

**An innovative method of extraction of coffee oil using an advanced microwave system:
in comparison with conventional Soxhlet extraction method**

Sam Hibbert¹, Kevin Welham², Sharif H. Zein^{1,*}

¹Department of Chemical Engineering, Faculty of Science and Engineering, University of Hull (UoH), Kingston Upon Hull, HU6 7RX, U.K.

²Department of Chemistry and Biochemistry -School of Mathematics and Physical Sciences, University of Hull (UoH), Kingston Upon Hull, HU6 7RX, U.K.

Abstract

The production of energy and chemicals from waste biomass is an attractive alternative by comparison with first generation biofuels and fossil feedstocks. This paper investigates oil extraction from spent coffee grounds (SCG) by means of an advanced microwave process and compares this with a conventional Soxhlet extraction (SE) method. Microwave assisted oil extraction (MAE) from SCG was performed over different durations, varying solvent volumes and extraction temperatures. It was found that each of these parameters had an effect on the process, with the largest yield being over 11.54 wt %, oil extracted in 10 minutes using 160 ml of hexane at 95 °C. In 10 minutes, MAE was successful in extracting more oil than SE. MAE achieved a 24 fold decrease in duration for the extraction compared with SE and used less solvent per gram of oil produced. It is proposed that a certain moisture content in the SCG would be beneficial to the extraction process and might it also play a role in the heating process. The extracted oil can be converted into biodiesel and biochemicals leaving the remaining solids suitable for processing into bioethanol, fertiliser, adsorptive material and fuel pellets.

Key words: Coffee oil, Extraction, Microwave, Soxhlet, Spent coffee grounds

*Corresponding Author: E-mail: s.h.zein@hull.ac.uk, Tel: +40 1482 466 753.

Introduction

Accelerated release of carbon into the atmosphere and derived ecological consequences accompanied by increasing prices and falling production of crude oil, drives research into the utilisation and valorisation of waste materials into fuels and renewable chemicals. These alternative feedstocks include: agricultural, municipal, industrial and sewage wastes [1] and can be known practically as biomass. Coffee is one of the largest agricultural products and one of the most popular beverages worldwide [2]. Europe is the world's leading consumer [3] making for a fairly local concentrated supply of oily spent coffee grounds (SCG) that would typically go to landfill or possibly be used as garden fertiliser. More recently SCG has in-fact gained traction in research as a feedstock for biodiesel with first reports of oil extraction coming in 1927 [4 – 7]. Oil content in SCG varies from batch to batch of the coffee blend used but provides a maximum yield of 11.5%, which is significant in comparison with traditional oily crops, providing a maximum yield of 25%. This yield, when coupled with the fact that SCG is a cheap waste already having served its purpose as a consumable beverage, makes for a smart choice in feedstock for biodiesel production. SCG contain remaining oil that can be extracted and converted into fuels and commodity chemicals [6, 8]. It also contains antioxidants hence adding valuable oxidation stability to a biodiesel product [9,10].

Major constituents of the oil from SCG include monoglycerides (MAG), diglycerides (DAG) and triglycerides (TAG) with additional small quantities of free fatty acids (FFAs). The glycerides can be transesterified and then serve as a platform for biodiesel as well as commodity chemicals such as biolubricants, biosurfactants and biosolvents [8, 11]. Remaining solids produced as a waste from the oil extraction process retain value and can be upgraded into carbonaceous material – an effective adsorbent with applications in water treatment, combustion product capture and dye removal [12 – 17]. Other applications for SCG include bioethanol production [18], fuel pellets for small wood/pellet burning heaters and use as soil treatment [19].

Today, Soxhlet extraction (SE) is the most widely utilised solid liquid extraction (SLE) technique in research but is temperature limited by the boiling point of the selected solvent, long extraction times and large solvent losses [20]. Typical operation times can vary from 2 hours to 24 hours [21 – 25]. Tackling the shortcomings with using Soxhlet apparatus have acted as starting areas for development to produce alternative SLE procedures, particularly supercritical fluid extraction (SFE) ultrasound-assisted extraction (UAE), accelerated solvent extraction (ASE) and microwave-assisted extraction (MAE). SFE requires more energy

compared with conventional SE, hence, it is more dependent on the price of the product, which economically potentially limits the technology to high value products [26, 27]. UAE makes use of high-intensity, high-frequency sound waves which increase heat and mass transfer rates and aids rapid cell wall breakdown [28 – 30]. However, although relatively easy to achieve on a lab scale, scale-up for industry is challenging [31]. ASE combines elevated temperatures and pressures with liquid solvents. It uses high temperature and pressure to extract materials and is more time and solvent efficient. However, ASE use has been limited due to its high cost [32]. MAE offers rapid heating of the extraction mixture by simultaneous volume heating via microwave irradiation [17, 33].

