FACTORS AFFECTING THE EFFICIENCY OF PRESSURIZED SOLVENT EXTRACTION OF OIL FROM SPENT COFFEE GROUNDS

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ABSTRACT

Spent coffee grounds (SCG) are the main residues of the coffee beverage industry, and a potentially valuable source of energy-dense lipids. The present study investigates the effect of temperature, pressure and duration on the pressurized solvent extraction of lipids from dried SCG to evaluate their impact on oil extraction efficiency, composition and energy content. Solvent extraction trials at elevated temperatures performed by an Accelerated solvent extraction (ASE) unit revealed a beneficial effect of increased temperature on the crude lipid extracting efficiency of polar ethanol. Nuclear magnetic resonance (NMR) analysis showed that extraction temperature had a significant impact on the proportions of the ASE-extracted SCG oil constituents, with increasing temperature leading to lower concentration of triglycerides and higher levels of 1,2- and 1,3-diglycerides. Experiments performed in a closed pressurized vessel allowed individual selection of pressure and temperature and showed that pressure had a significant impact on oil extracting efficiency that largely depended on process temperature. There was no systematic effect of extraction temperature and pressure on the higher heating value (HHV) of SCG lipid samples, which ranged between 38.53 MJ/kg and 39.12 MJ/kg, while extraction pressure was found to have negligible effect on the free fatty acid (FFA) content of lipids extracted by pressure vessel experiments. Prolongation of pressurized extraction duration above 10 minutes was found to be counterproductive in terms of oil recovery, and consecutive short extraction static cycles with fresh solvent removed higher amounts of SCG oil relative to a single longer cycle.

1. INTRODUCTION

Spent coffee grounds (SCG) are the main residues of the coffee beverage industry, and a potentially valuable source of energy-dense C16-C18 triglycerides (Campos-Vega, Loarca-Piña, Vergara-Castañeda, and Oomah, 2015). Previous studies have shown that the lipid content of SCG ranges between 7 to 30.4% w/w on a dry weight basis (Ahangari and Sargolzaei, 2013; Al-Hamamre, Foerster, Hartmann, Kröger, and Kaltschmitt, 2012; Efthymiopoulos, Hellier, Ladommatos, Kay, and Mills-Lamptey, 2017; Haile, 2014; Jenkins, Stageman, Fortune, and Chuck, 2014), while the relatively high gross calorific value of SCG oil (36.4-43.2 MJ/kg) renders it a potential biodiesel feedstock (Abdullah and Bulent Koc, 2013; Berhe, Asfaw, and Asfaw, 2013; Caetano, Silva, Melo, Martins, and Mata, 2014). SCG oil mostly consists of triglycerides diglycerides, monoglycerides and free fatty acids (FFAs), along with smaller amounts of unsaponifiables (Efthymiopoulos, Hellier, Ladommatos, Russo-Profili, et al., 2018; Jenkins et al., 2014).

Supercritical fluid extraction and different variations of solvent extraction have most commonly been used for extraction of SCG lipids, however, the effect of pressure on the efficiency of solvent extraction from SCG has not been previously examined; generally pressure as a solvent extraction parameter is one that has been scarcely investigated in the case of vegetable oilseeds. Accelerated solvent extraction (ASE), also known as pressurized solvent extraction, is currently the only practical solvent extraction method that operates at pressures above the atmospheric. However, previous studies that investigated the pressurized solvent extraction of various compounds of interest from different matrices, and considered pressure as an extraction parameter, have suggested the effect of pressure to be of minor importance in ASE in terms of extraction efficiency relative to that of temperature, with its main advantage being that it enables solvents to remain liquid at temperatures above their boiling point (Camel, 2001;

Carabias-Martínez, Rodríguez-Gonzalo, Revilla-Ruiz, and Hernández-Méndez, 2005; Kaufmann and Christen, 2002; Mustafa and Turner, 2011).

The effect of pressure on the ASE extraction efficiency has been evaluated in the case of oil extraction from pistachio kernels, with pressure increase from 10 to 150 bar having a negligible impact on the oil yield obtained with hexane at 60°C (Sheibani and Ghaziaskar, 2008). On the contrary, Jalilvand et al., (2013) investigated the accelerated solvent extraction of rice bran oil with hexane at a temperature range of 40°C to 80°C and at pressures ranging between 20 and 140 bar through a modified supercritical fluid extractor unit, and found that the oil yield increased significantly with increasing pressure up to 75 bar, but with a further increase in pressure decreasing oil yield.

