (using adjusted peak integral values), and derived estimates of mass concentration.

Solvent	Apparent molar ratio					Estimated mass (%)				
	TAG	1-MAG	1,2-DAG	1,3-DAG	FFAs	TAG	1-MAG	1,2-DAG	1,3-DAG	FFAs
Dichloromethane	1.00	0.00	0.08	0.19	1.50	61%	0%	3%	8%	27%
Toluene	1.00	0.01	0.07	0.20	1.21	64%	0%	3%	9%	23%
Pentane	1.00	0.00	0.10	0.22	0.52	72%	0%	5%	11%	11%
Hexane	1.00	0.00	0.07	0.22	0.79	69%	0%	3%	11%	16%
Heptane	1.00	0.00	0.08	0.19	0.52	74%	0%	4%	10%	12%
Ethanol	1.00	0.03	0.09	0.44	2.33	48%	1%	3%	15%	33%
Propanol	1.00	0.11	0.17	0.57	1.92	47%	2%	5%	19%	27%
Butanol	1.00	0.01	0.15	0.41	1.68	53%	0%	6%	15%	26%
Pentanol	1.00	0.26	0.22	0.72	1.66	44%	5%	7%	22%	22%
Hexanol	1.00	0.36	0.29	0.83	2.01	39%	6%	8%	23%	24%

TAG, Triglyceride; 12-DAG, 1,2-diglyceride, 1,3-DAG, 1,3-diglyceride, 1-MAG, 1-monoglyceride, FFA, free fatty acid.

transesterification of SCG oil without a catalyst.

Therefore, it is hypothesized that the relatively high temperatures applied during oil extraction from SCGs with higher alcohols and the prolonged process duration (8 h) might have created suitable conditions for partial single-step biodiesel production despite the absence of a catalyst, thus resulting in limited esterification of oil and formation of esters. Alternatively the result could simply indicate that the higher alcohols extract relatively higher levels of mono- and diglycerides. The FFA results obtained from titration suggest that selection of solvent used for extraction could have direct implications for the intended use of the extracted oil, depending on whether greater proportions of glycerides or FFAs are desirable. If the intention is to produce biodiesel, then a high temperature extraction with a long chain alcohol is a potential route to one step extraction and transesterification, however, elevated temperatures and polar alcohols may result in a higher FFA content, which is undesirable for a final biodiesel product. Furthermore, the ester alcohol moiety chain length can have implications for diesel engine combustion and emission characteristics (Hellier et al., 2012). Further work is required to confirm whether fatty acid alkyl esters are present, which may or may not be advantageous.

An interesting observation from the NMR data is that of the SCG oil extracted by ASE with ethanol at temperatures of 125 °C and 185 °C. The spectra are unique in that the presence of caffeine was indicated by four identifying singlet peaks. It is tentatively suggested that the high temperature of the ASE extraction coupled with the use of the polar ethanol extracted residual caffeine contained in the SCGs; the caffeine peaks were not present in the spectra of oil obtained from the lower temperature Soxhlet extraction using ethanol or any other alcohol, nor in the spectra of oil obtained by ASE with *n*-hexane at temperatures of 125 °C, 145 °C and 165 °C. The presence of the caffeine could have implications for the properties of the oil and its derivatives (for example as a carrier of molecular nitrogen), and therefore potentially impacts on the suitability of ethanol as an extraction solvent under high temperature conditions.

4. Conclusions

1. A correlation between increasing solvent boiling point and oil extraction efficiency was observed in Soxhlet experiments, however, no systematic impact of solvent dielectric constant or molecular weight was observed.
2. Extraction by ASE at elevated temperatures extracted considerable oil quantities at significantly shorter duration and higher SCG-to-solvent ratios relative to Soxhlet.
3. Increase of extraction temperature in ASE resulted in higher oil extraction ratios for polar solvents than for non-polar ones. Oil extraction ratios obtained with non-polar solvents increased with increasing extraction temperature until an optimum temperature, with further increase above this point leading to slight decrease in extraction ratio.
4. Solvent selection appears to have implication for the relative proportions of mono-, di- and triglycerides and FFAs present in the extracted oil, while the FFA content of the oil was found to increase with increasing polarity of the extraction solvent used, with NMR providing comparable results to the conventional titrimetric method in determining the FFA content of oil samples.
5. Higher relative proportions of mono- and diglycerides were identified in oil samples extracted with long-chain alcohols based on the obtained ^{1}H NMR spectra, tentatively suggesting that partial esterification of SCG lipids may have occurred simultaneously with the extraction process leading to limited formation of alkyl esters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.indcrop.2018.04.008.

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