This paper investigates oil extraction from SCG by means of MAE using an advanced microwave system and compares this with the traditional SE method. To the best of our knowledge, non-soxhlet MAE from SCG by continuous microwave irradiation is yet to be published. Research using microwaves as the sole heating source for vegetable oil extractions showed MAE to use less solvent, whilst producing 91.8% and 270% more vegetable oil in 1/8th of the duration when compared with traditional SE [33]. We have shown that MAE was successful in extracting more oil than SE with a 24 fold decrease in duration and used less volume. These results are due to the rapid microwave volume heating and availability of a pressurised system which allows the solvent to proceed in the extraction at temperatures above its own boiling point, further increasing the solubility of the solute into the solvent.

Materials & Methodology

SCG were collected directly after the brewing process from the Costa outlet situated at Staff House of the University of Hull. Initially SCG was dried in an oven overnight at 50 °C and for 1 hour at 110 °C to remove moisture from brewing and then placed in the desiccator. Moisture content value was 55.3%.

Analytical grade hexane was obtained from Sigma Aldrich. Hexane was selected as the solvent to be used during extractions due to its very low polarity, high availability and low boiling point for ease of separation. The MAE was carried out in a Milestone microwave laboratory system (Ethos EX, Milestone Italy). The first set of extractions was performed at 85 °C for durations of 10, 17.5, 25 and 32.5 minutes. The second set of extractions was performed at 69, 75, 85, 95 and 105 °C for the duration of 10 minutes, and the third set of extractions used 25, 30, 35 and 40 mL of hexane for every 6 g of SCG used. All experiments incurred a 2.5 minutes

warm-up period to bring the extraction mixture to the desired temperature. The additional 2.5 minutes for each run are not used in labels in graphical or tabulated data and so are discussed as 10, 17.5, 25, 32.5 minutes instead. The power and energy consumption accounting for the warm up period and were recorded in Table 2. Each run was performed 3 times in total.

SE was also performed 3 times for comparison purposes. The Soxhlet apparatus was set-up with 6g of SCG in the extractor, again using n-hexane as the solvent in the quantity of 260 mL per extraction. SCG was subjected to extraction for 4 hours and no additional solvent was supplied. For MAE, 24 g of SCG were used per extraction run with 6 g weighed out for each microwave vessel (4 total). SCG and the desired solvent volume (25 - 40 mL for every 6 g of SCG used) was added to the vessels along with a magnetic stirrer and the vessels were sealed tight with a wrench and placed on a turntable and then subsequently placed in the microwave oven. Once extraction completed, the hexane containing coffee oil and SCG was transferred into centrifuge vials to perform solid-liquid separation, with the resulting hexane and oil mixture then separated by rotary evaporator. All hexane used was recycled for following extractions.

Analysis of the coffee oil was performed using gas chromatography mass spectrometry (GC MS), on an Agilent 5973N MSD with an Agilent 6890+ GC and an Agilent 6783 autosampler system. GC conditions used for the oil are given below. The total run time for the procedure was 45 minutes, starting at 40 °C held for 3 min, then ramping the temperature at a rate of 15 °C per min up to 310 °C. The capillary column employed was a Thames Restek Rxi-5MS 30 m x 0.25 mm with a 0.25µm stationary phase film thickness. Helium gas was used as the mobile phase. The MS detector was set to scan from m/z 20 to m/z 650 in 0.4 sec and measured mass spectra were compared to the NIST library 2002 for confirmation of molecular structures. Samples were analysed both with and without derivatisation to provide direct analysis of the free fatty acids and their corresponding methyl esters. Derivatisation was carried out using a small amount (0.5 mL) of methanolic KOH in 1.0 mL of hexane, in a sealed vial, heated to 60 °C for 1 hour. The hexane layer was then removed and analysed by GCMS as described above.

