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Original article

Integrated strategies for water removal and lipid extraction from coffee industry residues

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ABSTRACT

Spent coffee grounds (SCGs) and roasted defective coffee beans (RDCBs), are a potentially sustainable source for biofuel production if the processing of these residues, and the recovery of energy-dense lipids, can be undertaken in an energy efficient way. A necessary step in solvent extraction of lipids is prior drying of the feedstock, and this can incur a significant energy cost in the case of SCGs. This study investigates solvent extraction strategies for crude lipid recovery from wet or partially dried SCG samples, with mechanical pressing used as pre-treatment and alternative to thermal drying. Dewatering of SCGs by application of pressures up to 550 bars removed 42% of the moisture present, while lipid expression from whole RDCBs was achieved, with a maximum crude lipid recovery of 77.1% relative to available oil obtained. Crude extracts removal from partially wet pressed SCGs through accelerated solvent extraction (ASE) with ethanol was not impeded by moisture presence, and the obtained extracts had high energy density (~39 MJ/kg) comparable to hexane-extracted crude lipids. SCG and RDCB crude oil removed through solvent extraction and mechanical pressing respectively had similar fatty acid (FA) compositions, but a higher proportion of free fatty acids (FFAs) in solvent-extracted oil.

Introduction

The majority of worldwide energy consumption continues to come from fossil sources [1]. However, price fluctuations, increasing energy demand, dependency on imported products and environmental concerns render the research for alternative and renewable fuels a critical matter [2–4]. For example, biodiesel has been recognized as a feasible source of energy for the transport sector as it is compatible with current diesel engine technology and existing distribution networks, and offers advantages over petroleum diesel such as negligible aromatic and sulfur content, inherent lubricity and higher flash point [4–6]. Furthermore, biodiesel is a potentially carbon neutral fuel with emissions of SO_2, SO_3, CO, unburnt hydrocarbons and particulate matter lower than that of diesel according to several studies [4,5,7–9]. Nevertheless, the high cost of biodiesel production from biomass sources has restricted its further commercialization as a sustainable fuel [5,9].

There is a high economic and indirect environmental cost of utilizing edible oils for fuels, as they have high energy requirements during cultivation, compete with food resources and are subject to potential future depletion [4,5,9–11]. The feedstock used for biodiesel production accounts for approximately 70% up to 95% of the total process cost [4,7,9,12]. Therefore, if food grade lipids could be replaced by non-edible oils, such as waste cooking oils, animal fats or other agro-industrial waste residues that contain suitable lipids, for example coffee industry residues, this would significantly reduce biodiesel costs [4,5,9,12].

SCGs are the main residual products of the coffee industry with an average annual production of 8 million tonnes worldwide, and contain a significant amount of lipids, ranging from 7 to 30.4% w/w on a dry weight basis, with most researchers reporting values between 11 and 20% w/w [9,10,13–17]. RDCBs are also residues of the coffee industry, constitute about 20% of the total mass of the coffee bean production and can be classified as black, sour and immature beans which roast to a lesser degree than other types of beans under the same roasting conditions [18–20]. RDCBs can be differentiated by non-defective ones only by an evaluation of their volatile profile [21]. According to previous studies, RDCBs have a slightly lower lipid content of 9.2–10% w/w than non-defective roasted beans, and a moisture content as low as zero immediately after roasting, which can increase up to 3% w/w as the beans tend to absorb water from surrounding air [18–20]. Table 1 shows the energy content of SCGs, defatted SCGs, SCG oil and SCG derived biodiesel found in previous studies. To the best of the authors'

Abbreviations: SCG, Spent coffee grounds; RDCB, Roasted defective coffee bean; ASE, Accelerated solvent extraction; FFA, Free fatty acid; FA, Fatty acid

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Table 1
Higher heating values of SCGs, SCG oil, defatted SCGs and SCG derived biodiesel.

Reference	HHV of SCGs (MJ/kg)	HHV of Defatted SCGs (MJ/kg)	HHV of SCG lipids (MJ/kg)	HHV of SCG biodiesel (MJ/kg)
Al-Hamamre et al. [9]	20.79	–	35.86–39.00	39.65
Haile [10]	–	19.3–21.6	38.22	39.6
Campos-Vega et al. [14]	19.61	17.86	–	–
Silva et al. [22]	24.9	–	–	–
Tsai et al. [23]	23.5	–	–	–
Go et al. [24]	22.83–24.39	20.03–20.27	–	–
Bok et al. [25]	22.74	–	–	–
Romeiro et al. [26]	25.7	–	–	–
Zuorro and Lavecchia [27]	23.72–24.07	–	–	–
Vardon et al. [28]	23.4	20.1	–	39.6
Berhe et al. [29]	–	20.8	37.88	38.4
Abdullah and Bulent Koc [30]	–	–	43.2	–
Caetano et al. [31]	19.3	–	36.4	–
Deligiannis et al. [32]	21.16	–	–	39.49
Caetano et al. [33]	19.3	19.0	40.8	–

knowledge, data is not available in the literature regarding the higher heating value (HHV) of RDCBs.

Based on the findings of previous studies presented in Table 1, it can be seen that SCGs have a HHV greater than most agro-industrial residues and woody biomass (HHV: 19–21 MJ/kg) [25,27,28,33,34]. SCG lipids have a HHV slightly lower than that of petroleum crude oils (41–48 MJ/kg) but similar to that of other vegetable oils or animal fats [10,35]. The variation in SCG energy content can be possibly attributed to variation in lipid content and overall composition due to the origin, upstream processing and different blends of coffee varieties [9,16,36].

One disadvantage of SCGs as a source of renewable energy is the high moisture content of the grounds, which usually ranges between 50 and 60% w/w [9,13], but can be as low as 18% w/w [32], or as high as 80% w/w [37]. The water is present either as unbound excess moisture resulting from the brewing process, with coffee grounds used in the industrial production of instant coffee retaining higher moisture levels than retail, or bound moisture entrapped within the microstructure of the solid particles [9,37]. For recovery of oils from SCGs, the main extraction techniques previously reported are solvent extraction and Supercritical fluid extraction (SFE), methods that require dried materials and thus necessitate removal of moisture from SCGs [9,10,13,15,17,37,38].