In general, increase of pressure has been suggested to favour solvent penetration into the matrix pores and to enhance solubility and desorption kinetics (Camel, 2001; Kaufmann and Christen, 2002; B. Kaufmann, Christen, and Veuthey, 2001; Matthäus and Brühl, 2001; Mustafa and Turner, 2011; Richter, Jones, Ezzell, and Porter, 1996). Luthria et al., (2004) and Richter et al., (1996) have also suggested that an ASE system pressure above the threshold required to maintain the solvents in liquid state (~100 bar), provides rapid filling and flushing of the extraction cells used. Nevertheless, an increase in extraction pressure is also likely to result in increase of the viscosity and surface tension of the solvent (Mezger, 2006; Rusanov and Prokhorov, 1996).

Regarding the effect of process temperature on the pressurized solvent extraction of oil from SCG, temperature increase has been found to result in improved crude oil recoveries, with higher temperatures being more beneficial for the extracting efficiency of polar solvents (Efthymiopoulos, Hellier, Ladommatos, Russo-Profili, et al., 2018). Generally, higher extraction temperatures improve the solubility of lipids and the mass transfer properties of the solvent (Johnson and Lusas, 1983; Richter et al., 1996; Yao and Schaich, 2015), however, may decrease the selectivity of the process (Campos-Vega et al., 2015; Efthymiopoulos, Hellier, Ladommatos, Russo-Profili, et al., 2018; Quinn, 1988; Zuorro and Lavecchia, 2012). The combined effect of controlled pressure and temperature on the efficiency of solvent extraction of oil from SCG has not been previously studied.

While the effect of pressurized solvent extraction duration on the process efficiency has not been investigated for SCG, limited information does exist in the literature for oil extraction from other sources. Jalilvand, Kamali, and Nematollahi, (2013) and Sheibani and Ghaziaskar, (2008) performed extraction of rice bran oil and pistachio oil through ASE at temperatures up to 100°C for durations ranging between 5 and 30 minutes and reported no significant change in the extraction yield. Yao and Schaich, (2015) investigated lipid removal from dry pet food through ASE (40°C, 103 bar) at static extraction durations of 5, 10 and 20 minutes and found a prolonged process duration to be counterproductive for extraction efficiency.

The present study investigates the effect of pressure, temperature and static cycle number and duration on the efficiency of pressurized solvent extraction of oil from dried SCG using a prototype closed pressure vessel and a Dionex ASE 150 unit. The composition of ASE-extracted lipids obtained at varying conditions in terms of mono-, di- and triglycerides and free fatty acids (FFA) was determined through 1H Nuclear Magnetic Resonance (NMR), whereas the FFA content of lipids obtained through solvent extraction in the pressure vessel was measured by titration. The HHV of selected oil samples was determined by a Bomb Calorimeter.

1.1 Abbreviations

ASE	Accelerated solvent extraction
FFA	Free fatty acids
HHV	Higher heating value
ICG	Instant coffee grounds
NMR	Nuclear magnetic resonance
RCG	Retail coffee grounds
SCG	Spent coffee grounds

2. MATERIALS AND METHODS

2.1 Materials

Two SCG samples were used in this study due to supply issues, a retail SCG sample, which will be referred throughout as RCG, was used in pressure vessel experiments and an instant SCG sample, which will be referred to as ICG, was used in ASE trials. All the samples used were thermally dried at a temperature of 100°C for 5.5 h prior to lipid extraction to remove residual moisture. The term moisture refers to the amount of liquid component that could be thermally removed from SCG and is not intended as an absolute measure of the presence of elemental H_2O (Efthymiopoulos et al., 2017). The oil yield of RCG and ICG samples was found by 8 hour Soxhlet extraction with hexane (SCG-to-solvent ratio of 1:9 w/v) to be 14.8±2.1% w/w and 25.1±1.1% w/w respectively, with the standard deviations calculated by three experimental repeats.

2.2 Accelerated solvent extraction

ASE static experiments without continuous solvent flow were performed with hexane and 99.8 pure anhydrous ethanol at temperatures up to 185°C and in SCG-to-solvent ratios ranging between 1:5.8 and 1:6.6 w/v determined by the instrument. The high pressure inside the extraction cell (70-140 bar) was automatically selected and allowed the solvent to remain in liquid state at temperatures above its atmospheric boiling point (Camel, 2001). A maximum of 5 static cycles could be performed per extraction and the maximum selectable duration for each cycle was 10 minutes.

2.3 Pressurized vessel

A prototype two-piece cylindrical stainless steel vessel that allowed independent control of both temperature and pressure was used to investigate the combined effect of pressure (up to 110 bar) and temperature (25-65°C) on the solvent extraction of lipids from SCG. Hexane was the solvent used at a SCG-to-solvent ratio of 1:6 w/v and static extraction durations between 5 and 60 minutes were inves-

tigated. The vessel was pressurized by compressed nitrogen gas supplied through a stainless steel pipe connecting the vessel with a N_2 bottle and a band heater was used to achieve the desired temperature conditions. Pressure and temperature inside the vessel were constantly measured by a pressure transducer and a thermocouple respectively. Dried SCG were mixed with hexane in the vessel for 20 minutes prior to pressurization in order to achieve the desired experimental temperature. After depressurization the solvent and SCG mixture was passed through a funnel equipped with a mesh of 0.1 mm aperture and subsequently filtrated through a cellulose filter paper with pore size of 20 μm so as to separate the oil and solvent mixture from SCG.