A Thermo Separations high performance liquid chromatograph (HPLC) was employed as a separation technique to analyse the extracted oil. A Phenomenex Kinetix C18 150 x 2.1 mm column was packed with SPP particles with a diameter of 2.7 µm. Solvent A was selected as acetonitrile plus 0.1% formic acid and ethyl acetate was selected for solvent B. The initial solvent flow was 60% A, 40% B until 16 minutes where solvent B flow was increased to 90%

until 21 minutes at which the flows were returned to 60% (A) and 40% (B). This condition remained for the final 9 minutes to re-equilibrate the column, making for a 30 minute program. The injected volume was 10 μ L, with a dilution of 1:10 in ethyl acetate. Additional specifics include minimum and maximum pressures of 25 and 4000 PSI respectively and the column and tray temperatures remained at 25 $^{\circ}$ C throughout. Positive mode atmospheric pressure chemical ionisation (APCI) was employed for mass spectrometry using a Thermo-Finnigan LCQ Classic instrument, detecting molecular masses between 150 and 2000 Da.

Results

Soxhlet Extraction (SE) Method

As previously mentioned, conventional SE was employed as a technique used for comparison with the MAE process. The results for SE method are presented in Figure 1.. The extraction yielded, on average, 0.51 g (8.6 %) of oil from 6 g of SCG after 4 hours of operation. Hexane losses per gram of oil produced averaged 39.3 g/g. The oil percentage extracted is calculated using equation (1):

$$\text{Percentage Oil Extracted} = \frac{m_1}{m} \times 100 \quad \text{Eq (1)}$$

where m_1 represents the mass of the oil extracted and m represents the mass of the SCG used in the extraction.

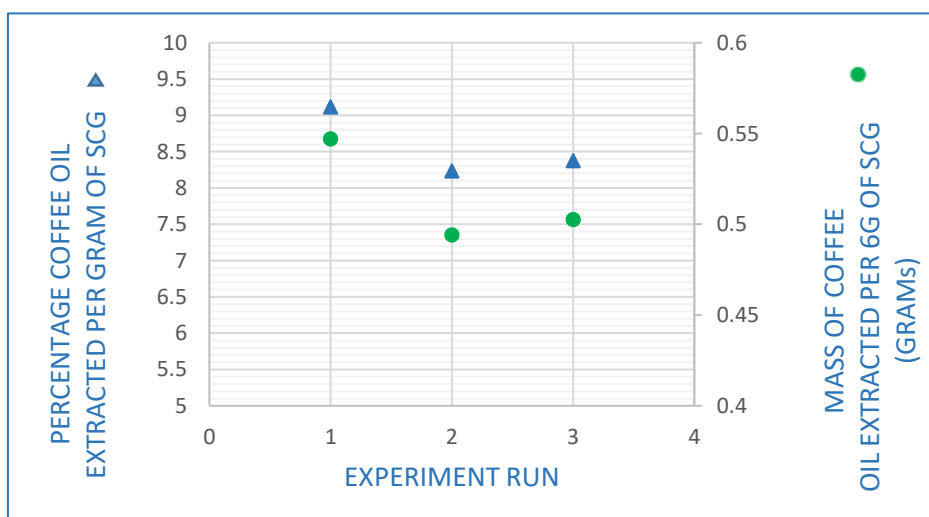


Fig. 1 Graph showing oil extraction values for SE over 4 hours. The average yield produced was 0.51 g of oil using 6 g of SCG

Microwave Assisted Extraction (MAE) Method

Varying Duration

Results in Table 1 show the increase in percentage oil extracted for each experimental run. It is important to note that the ‘Extraction Duration’ is presented with an additional 2.5 minutes to account for the ‘warm-up’ phase and these total durations are used for energy consumption calculations. Table 1 also shows how the average power consumed (APC) and total energy used (TEU) during extractions (including heating period) are influenced by the duration of the extraction. The APC measurements were recorded by the microwave system itself and displayed on the computer interface. Minimal energy consumption, in the 10 minutes extraction, equated to 55% of the energy consumption for the 32.5 minute extraction. Figure 2 shows the effect of extraction duration on oil yields from SCG, presenting volumes and masses of coffee oil extracted. Yields were highest after 32.5 minutes of extraction, totalling 2.4 g from 24 g of SCG. It was observed that on average 2.13 g of oil was extracted over 10 minutes, equivalent to just under 90 % of the oil extracted over 32.5 minutes and using just 55 % of the power (Table 1).