Thermal drying has most commonly been used for dewatering SCGs at laboratory scale prior to further processing [9,10,13,15,28,33], however, at large scale this would likely be a time and energy intensive procedure [24,30]. Extraction of lipids from wet or partially dried SCGs through Soxhlet with *n*-hexane showed that moisture contents greater than 2% w/w inhibit oil extraction, with increasing moisture content of the grounds leading to lower crude lipid yields, while extraction at a pilot plant with countercurrent contact of *n*-hexane and SCGs was found to be less sensitive to water presence of between 5 and 10 % w/w [13]. Abdullah and Bulent Koc (2013), attempted to circumvent the necessity for water removal by extracting lipids from wet SCGs through ultrasound-assisted two-phase oil extraction and obtained a crude lipid recovery of 98% relative to total available oil in 30 min [30].

Solvent extraction of lipids at elevated temperature, commonly known as ASE, or pressurized fluid extraction, is another extraction method that partly derives from SFE but which can operate successfully with partially wet oilseeds such as rice bran and corn kernels [39,40], and one that has not been previously used for the extraction of lipids from wet or partially dried SCGs. Jalilvand et al. (2013) investigated the dynamic (i.e. continuous solvent flow) pressurized fluid extraction of oil from rice bran with a moisture content of 10.2% w/w with n-hexane at temperatures ranging between 40 and 80 °C, and achieved a 100% crude lipid recovery at 77 °C after 34 min with a flow rate of 0.2 ml/min [39]. Moreau et al. (2003) examined the extraction of oil from corn kernels with a moisture content of 14–16% at temperatures between 40 °C and 100 °C using hexane, dichloromethane, isopropanol and ethanol and obtained crude lipid yields varying between 2.9 and 5.9% w/w [40]. A correlation between increasing solvent polarity and higher crude lipid yield was observed in this study with ethanol being the most efficient solvent, while the highest crude lipid yields were achieved at 100 °C irrespective of the solvent used [40].

Mechanical expression is another method that has been extensively used for oil removal from vegetable oilseeds such as soybean [41,42], palm fruit [41], rapeseed [43], sesame seed [43] flax seed [43,44] and rubber seed [45], while it has also been used before for the recovery of lipids from RDCBs by Oliveira et al. (2006), without specifying though the pressing conditions and crude lipid yields obtained [18]. Mechanical pressing of oilseeds is usually combined with thermal drying for better results, with materials that undergo mechanical expression partially dried prior to the pressing procedure [42–44,46]. Ali and Watson (2013) investigated oil expression from flax seeds of water content between 4 and 12% w/w with a screw press, and found that the crude oil yield increased with increasing moisture within the range investigated [44]. Willems et al. (2008) investigated the expression of oil from sesame seeds with a hydraulic press at feedstock moisture contents of between 0% and 5.5% w/w and found that the highest crude oil yield was obtained at a moisture level of 2.1% w/w [43].

Generally, an increase in the mechanical pressure applied leads to a crude oil yield increase in mechanical expression from oilseeds at pressures ranging from 100 to 700 bars [43,45], while pressures greater than 450 bars can improve the crude oil recovery up to 15% w/w (oil/oil) relative to presses operating at lower pressures [43]. Santoso et al. (2014), who examined the hydraulic expression of oil from rubber seed at pressures between 80 and 120 bars, found a relationship between increasing duration of pressing (30–90 min) and higher crude oil yield [45].

Mechanical expression has also been used for water removal from SCGs, as was demonstrated by Schwartzberg (1997), who removed 63% w/w of the moisture content from SCGs by applying 600 bars of pressure (ram speed of 500 mm/min) at room temperature [47]. A previous study considering lignite, bio-solids and bagasse investigated temperatures ranging between 20 and 200 °C and pressures from 15 to 240 bars, for a constant duration of 5 min, and found that processing conditions of 150 °C and 120 bars removed approximately 55–75% of the water present [48].

In this work, SCGs, RDCBs, crude coffee lipids extracted at different conditions and defatted SCGs and RDCBs were characterized in terms of energy content, and various processing strategies investigated for energy efficient recovery of lipids. Mechanical pressing was utilized for crude lipid and water expression from coffee residues, with only one previous report of the use of pressing for water removal from SCGs [47], and none for lipid expression. Solvent extraction of oil from wet

and partially wet pressed SCGs at elevated temperature was investigated through ASE for the first time, and in addition, crude coffee lipids recovered through mechanical pressing and solvent extraction were compared in terms of FA profile and FFA content so as to determine the effect of the extraction method on the composition of the oil obtained, and evaluate the potential suitability of these crude lipids for biodiesel production.

Materials and methods

The SCG and RDCB samples used were provided by Bio-bean Ltd. Three separate wet SCG batches were used due to supply issues, and these had different initial moisture contents and resulted in different crude oil yields after Soxhlet extraction at constant conditions (method described in Section "Soxhlet method"). Information regarding the origin and upstream processing of the samples used was not available, however, 2 samples had been used for instant coffee production and will be referred to throughout as ICG1 and ICG2, where ICG stands for instant coffee grounds and the other was a product of the retail market for use in espresso machines and will be referred to as RCG, where RCG stands for retail coffee grounds. The SCGs and RDCBs were subjected to complete or partial moisture removal for subsequent oil extraction through thermal drying in an oven at 100 °C, or via mechanical expression of water (method described in Section "Hydraulic ram press").

Oil yield calculation

The crude lipid yields obtained from the various lipid extracting methods were calculated as per Eq. (1).

$$\%crude\ \ lipid\ \ yield = \frac{W_1}{W_2} \times 100 \quad (1)$$

Where W_1 is the weight of the crude oil extracted and W_2 the weight of the dry SCG sample. The crude lipid recoveries obtained relative to available oil were calculated based on Eq. (2):

$$\%\ crude\ lipid\ recovery = \frac{\%\left(\frac{w}{w}\right) oil\ exracted \cdot 100}{\%\left(\frac{w}{w}\right) crude\ lipid\ yield} \quad (2)$$

Where the % (w/w) crude lipid yield corresponds to the average *n*-hexane-extracted oil yield of the specific SCG batch used in each case as calculated after 3 experimental repeats (Table 2). In the case of oil extraction with ethanol and extraction from wet SCGs, the term crude extract recovery will be used instead of crude lipid recovery as polar non-lipid compounds may have been extracted along with the coffee lipids.

In extraction methods where a solvent was used for lipid extraction, the obtained oil remained dissolved in the solvent and further processing was required to remove residual solvent from the oil-solvent mixture. Rotary evaporation was used to rapidly remove excess solvent by applying heat to a rotating round bottomed flask at a reduced pressure. Any remaining traces of solvent in the oil were then removed by nitrogen-assisted evaporation or thermal drying at 100 °C.