2.4 Oil yield calculation

The obtained oil was separated from the solvent by rotary evaporation followed by thermal drying at 100°C for 2 hours to remove any remaining solvent traces. The Soxhlet lipid yields of the two SCG batches were calculated as per Equation 1.

$$\% \text{ lipid yield} = W_1/W_2 \times 10 \qquad (1)$$

Where W_1 is the weight of the oil extracted and W2 the weight of the dry SCG sample. The lipid extraction ratio was measured by Equation 2.

$$\% \text{ lipid extraction ratio} = (\%(w/w)\text{oil extracted} \cdot 100)/(\% (w/w) \text{ lipid yield}) \qquad (2)$$

Where the % (w/w) lipid yield corresponds to the average hexane-extracted oil yield of the specific SCG batch used in each case obtained through Soxhlet.

2.5 Oil characterization

The composition of ASE-extracted SCG oil was determined by ^{1}H NMR analysis, in which 0.025 mL of oil was diluted into 1 ml of $CDCl_3$. The analysis was performed at 298 K by using a Bruker Advance III 600 spectrometer, operating at 600.13 MHz, and equipped with a cryoprobe.

Component mass percentage estimations were made using an assumed molecular weight for all lipid chains, corresponding to that of palmitic acid which is representative of lipids found in oil from SCG (Jenkins et al., 2014). More information on the NMR method used can be found in a previous study (Efthymiopoulos, Hellier, Ladommatos, Russo-Profili, et al., 2018). The FFA content of SCG oil samples obtained by pressure vessel experiments was determined through a method of titration with phenolphthalein as the indicator (Kardash and Tur, 2005). Higher heating values of oil samples were determined by using an IKA® C 1 Bomb calorimeter system operated with oxygen supply (30 bar) and with water at a constant temperature of 19°C.

3. RESULTS AND DISCUSSION

3.1 Accelerated solvent extraction trials

ASE experiments were performed at a constant temperature of 125°C so as investigate the effect of static cycle duration and number of static cycles on oil extraction ratio, and identify suitable conditions for subsequent extractions. Figure 1 shows the oil extraction ratios obtained from dried ICG with hexane at different conditions, while each point represents a separate experiment.

It can be seen in Figure 1 that addition of static extraction cycles initially resulted in improved oil recoveries for both of the examined cycle durations, with 3 static cycles of 5 minutes duration and 4 static cycles of 10 minutes duration resulting in the highest oil extraction ratios, while any further increase in the number of cycles resulted in a decrease in extraction ratios. The initial increase of the oil extraction ratio with additional extraction cycles can be explained by the introduction of fresh solvent and insufficient process duration of a single cycle, however, the subsequent slight decrease of oil extraction ratio is possibly related to reduced stability and degradation of lipid components due to prolonged exposure to conditions of high temperature and pressure in the extraction cell (Campos-Vega et al., 2015; Novaes, Oigman, De Souza, Rezende, and De Aquino Neto, 2015). The obtained results did not show any clear
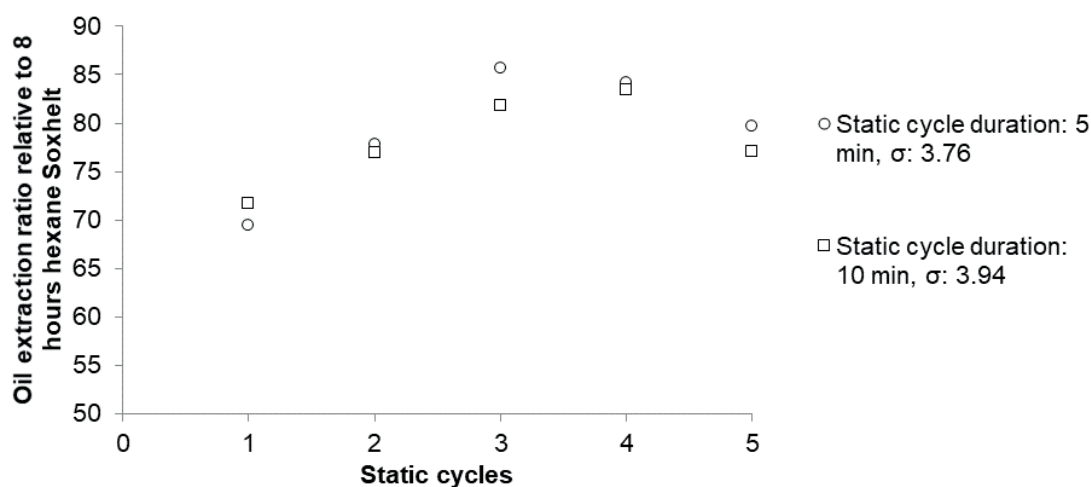

FIGURE 1: Oil extraction ratios obtained through ASE with hexane and varying number of static extraction cycles and static cycle duration. Standard deviation of the mean was calculated by three repeats at each experimental set of conditions.