Table 1: Percentage oil extracted from SCG (mass basis) with power and energy consumed during the extractions (Note: The ‘Extraction Duration’ is presented with an additional 2.5 minutes to account for the ‘warm-up’ phase and these total durations are used for energy consumption calculations).

			Other Parameters	Percentage Oil Extracted, wt%	Average Power Consumption, W	Total Energy Consumed, MJ
1	Duration, minutes	10	85 °C, 120 mL hexane	8.88	218.33	0.164
2		17.5		9.15	157.7	0.189
3		25		9.42	123.7	0.204
4		32.5		9.87	122.3	0.257
5	Temperature, °C	69	10 minutes, 120ml hexane	7.85	144.00	0.108
6		75		8.06	170.67	0.128
7		95		9.84	155.50	0.117
8		105		10.59	201.33	0.151
9	Solvent Volume, mL	100	95 °C, 10 minutes	8.39	140.67	0.106
10		120		9.84	155.5	0.117
11		140		10.16	178.67	0.134
12		160		11.54	188.8	0.141

Unlike

SE

which makes use of continuous distillation, encouraging the greatest concentration gradient

for diffusion of solute into solvent, MAE uses shorter extractions by temperature and solvent volume. Within 10 minutes, MAE was successful in extracting more oil than after 4 hours of SE.

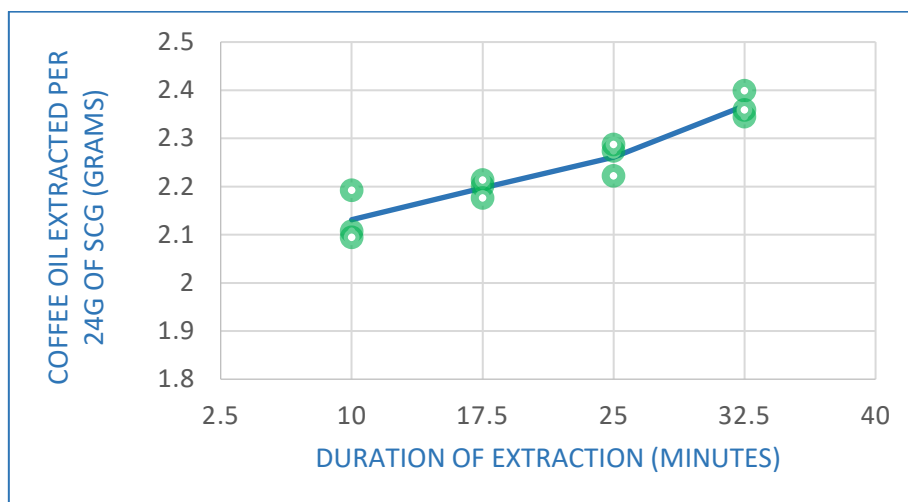


Fig. 2 The effect of extraction duration on oil yield from SCG using MAE at 85°C with 120 mL n-hexane

Varying Temperature

Increasing the extraction temperature from 69 °C to 105 °C whilst maintaining duration and solvent volume constant saw an increase in yield from 1.88 to 2.54 g of oil (Figure 3). This 35% increase could be attributed to increased solubility of oil in hexane and greater penetrative power of a more energised solvent. However, with reference to Table 1, extractions at 95 and 105 °C showed a decrease in energy consumption and increase in oil yield in comparison with the previous 85 °C extraction (10 minutes). Nearly the same mass of oil was yielded at the 95 °C extraction as was in the longest extraction (32.5 minutes) yet with a beneficial 54% decrease in energy consumption. Although, removal of moisture from the SCG took place, it is suggested that traces of water still remain but importantly are ‘locked’ deep within the SCG particles. On the approach to the boiling point of water in extractions 95 °C and 105 °C it is likely that the traces of water vaporise and burst open previously inaccessible (at lower temperatures) matrices containing oil. This allows for the hexane to dissolve and extract more oil. The vaporisation of trace moisture also likely plays a small role in increasing turbulence within the

mixture, resulting in accelerated heat transfer. It is suggested that for MAE it is in fact beneficial during oil extraction that the SCG should contain water, saving both time and energy. Further investigation is needed into the amount of water beneficial for extraction vs costs saved in drying before and after extraction. Extractions were continued at 95 °C whilst changing solvent volume to further support this hypothesis.