Mechanical pressing

Hydraulic ram press

A hydraulic mechanical ram press was used in the experiments that investigated the effect of pressure applied via a flat piston on wet and dry SCGs and RDCBs. The stainless steel cylindrical press had an available internal volume of ~470 ml and was designed to withstand pressures up to 600 bars at temperatures up to 200 °C. A stainless steel pipe connected the press with a diesel engine common rail that provided fossil diesel fuel at a range of precisely controlled pressures (150–550 bars, with a deviation of ± 1 bar) as a hydraulic fluid to move the piston and apply mechanical pressure on the SCGs.

Fig. 1 shows a schematic form of the press, which consisted of 5 parts including: a free moving piston, a cylinder that was secured in a clamp in which the piston could move, a removable upper cap with two holes, one of which was used to supply hydraulic fluid pipe and the other for a pressure transducer which constantly transmitted pressure readings to a Labview program, and a removable cylinder that could hold a perforated supporting plate on which the SCGs were placed on top of a mesh of 0.1 mm aperture. Approximately 100 g of wet or dry SCGs were used in all the experiments and the pressing time was varied between 5 and 30 min. Some experiments were conducted at a temperature above ambient, where heat was applied by a 550 Watt band heater. These experiments included a preheating time of 30 min and pressing time of 20 min with the temperature of the outer press wall maintained constantly at 100 °C and measured by a thermocouple (± 1 °C).

Following an experiment, the cylinder containing the SCGs was removed and a lab jack used to push the piston to its starting position and consequently drive the excess diesel to the fuel tank of the engine. Any water or oil removed from the SCGs and RDCBs was collected in a petri dish positioned below the perforated supporting plate and in the case of wet SCGs, the pressed cake was subjected to prolonged drying at 100 °C in an oven so as to determine by mass difference the amount of moisture remaining within the grounds.

Screw press

A screw press with a capacity of approximately 30 kg/h was used for expressing lipids from partially dried SCGs and whole RDCBs. The raw material was fed into the press hopper and the press was pre-heated at 100 °C before starting with a shaft speed of 12 rpm that was later increased up to 30 rpm, while various gap settings and nozzle sizes were used during process optimization so as to achieve better oil release. Any derived oil was concentrated in a trough beneath the screw press and filtered through a bag filter with pore size of 25 μm, followed by a further filtration with filter paper of 5 μm pore size, to remove any fine seed debris, while the pressed raw material was discarded.

Solvent extraction

Soxhlet method

Oil extraction from dry SCGs and ground RDCBs was undertaken with a Soxhlet extractor, consisting of a percolator that allowed the circulation of the solvent, a thimble containing SCGs and a siphon

Table 2
Moisture, oil and energy content of SCGs and resulting defatted grounds, lipids and biodiesel.

Sample	% (w/w) Moisture content	% (w/w) Crude lipid yield (Soxhlet)	HHV of dried raw samples (MJ/kg)	HHV of extracted crude lipids (MJ/kg)	HHV of dried defatted samples (MJ/kg)
ICG1	57.45 ± 1.04	24.26 ± 1.62	25.5 ± 0.30	38.84 ± 0.30	20.17 ± 0.69
ICG1-Ethanol*	”	23.52 ± 2.67	”	38.23 ± 0.21	20.45 ± 0.24
ICG2	67.73 ± 1.75	25.16 ± 1.09	25.86 ± 0.10	39.30 ± 0.15	20.58 ± 0.26
RGC	62.15 ± 1.41	14.80 ± 2.11	22.37 ± 0.07	38.95 ± 0.34	19.85 ± 0.11
Ground RDCBs	2.66 ± 0.37	11.41 ± 0.75	21.34 ± 0.18	38.80 ± 0.16	19.60 ± 0.54

* Crude extract yield and HHV of crude extract is shown.

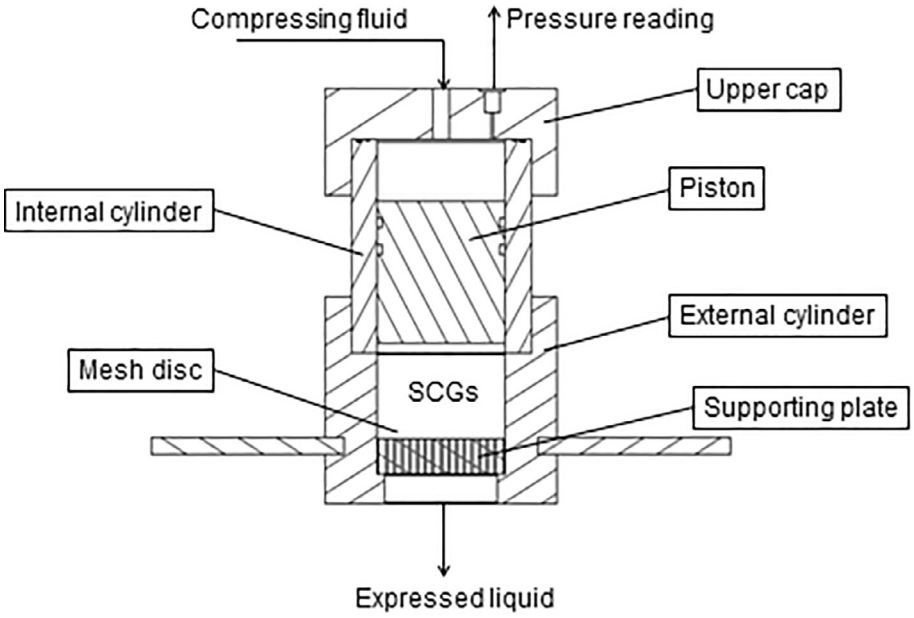

Fig. 1. Diagram of mechanical ram press experimental set up.

mechanism. RDCBs were grinded by a seed grinder into particles with diameter < 1.0 mm prior to solvent 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 [9,10,15], while ethanol was also used for comparison purposes due to its polar character. For all the extractions, a 250 ml Soxhlet apparatus was used in conjunction with a high purity glass microfiber thimble of 30 mm diameter and 100 mm height. Extractions of 8 h were performed at a constant coffee to solvent ratio of 1:9 w/v with an average cycle time of 15 min.

Accelerated solvent extraction

Solvent extraction experiments at conditions of elevated temperature were performed in an ASE 150. The high pressure applied inside the extraction cell (70–140 bars) increases the boiling point of the solvent and allows it to remain in liquid state at elevated temperatures (100–200 °C) [49]. For each extraction, approximately 23 g of sample was loaded into the stainless steel extraction cell (66 ml capacity), and capped with two filtration end fittings, and then fitted into the ASE oven which had been 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 flow of solvent was then performed, followed by pressure release and rinsing of the extracted lipids and solvent used during the extraction into the collection vial through a filter inserted at the bottom of the cell. This was accomplished by a second volume of solvent which filled the cell and initiated the second static period.