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correlation between the static cycle duration and the lipid extraction efficiency. The optimum conditions of 3 static cycles with cycle duration of 5 minutes were used for subsequent ASE experiments. Compared to Soxhlet extraction, ASE trials recovered less oil from SCG but at a significantly shorter duration and with higher SCG-to-solvent ratio.

3.1.1 Effect of elevated temperature on pressurized solvent extraction efficiency

The polar ethanol and the non-polar hexane were used in ASE trials in order to investigate the effect of temperature on the lipid extraction efficiency from ICG. Table 1 shows the oil extraction ratios achieved relative to the oil yield obtained through 8-hour Soxhlet extraction with hexane, with an extraction ratio above 100% indicating that the actual oil yield was higher than that obtained through Soxhlet. The estimated relative mass composition of extracted SCG oil glycerides and FFAs was determined by ^{1}H NMR analysis, while the apparent molar ratios of the identified oil constituents, normalised to the triglyceride component, can be found in Table A.1 of the Appendix.

It can be seen in Table 1 that the SCG oil extraction ratio achieved with hexane slightly reduced at the highest investigated process temperature, potentially due to lipid degradation. However, an increase of temperature resulted in a consistently higher oil extraction ratio when ethanol was used, possibly attributed to reduced selectivity of the extraction process, which may have resulted in extraction of non-lipid polar compounds such as proteins, phosphatides and carbohydrates (Al-Hamamre et al., 2012; Johnson and Lusas, 1983; Kondamudi, Mohapatra, and Misra, 2008). The oil extraction ratios achieved with hexane and ethanol at the same experimental conditions (125°C) offer an indication for the actual hexane-soluble lipids in ethanol-extracted oil. In particular, the additional 9.5% w/w extracted with ethanol possibly corresponded to non hexane-soluble lipid components.

Table 1 also shows that the main components identified in lipid samples extracted through ASE were triglycerides, FFAs and 1,3-diglycerides in a decreasing order of magnitudes, while 1,2-diglycerides were also found in small amounts in most of the samples examined. There is no clear correlation apparent between increasing extraction temperature and FFA content in oil samples extracted either with hexane or with ethanol, however, higher extraction temperatures resulted in lower concentration of triglyc-

erides and higher quantities of 1,2- and 1,3-diglycerides in both sample sets. The NMR analysis performed did not reveal any spectral peaks unique to other lipid components, however this does not necessarily rule out their presence in the examined oil samples.

The decreased portion of triglycerides in oils extracted at higher temperatures in combination with the increased concentration of diglycerides and the relatively high quantities of FFAs suggest that the high extraction temperature may have resulted in enhanced thermal degradation of lipids due to glyceride hydrolysis with any residual bound water held within the grounds after thermal drying. In addition, FFAs could have been formed by the breakdown or hydrolysis of unidentified structural lipids other than mono-, di- and triglycerides, such as wax esters and phospholipids (Ratnayake, Hollywood, O'Grady, and Stavric, 1993; Speer and Kölling-Speer, 2006), with SCG residual water traces (Tran Nguyen, Go, Huynh, and Ju, 2013).

The increased presence of FFAs in ASE-extracted lipids relative to ICG oil extracted though Soxhlet, which was found to be 24.2±1.6% w/w, can also be partly attributed to preferential recovery of FFAs in the short ASE extraction duration (Efthymiopoulos et al., 2017). The fatty acid profile of ICG oil obtained through solvent extraction at atmospheric pressure conditions has been previously determined by gas chromatography, with linoleic (42% w/w), palmitic (32% w/w), oleic (10%w/w), stearic (8% w/w), eicosanoic (4% w/w) and linolenic acid (1% w/w) being the main fatty acids present (Efthymiopoulos et al., 2017). Previous studies have also shown that the unsaponifiable content of SCG oil extracted with hexane represented approximately 3% w/w to 5% w/w of total oil mass, based on transesterification yields achieved (Efthymiopoulos, Hellier, Ladommatos, Kay, and Mills-Lamptey, 2018; Kwon, Yi, and Jeon, 2013; Rocha et al., 2014).