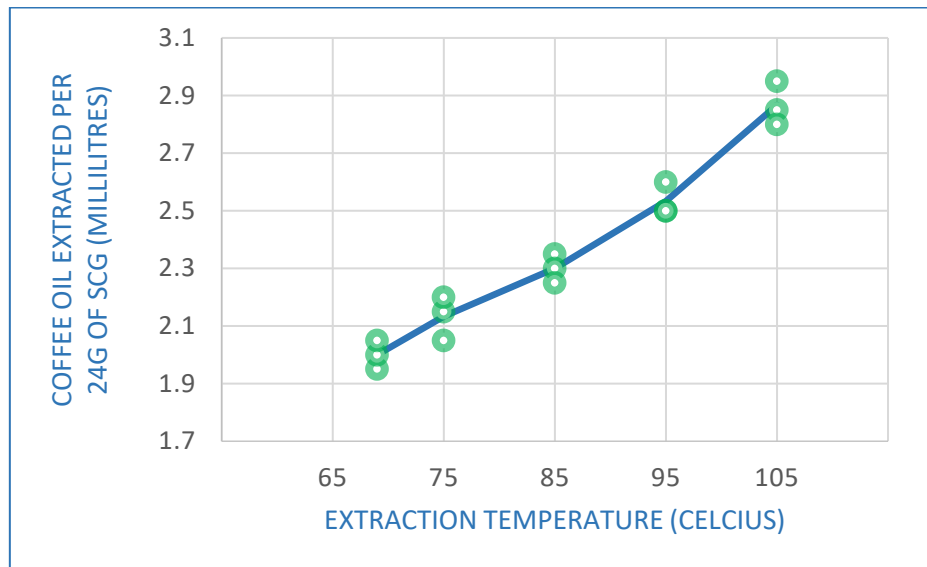


Fig. 3 The effect of extraction temperature on oil yield from SCG using MAE with 120 mL hexane for 10 minutes.

Varying Solvent Volume

Extractions were continued at 95 °C whilst changing solvent from 100 mL to 160 mL. The effects of increasing solvent volume positively influence mass diffusion by providing a greater concentration gradient of oil in SCG and oil in hexane. The highest yield achieved was 11.54 % mass of the SCG supplied. The results are presented in Figure 4 and in Table 1.

These extraction results (at 95 °C) remained correlated with extractions at varying temperatures (Table 1) and support the theory that water content benefits the oil yield. Increasing the solvent volume from 100 mL to 160 mL (per 24 g of SCG) produced 38 % more oil. Even though hexane is nearly without any polarity, heating 160 mL to 95 °C was less energy intensive than heating 120 mL of hexane to 85 °C. This result suggests that the trace water additionally promotes more efficient heating of the mixture by microwave irradiation. For this set of

experiments, hexane losses were also recorded (Table 2) for comparison with Soxhlet hexane losses. During the MAE and in contrast to the SE experiments, no solvent losses occurred. However, post-extraction, in transferring the hexane and oil into centrifuge vials to separate the oil from the majority of SCG, the SCG remained mixed with hexane and so the solvent losses at this stage were recorded. The average hexane loss per gram of oil extracted equated to 11.4, 8.9, 8.8, 6.5 g/g for extractions 100, 120, 140, and 160 ml respectively.