Preliminary experiments were performed with the ASE in order to determine the optimum static cycle duration as well as the ideal number of static cycles in terms of crude lipid yield obtained from dry SCG at a constant temperature of 125 °C. The maximum static extraction cycle duration that could be selected was 10 min, while a maximum of 5 static cycles could be performed per extraction. The crude oil yields obtained are shown in Fig. S.1 of the Supporting Information section, and the selection of 3 static cycles of 5 min, with a total duration of 20–25 min, was found to be the most efficient in terms of crude lipid yield. All the subsequent ASE extraction experiments have been performed at these conditions. The coffee to solvent ratio was 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 was purged with compressed nitrogen gas to remove the residual solvent, extracted lipids and final solvent volume.

Determination of coffee oil fatty acid profile and acidity

The FA profile of selected oil samples was determined by gas chromatography (GC) coupled with a flame ionization detector, following transesterification of the oil sample with methanol in the presence of sulphuric acid at elevated temperature to yield FA methyl esters. The GC was equipped with an Agilent Capillary column CP-Wax 52 CB FS, the injector temperature set to 230 °C and the detector temperature set to 300 °C. The carrier gas was nitrogen supplied at a flow rate of 0.8 ml/min, with the oven temperature initially kept at 170 °C for 3 min and then heated at a rate of 4 °C/min up to 220 °C. Detailed settings of GC experiments can be found in Supporting Information – Table S.1. The conversion yield of crude lipids into fatty acid methyl esters was calculated as per Eq. (3):

$$\%biodiesel\ \ conversion\ \ yield = \frac{W_3}{W_4} \times 100 \quad (3)$$

Where W_3 represents the mass of fatty acid methyl esters and W_4 the weight of crude oil.

Quantitative analysis was carried out using standard FA methyl esters as internal standard. The FFA content of the oil samples was determined through a method of titration with phenolphthalein as the indicator [50].

Determination of gross calorific value

The gross calorific value of solid and liquid samples including dry SCGs, defatted SCGs and coffee oil was determined using an IKA® C 1 Bomb calorimeter system. The bomb calorimeter required an oxygen supply at a pressure of 30 bars and was connected to a water cooler that provided water at a constant temperature of 19 °C.

Results and discussion

Feedstock characterization

The different coffee samples used in this study were characterized in terms of moisture and crude lipid yield according to the methods described in Sections “Hydraulic ram press” and “Solvent extraction”,

while the energy content of dry raw and defatted samples, crude lipids and biodiesel was found based on the method explained in Section "Determination of gross calorific value". Table 2 shows the moisture, crude lipid yield and energy content of the SCG and RDCB samples studied, with the standard deviations presented calculated after three experimental repeats of each experiment. All the solvent extractions were conducted through Soxhlet with *n*-hexane, except for one in which ethanol was used.

Table 2 shows that the crude lipid yield obtained from ICG samples is significantly greater than that of the RCG sample, the crude lipid yield extracted from which is consistent with that reported in studies investigating the extraction of lipids from retail SCGs [9,15,17,31,32]. The higher crude lipid yield of industrial samples can be possibly attributed to the processing required for production of instant coffee, and in particular to the treatment of roasted grounds with water at high temperature and pressure which extracts water-soluble solid compounds and volatiles [51,52], and consequently increases the mass portion of oil in the ICGs.

It can also be seen in Table 2 that the crude lipid yield extracted from ground RDCBs is considerably lower than that obtained from the SCGs, also in agreement with previous studies [18–20]. This lower crude oil yield obtained from RDCBs can possibly be attributed to their lesser degree of roasting, and therefore to the reduced dry matter loss of the defective beans relative to healthy ones, while the removal of water-soluble compounds from SCGs during the brewing process results in increased mass portion of oil [19,20]. Solvent extraction from ICG1 with ethanol instead of *n*-hexane resulted in a slightly lower crude extract yield, potentially due to its strong polar character that hindered the diffusion of non-polar SCG lipids [53].

Table 2 also shows the HHVs of the ICG samples to be slightly higher than that of RCG and RDCBs, something that can likely be attributed to the lower lipid content of these samples. The HHV of the extracted crude lipids was similar for all samples, while crude extracts removed from dried ICG1 with ethanol through the Soxhlet method containing a HHV only slightly lower than that of the crude oil extracted with *n*-hexane at the same conditions. Further to the values presented in Table 2, the HHV of FA methyl esters derived from crude ICG1 oil through two-step transesterification was found to be 39.88 ± 0.24 MJ/kg, a value similar to biodiesel HHVs measured in previous studies (Table 1).

Mechanical pressing of SCGs and RDCBs

The hydraulic press described in Section "Hydraulic ram press" was used for pressing wet and dry SCGs samples from the ICG1 batch. The press was initially used to expel lipids from dry SCGs and SCGs with a moisture content of ~5% w/w. Pressing experiments of 30 min duration were conducted at pressures ranging from 150 to 550 bars and at both ambient and elevated temperature of ~100 °C, while at the beginning of each experiment the pressure was gradually increased to the desired pressure at a rate of approximately 50 bars/minute so as to avoid fine particles from blocking the outlet of oil capillaries. Nevertheless, the amount of oil expressed on all occasions was negligible, rendering the trials unsuccessful. This can possibly be attributed to the relatively high dynamic viscosity of waste coffee oil (50.989 mPa s) [9], the thick cell walls of SCGs (2.5 μm thick) that resist rupture [47], and the densely packed formation of the SCGs that potentially resulted in clogging of oil capillary channels between the grounds.

Thereafter, wet SCGs, which had not been subjected to thermal drying, were subjected to similar pressing conditions for durations ranging from 5 up to 30 min in order to investigate the efficiency of pressing as an alternative way of SCGs dewatering. Figs. 2a and 2b shows the percentage of moisture removed from wet SCGs at pressures between 150 and 550 bars at ambient and elevated temperature. The standard deviation of each point is 1.08 as calculated from 3 experimental repeats and represents the reproducibility of the results.

It can be seen in Fig. 2a that there is a relation between increasing applied pressure up to 450 bars, and higher percentage of moisture removed from wet SCG. In order to evaluate the strength of the relationship between the two variables, the Pearson's correlation coefficient (r) was determined and the obtained values ranged between 0.85 for experiments conducted at 100 °C for 20 min and 0.99 for experiments with pressing duration of 5 min. Moreover, the duration of the pressing experiment had an important effect on the moisture removing efficiency of the process, and a correlation between longer pressing durations and higher percentages of moisture removed was observed irrespective of the pressure applied (Fig. 2b). Again the Pearson's correlation coefficient (r) was determined, with the obtained values ranging between 0.94 and 0.99 and indicating a strong linear relation of the variables.