Regarding the impact of ASE extraction temperature on the energy content of the obtained lipids, the HHVs of ICG oil samples extracted with hexane at temperatures of 125°C, 145°C and 165°C were found to be 38.53 MJ/kg, 38.90 MJ/kg and 38.84 MJ/kg respectively, showing no systematic impact of extraction temperature on the oil energy density. It is also interesting to note that a previous study that examined the calorific value of SCG lipids obtained with hexane and ethanol through ASE found minor differences in their HHV, indicating that they contain similar amounts of carbon and hydrogen atoms, although

TABLE 1: Oil extraction ratios and estimated relative mass composition of glycerides and FFAs present in oils obtained with ASE at various conditions. Standard deviations were obtained by triplicate experiments.

Extraction conditions	Oil extraction ratio (%) w/w	Relative mass composition of glycerides and FFAs in extracted oil (%)				
		TAG	1-MAG	1,2-DAG	1,3-DAG	FFA
Hexane - 125°C	84.1±3.6	64%	0%	1%	8%	27%
Hexane - 145°C	85.6±3.6	53%	0%	2%	10%	35%
Hexane - 165°C	76.8±3.6	60%	0%	0%	13%	27%
Ethanol - 125°C	93.6±3.8	51%	0%	3%	15%	31%
Ethanol - 185°C	118.3±3.8	45%	0%	4%	22%	29%

TAG: Triglyceride, 1,2-DAG: 1,2-diglyceride, 1,3-DAG: 1,3-diglyceride, 1-MAG: 1-monoglyceride.

this does not necessarily signify an equivalent lipid content (Efthymiopoulos, Hellier, Ladommatos, Kay, et al., 2018).

3.2 Solvent extraction in pressurized vessel

3.2.1 Effect of pressure on pressurized solvent extraction efficiency

Static solvent extraction experiments in a closed pressurized vessel were performed with dried RCG and Figure 2 shows the oil extraction ratios achieved at different temperature and pressure condition. The pressurized static extraction duration was 20 minutes and was preceded by a pre-heating period of 20 minutes during which the dried grounds were in contact with the solvent.

It can be seen in Figure 2 that when the static extraction was performed at conditions of ambient pressure and temperature (approximately 25°C), ~31% w/w of the available oil was extracted. As the applied pressure was gradually increased, while temperature remained ambient, the oil extraction ratio increased to reach a maximum of 35.6% w/w at 75 bar, with further pressure increase resulting in decreased extraction ratios. An almost identical trend, but with consistently higher oil extraction ratios, was observed when the experimental temperature was raised to 45°C. When the temperature of the extraction was increased to 65°C, a temperature close to the boiling point of hexane, the oil extraction ratio achieved at atmospheric pressure was 40.2% w/w. Experiments at higher pressures showed that the obtained oil extraction ratio increased linearly with pressure increase (R2=0.96), and the highest extraction ratio (56.5% w/w) was extracted at the highest applied pressure of 110 bar. However, it can be seen that the gradient of this increasing trend decreased at the highest pressures tested, with only a 0.9% w/w increase in extraction ratio when the extraction pressure was increased from 100 to 110 bar.

The beneficial effect of pressure increase up to 75 bar in the efficiency of the process can be possibly attributed to improved penetration of solvent into the pores of the feedstock, and the enhanced lipid solubility, mass transfer and desorption kinetics caused by the increase in pressure (Camel, 2001; Kaufmann and Christen, 2002; B. Kaufmann et al., 2001; Matthäus and Brühl, 2001; Mustafa and Turner, 2011; Richter et al., 1996). In addition, high extraction pressure tackles problems related to air bubbles found within the matrix that impede the solvent from reaching the oil (Mustafa and Turner, 2011). However, high pressure is known to increase the surface tension and viscosity of the solvent, with increased surface tension impeding the penetration of the solvent into the matrix of the oilseed and consequently reducing the rate of lipid extraction (Johnson and Lusas, 1983). Viscosity is a measure of internal molecular friction, and as oil removal through solvent extraction is in part governed by capillary flow through a solid matrix, high solvent viscosities can hinder flow and lead to lower extraction rates (Johnson and Lusas, 1983). The reduction in extraction ratio obtained at pressures greater than 75 bar (Figure 2) suggests that the inhibition of extraction caused by an increase in solvent surface tension and viscosity becomes more important in determining the overall lipid extraction rate at temperature conditions of between 25 and 45°C.