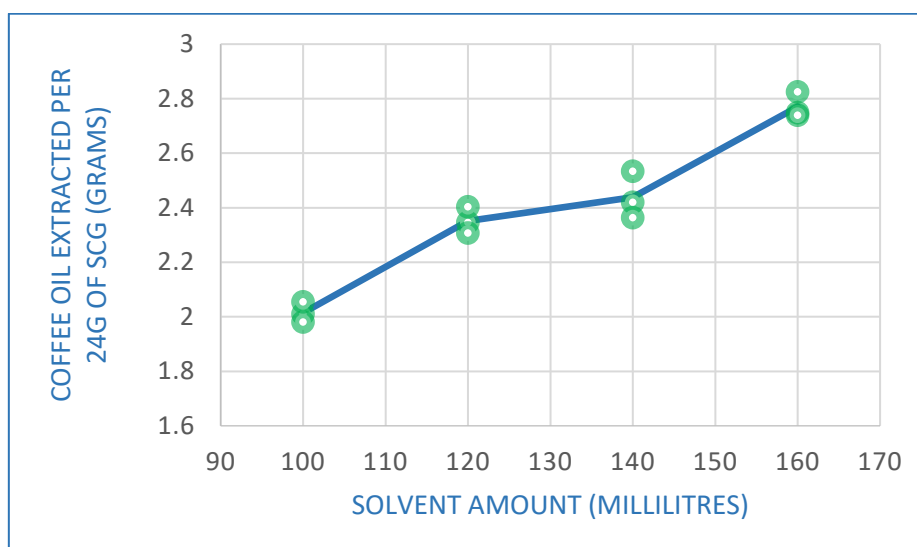


Fig. 4 The effect of extraction solvent on oil yield from SCG using MAE at 95 °C for 10 minutes.

Table 2 Comparison of hexane losses for MAE and SE processes

Process	Time (min)	Average Solvent used (g)	Average Solvent loss (g)	Percentage Solvent loss	Solvent loss for gram of oil extracted (g)
SE	240	170	20.09	11.8	39.3
MAE	10	65.5	22.9	35.0	11.4
MAE	10	78.6	21.0	26.7	8.9
MAE	10	91.7	21.4	23.3	8.8
MAE	10	104.8	18.1	17.3	6.5

Oil Analysis

GC MS results are given in Table 3. The produced coffee oil showed the presence of multiple FFAs with key peaks being n-hexadecanoic acid and linoleic acid, transpiring at 38.34 and

42.37 minutes respectively. Other major peaks at 41.11, 41.5 and 41.6 minutes correspond to octadecanoic acid, oleic acid and caffeine. HPLC separated the fatty acid derivatives in the oil indicating a major presence of di and triglycerides (acylglycerides) with small quantities of monoglycerides. HPLC coupled with positive mode APCI detection allowed for separation and detection of the larger component molecules in the oil for which GC is unsuitable.

Table 3: Identification and relative amounts of the extracted coffee oil using GC MS.

Ret Time (min)	Peak ID	RT Area %	Library Match %
38.35	n-hexadecanoic acid	41.9	98
41.11	n-octadecanoic acid	5.65	99
41.51	octadecenoic acid	5.29	97
42.38	octadecadienoic acid	20.92	99
41.61	Caffeine	6.43	94

Discussion

For SE experiments the average percentage oil extracted (8.6% wt.) was lower than previously reported values of 15% [6] but similar to 9.8% [34]. Differences in results could be derived from individual blends used and the method of brewing be it boiling, percolating or pressurised, which leave different amounts of substances in the SCG [35]. Using Soxhlet apparatus as an open system, which can only operate at the boiling point of the selected solvent, is limited by the amount of solvent contacting the solute, and so for more oil to be extracted more solvent must be used. However the nature of the apparatus gives the advantage that only nearly clean (of solute) solvent will interact with the intended extract and therefore the longer the extraction proceeds, the greater the initial difference in concentrations of solvent to solute as more solute is extracted. This will contribute to greater mass transfer rates and reduce the need for agitation to aid extraction.

To date, published work on SCG using MAE is not available and an ideal comparison cannot be made. In this study, MAE produced an extraction procedure that was quicker, more efficient and less wasteful than SE. All 10 minutes MAE produced a comparable or greater amount of

oil, achieved a 24 fold decrease in duration and used less solvent per gram of oil produced, when compared with SE (Table 2). These general results are a consequence of the microwave system that can rapidly heat the materials contained within the vessel as well as allowing extraction to take place above the boiling temperature of the solvent used. This sealed system also prevents the release of any solvent into the laboratory.