The highest percentage of moisture removed at ambient temperature was 40.7% w/w of the initial water content (57.67% w/w – Table 2) and was achieved after 30 min of pressing at 450 bars. The results shown in Figs. 2a and 2b suggest that when the duration of the extraction is longer than 5 min, an increase of pressure above 450 bars does not improve the moisture removing efficiency of the process. It is also interesting to note that at all pressures, increasing the pressing duration from 5 min to 30 min only results in a doubling of the level of moisture content removed (Figs. 2a and 2b).

When the pressing was conducted at an elevated temperature of approximately 100 °C, 41.9% w/w of the initial moisture was the highest portion of water removed after 20 min of pressing at 450 bars. This percentage is slightly higher than that removed at ambient temperature and similar conditions (38.8% w/w). Relative to tests conducted for 20 min at ambient temperature, heating of the press to 100 °C reduced the influence of pressure, with an increase in pressure above 250 bars resulting in the removal of only a further ~2% w/w (Fig. 2a). Based on the insensitivity to further pressure increases at elevated temperatures, and high initial rates of moisture removal at all conditions, it is suggested that a considerable fraction of the initial SCG water content is present as unbound excess moisture between individual particles that is easier to remove compared to bound moisture (held within individual particles). Mechanical pressing with the hydraulic ram press was also used as a pre-treatment for moisture reduction of wet SCGs prior to solvent extraction by ASE and these results are discussed in Section "Combination of mechanical pressing and solvent extraction".

Whole RDCBs were also pressed at ambient temperature in the hydraulic ram press for 60 min with the pressure applied increased from 350 to 550 bars at intervals of 20 min. Oil removal was negligible during the first 40 min at pressures between 150 and 350 bars but increased during the last phase of the experiment when a maximum pressure of 550 bars was applied. The amount of crude lipids expressed corresponded to a crude lipid yield of 2.47% w/w, or to a crude lipid recovery of 21.6% w/w relative to the average Soxhlet crude lipid yield achieved from ground RDCBs with *n*-hexane. While the application of sheer pressure was not as efficient in expressing crude lipids from RDCBs as Soxhlet extraction, it is suggested that a small portion of crude oil could be expressed from the RDCB sample because of the larger size of the beans relative to grounds. Whole RDCBs resulted in a loose sample formation when compared to the SCGs tested, allowing the formation of oil capillary channels.

The screw press described in Section "Screw press" was also used for expressing lipids from partially dried ICG2 with moisture contents of 5 and 10% w/w and from RDCBs. Similarly to the ram press trials, oil release from the SCGs was not achieved, rendering these trials unsuccessful. Lipid expression was achieved when whole RDCBs were pressed with the screw press and a crude oil yield of ~8.8% w/w, corresponding to a crude lipid recovery of 77.1% w/w relative to the average RDCBs Soxhlet crude lipid yield, was obtained. A significant amount of footings was expressed along with the coffee oil, however,

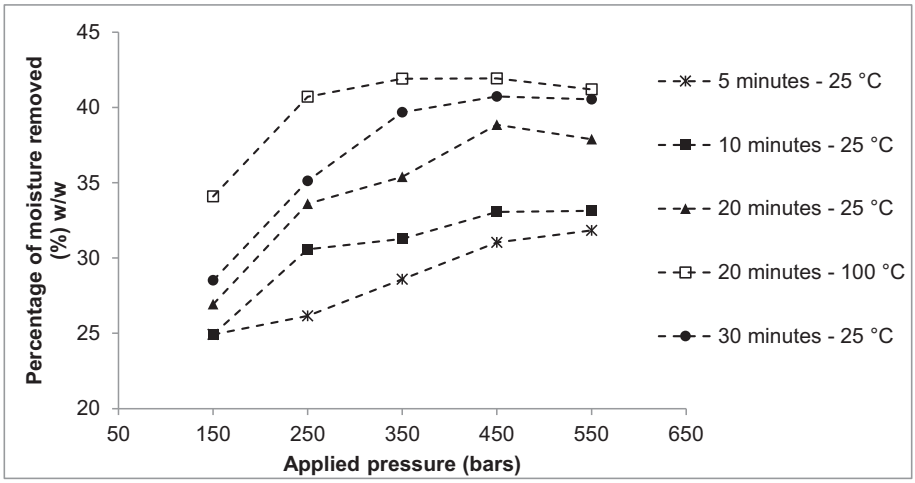

Fig. 2a. Percentage of moisture removed from wet SCGs versus applied pressure at various conditions of temperature and pressing duration.

the two-step filtering process ensured that only an infinitesimal amount of footings could have remained in the expressed oil.

Combination of mechanical pressing and solvent extraction

Solvent extraction from pressed and dried SCGs

Wet RCG samples were subjected to pressing for 20 min at pressures ranging from 150 to 550 bars in the ram press, followed by thermal drying in an oven to completely remove moisture prior to solvent extraction through ASE. These experiments were conducted so as to investigate any possible effect of SCG pre-pressing on the efficiency of the subsequent solvent extraction, independent of the effect of moisture present. *N*-Hexane was the solvent used and all ASE extractions took place at a temperature of 125 °C. Fig. 3 shows the crude lipid recoveries obtained when samples subjected to pressing at different pressures were used. The standard deviation for each point is 0.64 as calculated from 3 experimental repeats, representing the reproducibility of the obtained crude lipid recoveries.

Fig. 3 shows that when solvent extraction is performed with a sample that has not undergone pressing, the average crude lipid recovery is 71.6% w/w. The crude lipid recovery achieved slightly increased when the sample had been pressed at 150 bars and then significantly improved when samples pressed at 250 and 350 bars were used, with crude lipid recoveries of 80.9 and 85.7% w/w obtained respectively. It can also be seen in Fig. 3 that relative to pressing at 350 bars, pressing at 450 and 550 bars resulted in decrease in the crude lipid recovery with only 66.7% w/w extracted from the SCG samples pressed at 550 bars.

The apparent trend of increasing extraction efficiency with pre-pressing at pressures up to 350 bars can be likely explained by distortion of the cells due to the mechanical pressing, which also leads to the formation of a porous cake with structural integrity that increases the efficiency of solvent extraction [41,53]. However, it is suggested that pressing at 450 and 550 bars has an inhibitory effect on the efficiency of the subsequent extraction, possibly attributable to the packed formation of the grounds caused by pressing which results in clogging of the oil capillary channels.