The absence of any decrease in obtained extraction ratios at extraction pressure up to 110 bar when conducted at a temperature of 65°C suggests that any negative effects of increased solvent surface tension and viscosity were countered by improved lipid solubility and diffusion rate due to increased temperature (Johnson and Lusas, 1983; Richter et al., 1996). The positive effects of elevated temperature appear to overcome the negative impact of high pressure on surface tension and viscosity observed at lower temperatures, and, synergistically with the aforementioned beneficial effects of pressure, result in improved oil extraction ratios. Previous studies have reported that the
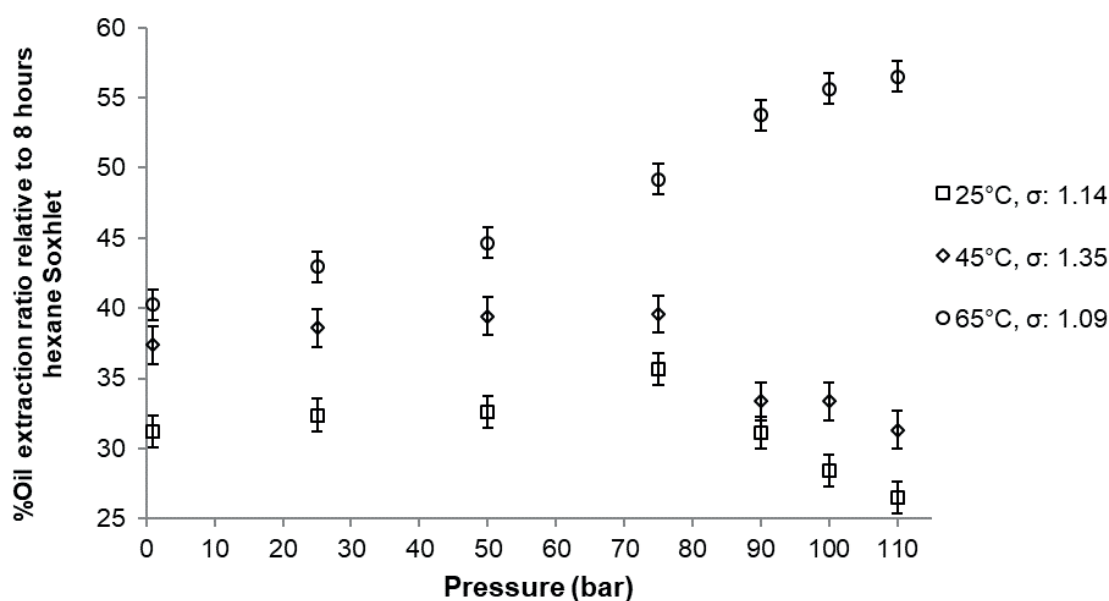

FIGURE 2: Oil extraction ratio obtained with hexane against applied pressure at extraction temperatures of 25, 45 and 65°C. Standard deviations were calculated from 3 experimental repeats and represent the reproducibility of the obtained results.

influence of applied pressure on oil yield is small, or even negligible, when compared to that of temperature (Camel, 2001; Mustafa and Turner, 2011), however, the obtained results suggest that pressure is also a significant factor when the extraction is performed at 75 bar and above. This is in agreement with the results reported from the pressurized solvent extraction of rice bran oil (Jalilvand et al., 2013).

Table 2 shows the average FFA content and HHV of samples extracted with varying pressure at a constant temperature of 65°C.

It can be seen in Table 2 that extraction pressure has a limited effect on the FFA content of the recovered lipids, with FFA levels ranging between 17.51% w/w and 19.22% w/w, while no clear correlation was found between applied pressure and FFA concentration. The FFA content of all the examined samples was higher than that of RCG lipids recovered through 8 hours Soxhlet extraction with hexane (15.46% w/w), verifying in this way the observation that prolonged solvent extraction duration can be associated with reduced presence of FFAs. Furthermore, the measured HHVs of the lipid samples showed only a small degree of variation, suggesting that extraction pressure does not significantly affect the energy content of recovered lipids.

3.2.2 Effect of pressurized solvent extraction duration and number of extraction cycles on lipid extraction efficiency

The effect of process duration on the efficiency of oil recovery through pressurized static solvent extraction in the pressure vessel was investigated with durations ranging between 5 and 60 minutes. Figure 3 shows the oil extraction ratios obtained from RCG2 with hexane at 45°C and 75 bar, against extraction duration.

It can be seen in Figure 3 that as the duration of the extraction increased from 5 to 10 minutes the obtained oil extraction ratio increased, while a further increase of the extraction duration to 20 minutes resulted in slight decrease of the oil extraction ratio. The initial increase in extraction ratio suggests that an extraction duration of 5 minutes did not allow sufficient time for the extraction of the available oil. Thereafter, and as the process duration increased up to 60 minutes, the obtained oil extraction ratio did not change significantly, suggesting that the extraction of the oil from SCG was accomplished during the first 10 minutes of the process under these temperature and pressure conditions of static solvent extraction.

TABLE 2: Average % w/w FFA content and HHV of oil samples extracted after 20 minutes at varying pressure conditions and a constant temperature of 65°C. Standard deviations calculated by three experimental repeats were 0.71 % w/w for FFA content and 0.43 MJ/kg for HHV.

Extraction Pressure (bar)	FFA content (%) w/w	HHV (MJ/kg)
1.013 (ambient)	18.74	38.93
25	17.51	38.82
50	19.22	39.12
75	18.08	39.03
100	18.91	38.91

The slight decrease of the oil extraction ratio when the duration of the process increased above 10 minutes can be possibly attributed to compression of the sample matrix under extended pressure and/or increased binding of lipids to protein (Yao and Schaich, 2015). The obtained results are in good agreement with previous studies that investigated pressurized solvent extraction of lipids from various sources such as rice bran (Jalilvand et al., 2013) pistachio kernels (Sheibani and Ghaziaskar, 2008) and dry pet food (Yao and Schaich, 2015) through ASE, and found that a prolongation of static cycle extraction duration could be either insignificant, or even counterproductive, in terms of oil extraction efficiency.

The effect of the number of static extraction cycles, with or without washing of the feedstock in between cycles, on the lipid extraction ratio achieved from SCG was also examined. The introduction of a second static extraction cycle of 20 minutes, with the same SCG sample but with fresh solvent at the same pressure and temperature conditions of 75 bar and 45°C, resulted in an average oil extraction ratio of 61.84±1.16% w/w. This is significantly higher than the extraction ratio of 39.57±0.35% w/w obtained with only one static cycle at the same conditions. This finding led to further experimentation with the number of static cycles at the same conditions of temperature (45°C), pressure (75 bar), pressurized extraction time (20 minutes) and SCG-to-solvent ratio (1:6 w/v or 120 ml of hexane), with washing stages of 1 minute with 120 ml of hexane following each static cycle. The average oil extraction ratios obtained from this set of experiments are presented in Figure 4.

Figure 4 shows that the introduction of a washing stage after the 1st extraction cycle removed a further 18.98% w/w of the available oil, a significant amount of lipids when compared to the oil extraction ratio of the 1st static cycle. This oil recovery can be possibly attributed to limited volume or saturation of the solvent used in the 1st static cycle, with the introduction of fresh solvent rapidly removing more oil. The 2nd static extraction cycle resulted in the recovery of an additional 12.85% w/w of the available oil, while the following washing stage achieved an extraction ratio of 1.78% w/w. These results suggest that the utilization of fresh solvent along with the extended total duration of the extraction allows recovery of lipids from the desorption-controlled phase, where the interactions between oil and sample matrix are stronger (Mustafa and Turner, 2011).

The addition of a 3rd static cycle followed by another washing stage removed a small further amount of oil and revealed the limit of the extraction efficiency of the process. The cumulative oil extraction ratio was 74.64% w/w, a significant amount of the total available oil, especially when considering the relatively low extraction temperature of 45°C and the total experimental duration of 63 minutes. Previous studies have also reported that several short consecutive static extraction cycles enhance the extraction efficiency of the process more than a longer single static cycle (Ramos, Kristenson, and Brinkman, 2002; Yao and Schaich, 2015).
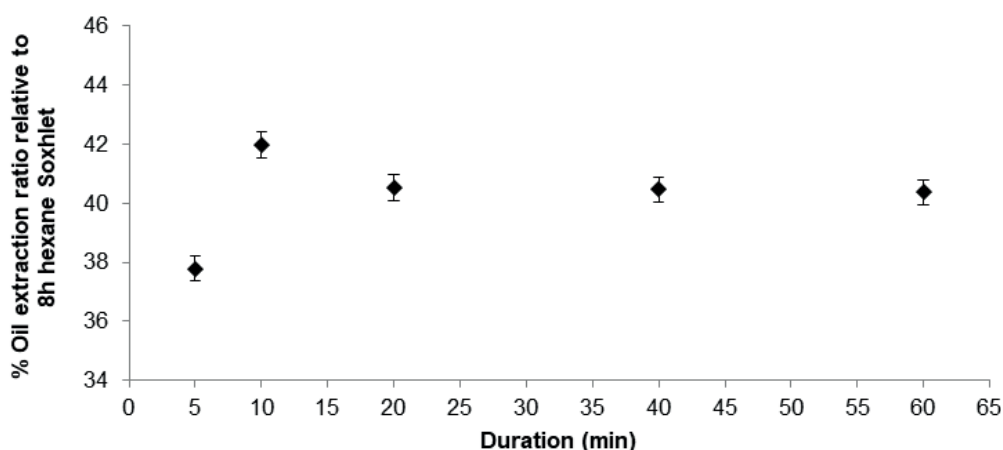
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FIGURE 3: Oil extraction ratios obtained with hexane against duration of static extraction at 75 bar and 45°C. The error bars shown represent the standard deviation of the mean.
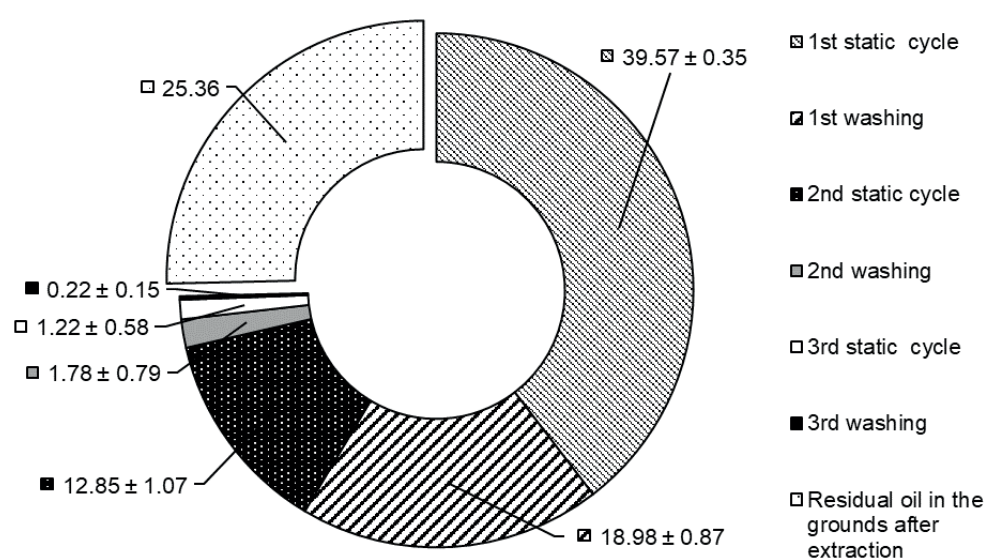