Solvent extraction from partially dried pressed SCGs and wet SCGs

This section presents the results obtained from solvent extraction of wet SCGs and SCGs which had been partially dried by mechanical pressing. Fig. 4 shows the crude extract recoveries obtained from ICG2 through Soxhlet with ethanol against the moisture content of the sample. The various moisture content levels of the samples presented in Fig. 4 were achieved with thermal drying, and the standard deviation of each point is 3.74 as calculated from 3 trials.

Fig. 4 shows that a moisture content of ~2% w/w resulted in increased crude extract recovery during Soxhlet extraction with ethanol (112.3% w/w), potentially due to enhanced extraction of polar compounds [53], while increase of moisture content above this limit resulted in decreased crude extract recoveries. The presence of water in the feedstock can seal the micropores which contain the lipids and

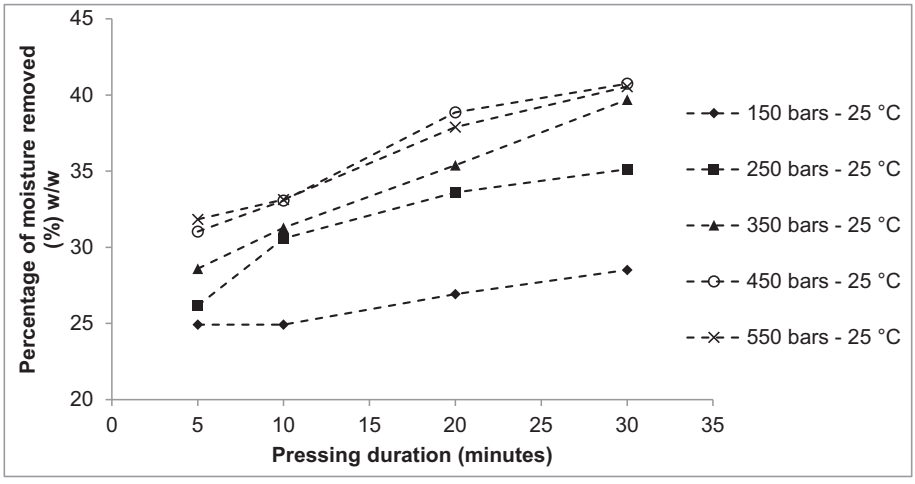

Fig. 2b. Percentage of moisture removed from wet SCGs versus pressing duration at ambient temperature and different pressures.

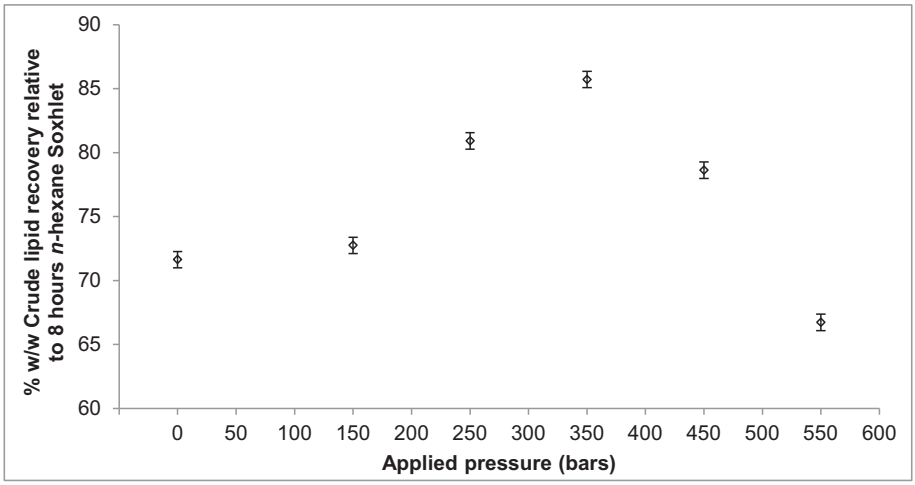

Fig. 3. Crude lipid recoveries obtained through ASE with SCGs pressed at various pressures and thermally dried.

therefore prevent their extraction by not allowing contact with the solvent, while is also responsible for emulsion formation [54,55].

Wet ICG2 samples were subjected to pressing in the hydraulic ram press for 20 min at pressures of 150, 350 and 550 bars, and ambient temperature, and resulted in samples with moisture contents of 49.50, 44.72 and 42.07% w/w respectively. Fig. 5 shows the crude extract recovery obtained through ASE with *n*-hexane and ethanol at 125 °C against the moisture content of the samples. The error bars show the standard deviation for each point as calculated from 3 repeats and represent the reproducibility of the obtained results.

It can be seen in Fig. 5 that there is a correlation between increasing moisture content of the sample and decreasing crude extract recovery when *n*-hexane was the solvent used. The Pearson's correlation coefficient (r) was used to evaluate the strength of this negative relationship between increasing moisture content and decreasing crude extract recovery, and was found to be −0.96 indicating strong linear relation of the variables. *N*-hexane resulted in crude extract recoveries of 9.23 and 52.92% w/w when samples with 67.73% and 42.07% w/w moisture content were tested respectively. Furthermore the effect of moisture content in hexane extractions appears to be more important than that of pre-pressing at different pressures, as pressing at 550 bars led to the highest crude lipid recovery (Fig. 5), in contrast with SCG samples that had been pressed and subsequently dried in an oven, where it slightly inhibited the process of extraction after complete drying (Fig. 3).

On the contrary, the crude extract recovery obtained with polar ethanol increased when a sample with a moisture content of 42.07% w/w was used, and then slightly reduced when the moisture content of the samples tested further increased. Ethanol was found to be considerably more efficient than *n*-hexane in removing crude extracts at all moisture contents, resulting in crude extract recoveries ranging between 93.29 and 108.67% w/w when samples with moisture contents of 67.73 and 42.07% w/w were tested respectively. It is interesting to note that almost identical crude extract recoveries were obtained from dry and wet SCGs when ethanol was used at these conditions (Fig. 5).