FIGURE 4: Oil extraction ratios obtained from multiple pressurized vessel static extraction cycles and washing stages when hexane was the solvent used. The standard deviations of the mean that are shown were calculated by sets of three experimental repeats.

4. CONCLUSIONS

- Increase of extraction temperature in ASE resulted in higher SCG oil extraction ratio when ethanol was used, suggesting that compounds other than lipids were extracted from SCG. Process temperature had a significant impact on the proportions of di- and triglycerides and FFAs present in the extracted oil, with increasing temperature leading to lower concentration of triglycerides and higher levels of 1,2- and 1,3-diglycerides, potentially due to enhanced hydrolysis with residual bound water traces remaining in the grounds after thermal drying;

- A process pressure of up to 75 bar improved the oil extraction ratio obtained through pressurized solvent extraction regardless of the process temperature, however, extraction above 75 bar at temperatures significantly below the boiling point of the solvent resulted in a decrease in oil extraction ratio, while an extraction temperature close to the solvent boiling point led to a linear increase in oil extraction ratio with increasing pressure;

- There was no systematic effect of extraction temperature and pressure on the HHV of SCG lipid samples recovered by ASE and closed pressurized vessel extractions, while the extraction pressure was found to have little effect on the FFA content of recovered lipids;

- Experimentation with the number of ASE static cycles revealed an optimum setting (3 cycles), while prolonged duration of ASE and closed pressure vessel trials was found to be counterproductive in terms of obtained oil yield;

- The introduction of fresh solvent after a single pressurized static extraction, either through a rapid washing stage or via a subsequent extraction cycle, improved significantly the oil recovery from SCG, and relatively short consecutive extraction cycles with fresh solvent were found to be more efficient than a single long cycle in terms of oil extraction ratio.

- This study has shown that pressurized solvent extraction can recover considerable oil quantities from SCG, at a significantly shorter duration relative to solvent extraction performed at atmospheric pressure conditions, while requiring a lower solvent quantity (Abdullah and Bulent Koc, 2013; Caetano, Silvaa, and Mata, 2012; Efthymiopoulos et al., 2017; Vardon et al., 2013). In addition, the closed pressurized vessel experiments demonstrated that extraction temperatures below the boiling point of the solvent can result in sufficient oil recoveries when multiple cycles are employed, therefore enabling extraction at less energy-intensive conditions. Finally, pressurized solvent extraction operates at a lower pressure range relative to supercritical fluid extraction, where pressures between 150 and 300 bars are typically employed, while achieving comparable oil recoveries (Ahangari and Sargolzaei, 2013; Couto, Fernandes, da Silva, and Simões, 2009).

ACKNOWLEDGEMENTS

APPENDIX

TABLE A1: Apparent molar ratios of SCG oil components obtained from 1H NMR spectra by using adjusted peak integral values.

Extraction conditions	Apparent molar ratio				
	TAG	1-MAG	1,2-DAG	1,3-DAG	FFA
Hexane - 125°C	1.00	0.00	0.02	0.15	1.24
Hexane - 145°C	1.00	0.00	0.06	0.25	2.03
Hexane - 165°C	1.00	0.00	0.00	0.27	1.33
Ethanol - 125°C	1.00	0.00	0.08	0.38	1.82
Ethanol - 185°C	1.00	0.00	0.13	0.65	2.04

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