These results suggest that the moisture content of the SCG sample is a serious inhibitory factor for the extracting efficiency of the non-polar *n*-hexane due to its hydrophobic nature which renders it insoluble in water, but does not appear to impede the removal of crude extracts when ethanol is used. Generally, as water content increases, alcohol solvents become more polar and the solubility of lipids decreases, while solubility of other polar compounds like phosphatides, sugars and pigments increases, suggesting that the extraction of compounds other than triglycerides might be responsible for the high crude extract recoveries in the case of ethanol [53]. Furthermore, the relatively high crude extract recoveries achieved with ethanol in ASE experiments relative to Soxhlet (Fig. 4) when wet or partially dried SCG samples were used can be can be possibly attributed to operation at high temperatures that improves the solubility of oil in the ethanol-water mixture, increases the diffusion rate of the lipids and the mass transfer properties of the solvent and decreases the selectivity of the extraction [49,53,54]. In addition, the heated and vaporized moisture generates internal pressure which ruptures the matrix cells and facilitates oil

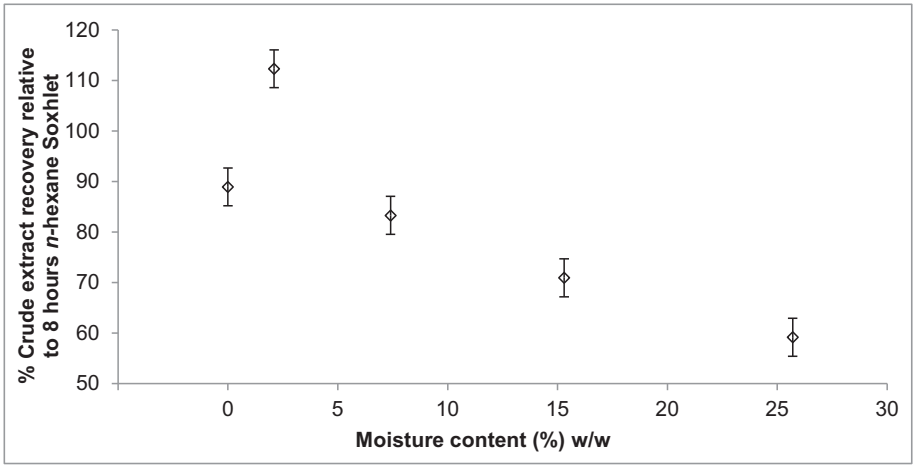

Fig. 4. Crude extract recovery obtained through Soxhlet with ethanol against the moisture content of the SCG sample.

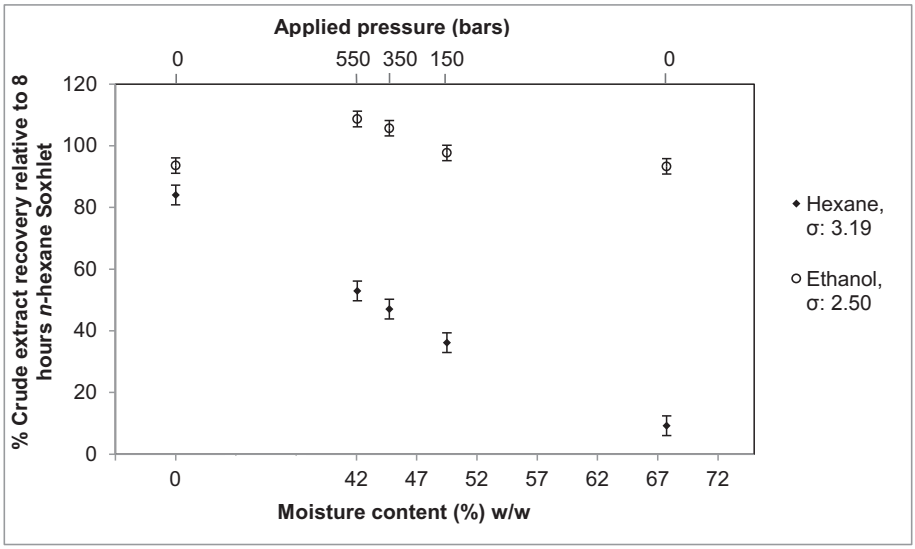

Fig. 5. Crude extract recoveries obtained through ASE with *n*-hexane and ethanol against the moisture content of the SCG sample.

release [56].

The energy densities of selected crude extract samples obtained through Soxhlet and ASE experiments from dried and partially wet ICG2 samples were determined by bomb calorimeter trials. Table 3 shows the measured HHVs, while the standard deviation of the shown values was found to be 0.22 MJ/kg, calculated by three experimental repeats with the same sample.

It can be seen in Table 3 that there is no significant effect of ICG2 moisture content up to 25.7% w/w on the HHV of crude extracts obtained with ethanol through Soxhlet, with the measured energy density values being similar and in most cases slightly lower than that of hexane-extracted crude oil removed from dry ICG2 grounds. Regarding the samples recovered in ASE trials, the HHV of crude extracts recovered with ethanol from partially wet pressed samples was found to be slightly lower than that of extracts removed from dry ICG2, while moisture presence had little effect on the HHV of hexane-extracted samples.

The similar HHVs of crude extracts obtained with ethanol from dry and partially wet ICG2 samples and crude lipids extracted with hexane do not mean that they have an equivalent lipid content, but indicate that these two types of extracts possibly contain similar amounts of carbon and hydrogen atoms, since a high presence of nitrogen and oxygen atoms in the extract would presumably result in significant decrease of its energy density. Nevertheless, the slightly lower HHVs of ethanol-removed extracts from samples with high moisture contents through ASE can be possibly attributed to the presence of non-lipid compounds of lower energy density compared to glycerides and FFAs.

A previous study which investigated the effect of solvent selection and process temperature on the composition of lipids extracted from dry SCG through Soxhlet and ASE reported that ASE extraction with ethanol at temperatures above the boiling point of the solvent (125–185 °C) resulted in extraction of small amounts of caffeine, while no other non-lipid compound was identified [57]. The determination of lipid composition was carried out through ^{1}H NMR analysis and caffeine or other non-lipid components were not found in samples extracted with ethanol through Soxhlet or in lipid samples extracted with hexane, suggesting that high temperature conditions and solvent polarity were responsible for the extraction of caffeine traces along with the lipids [57]. The presence of caffeine and other non-lipid compounds in the crude extract can potentially impact on the use of ethanol for extraction of SCG lipids, as they could have implications for the properties of the oil and its derivatives (e.g. biodiesel), and further research is needed to determine the composition of ethanol extracted SCG crude extracts and identify non-lipid compounds.

Table 3
HHVs of crude extracts obtained by Soxhlet and ASE experiments from dried and partially wet ICG2 samples.

Extraction method	% w/w moisture content of ICG2 sample	HHV of crude extract removed with ethanol (MJ/kg)	HHV of crude extract obtained with *n*-hexane (MJ/kg)
Soxhlet	0	39.11	39.30
	2.1	39.18	–
	15.3	39.46	–
	25.7	39.28	–
ASE	0	39.07	39.16
	42.07	38.73	–
	67.73	38.95	39.35

Fatty acid profile and free fatty acid content of derived lipids

The determination of the FA profile and FFA content of RCG oil, obtained after Soxhlet solvent extraction with *n*-hexane, and RDCBs oil expressed through a screw press was carried out according to the method described in Section “Determination of coffee oil fatty acid profile and acidity”, while additional information can be found in Table S.1. Table 4 shows the FA composition and FFA content of the oil samples.

Table 4 shows that in both oil samples tested linoleic (C18:2), palmitic (C16:0), oleic (C18:1), stearic (C18:0), eicosanoic (C20:0) and linolenic (C18:3) were the FAs present with the highest weight percentages in decreasing order of magnitude. Detailed fatty acid profiles can be found in the Supporting Information section (Tables S.2 and S.3). The FA profiles obtained are in good agreement with coffee oil FA profiles found from previous studies [10,16,18,58], while Haile (2014) produced biodiesel from SCG oil with a similar FA profile that was found to be within the standard limits (EN 14214) for density, viscosity, iodine and acid value and flash point [10].

In addition, it can be seen in Table 4 that both defective and healthy roasted beans, from which the RCG sample derived, contain oil of very similar FA profile, in agreement with the findings of Oliveira et al. (2006) [18]. Furthermore, it suggests that the brewing process that the RCGs have been subjected to does not significantly alter the FA profile of the oil sample, coinciding with the findings of Jenkins et al. (2014), who demonstrated that the majority of coffee oils examined from fresh

Table 4
% w/w FA composition, FFA content, and biodiesel conversion yield of RCG and RDCB crude oil samples.

Sample	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	Other	% (w/w) FFA content	% (w/w) Biodiesel conversion yield
RCG solvent extracted oil	32.7	7.1	8.5	44.9	1.3	2.7	2.8	15.46	95.6
RDCB pressed oil	32.2	7.3	8.8	43.5	1.7	3	3.5	4.42	93.9

and waste samples have similar FA composition [16]. Moreover, the similar FA profiles of the two samples shows that the oil removal method does not significantly affect the composition of the oil, an observation that is in agreement with a study performed by Ali and Watson (2013) on the extraction of oil from flax seeds [44].

Table 4 also shows that the FFA content of the pressed oil sample is significantly lower than that of the solvent extracted one, coinciding with the findings of previous studies which investigated oil extraction from other oilseeds [43,59], and suggesting that it may be a better feedstock for biodiesel production as high FFA content increases oil acidity, kinematic viscosity, susceptibility to oxidation and speeds up degradation [9,60], while FFA content above 1–1.5% w/w inhibits alkaline transesterification of the oil by forming stable emulsions that impede separation of fatty acid methyl esters from glycerol [9,31]. Based on these results, it is tentatively suggested that mechanical expression extracts the oil predominantly as triglycerides, while solvent extraction appears to preferentially extract FFAs from the feedstock.

The considerably higher amount of FFAs in the oil extracted from RCG relative to that obtained from RDCBs can also be justified by the treatment of RCGs with water during the brewing process, which results in increased FFA content due to hydrolysis of triglycerides [61]. Previous studies examining the acidity of SCG solvent extracted lipids have found FFA contents ranging between 0.31 and 20% w/w [5,9,15,32], while Oliveira et al. (2006) who examined the FFA content of pressed oil from RDCBs found a value of 4.97% w/w [18].

Finally, the high biodiesel conversion yields achieved from both samples indicate a relatively small presence of unsaponifiables in the examined coffee oil, which based on the obtained biodiesel yields, was higher in the case of oil expressed from RDCBs. This can be potentially justified by the brewing process that RCGs had been subjected to, which has been previously reported to remove part of the unsaponifiable matter originally present in the coffee oil [16], while mechanical pressing has been found to result in crude oil with higher unsaponifiable content relative to solvent extracted oil in a study performed by Oliveira et al. (2006), due to reduced selectivity of the process [18]. The achieved biodiesel conversion yields are comparable to those obtained in previous studies that performed acid-catalyzed transesterification of waste coffee oil with sulphuric acid as the catalyst and obtained biodiesel yields ranging between 97 and 99% w/w [5,16,62].

Conclusions

1. Soxhlet extraction from partially wet SCGs with ethanol revealed an optimum moisture content of ~2% w/w in terms of crude extract recovery, with higher levels of moisture resulting in decreased crude extract recoveries. High SCG moisture presence (up to 67% w/w) did not impede the removal of crude extracts when ethanol was used in ASE experiments at an extraction temperature of 125 °C. Crude extracts obtained with ethanol from wet or partially wet SCG had a similar, and in the case of ASE trials, slightly lower HHV relative to hexane-extracted crude lipids which could be potentially attributed to the presence of non-lipid compounds.
2. Solvent extraction with ASE from wet and partially wet pressed SCGs with *n*-hexane resulted in a significant decrease in crude extract recovery relative to crude lipid recoveries obtained from completely dry SCGs, however, both types of extracts contained similar HHVs.
3. The effect of mechanical pressing as a pre-treatment method of wet SCGs prior to drying and solvent extraction of lipids from dried SCGs was beneficial until a maximum increase in crude lipid recovery was reached at 350 bars. Pressing at higher pressures appeared to inhibit the subsequent process of crude oil extraction from dry SCGs, possibly due to compaction of the feedstock and reduction of gaps between particles.
4. Significant moisture removal from SCGs was achieved through the ram press (up to 42% w/w of the total water present), and a relation between increasing pressure from 150 to 450 bars and higher percentage of moisture removed was observed. An increase of pressure from 450 to 550 did not improve the moisture removing efficiency of the process and in some cases resulted in reduced water removal. In addition, longer durations of pressing resulted in the removal of significantly higher moisture percentages. Moisture reduction through pressing was improved at pressures of 350 bars and below at an elevated temperature of 100 °C.
5. Expression of oil from RDCBs with a ram press resulted in crude lipid recovery of 21.6% at an applied pressure of 550 bars, with lower pressures leading to negligible recoveries, while oil expression from RDCBs through the screw press resulted in crude lipid recovery of 77.1% w/w relative to hexane-extracted crude lipid yield.
6. The FA profile of crude oil obtained from RCGs and RDCBs through solvent extraction with *n*-hexane and pressing respectively was almost identical, however, *n*-hexane-extracted crude lipids were found to have a considerably higher FFA content relative to oil expressed from RDCBs but a slightly lower unsaponifiable content.

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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.seta.2018.06.016.

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