Naturally, polar molecules such as water or methanol have large permanent dipole moment allowing for a strong interaction with microwaves. Hexane, with a very small dipole moment and dielectric constant should therefore not heat up when subject to microwave irradiation. On the contrary, the hexane and SCG mixture not only reached the extraction temperatures but did so more rapidly than using a heating mantle (SE extractions). The reasoning behind successful dielectric heating of the extraction mixture could lie with a couple of factors or a combination of both. Firstly hexane may absorb the supplied electromagnetic energy, albeit not as rapidly as a polar substance such as water or methanol, which then heats the coffee and oil through molecular friction and convection in the same way water or methanol would [36]. Secondly the SCG may convert the supplied microwave energy to heat and so the coffee itself may be a driver in the heating of the mixture. It is likely that both hexane and SCG, although small, have significant dielectric properties that contribute to the rapid heating of the mixture.

The rate of dissolution of a desired solute into the extraction solvent is most influenced by the mass transfer rate of the solute (oil) from the solid matrix into the solvent. This flux of solute occurs because of the concentration gradient relative to the solute across the solid-liquid interface and is described by the following equation based on Fick's law for a steady state, isothermal process [36]:

$$\frac{N_C}{A_T} = -D_{BC} \frac{dC_C}{dz} \quad 2$$

where, N_C is the rate of dissolution of solute C in the solution (kg/s), A_T is the area of the solid-liquid interface (m^2), D_{BC} is the diffusivity coefficient for the solute into the solvent from the solid (m^2/s), C_C is the concentration of solute in solution (kg/m^3), and z is the distance in the porous solid the desired solute must move across (m). Generally, increasing solvent volume will increase the concentration gradient, decreasing the particle size of the solid parent material will allow for a greater surface area on which the solvent can contact the solid. Presumably then, the particle size from grinding the coffee beans prior to brewing will also affect the extracted oils as well as the taste of the coffee itself. Although increasing extraction duration does not directly change variables set out in the mass diffusion equation based upon Fick's

Law [36], an increase in MAE duration allowed for mass transfer of oil into hexane to proceed over a longer period, consequently increasing the amount of oil extracted from the SCG matrix. It is expected that some distillation of the hexane will occur within the extraction vessel; however, this experiment is ultimately limited by solvent volume as the hexane becomes more saturated with oil as the extraction proceeds. The 10 minutes MAE extraction produced almost 90 % of the oil extracted over 32.5 minutes (Table 1) with the limiting factor being the rate of mass diffusion of oil into hexane as the concentration gradient of the oil in species A (SCG) and in species B (hexane) decreases. Here, the initial concentration gradient will be the same for all durations of extraction, and similar to that of SE. It is the case that in a batch system such as described and used in this project, the rate of mass transfer of the oil will be greatest with the largest concentration gradient of oil in species A compared with species B, ie. at the beginning of the extraction. It is therefore assumed that the rate of mass diffusion will be highest at the start (of the extraction) and so the most oil mass will diffuse at the start with less and less oil diffusion as the extraction proceeds – thus the 10 minutes extraction is nearly as successful as an extraction with over three times the duration. Moreover, the 10 minutes extraction achieves such a similar oil yield whilst only requiring 55% of the energy of the 32.5 minutes extraction, highlighting the shorter method as the most efficient. In addition, this 10 minute extraction yields slightly more oil than the SE run and in under 5 % of the time; a credible improvement to conventional extraction.

Varying the temperature manipulates the solubility of the oil in hexane, and with an increase in temperature comes an increase in solubility. This increase in solubility then enables the hexane solvent with a higher saturation threshold of oil relatively increasing the concentration gradient of oil in SCG to hexane. A decrease in temperature would provide the opposite effects. Relating back to the mass diffusivity (equation 2), temperature manipulation specifically affects the diffusivity coefficient of the oil in SCG as the coefficient is defined for a given temperature. The oil yields observed from 69 - 105 °C, showed extractions increased 35% on a mass basis (Figure 3, Table 1). The increase is derived from an increase in solubility of oil in hexane which in turn increases mass transfer rates. Additionally, the hexane solvent itself being at a higher temperature has more energised molecules which permeate through the solid matrix more rapidly by breaking intermolecular bonds with relatively less resistance [36]. This mechanism promotes faster and more thorough solvent-oil contact, producing more oil in a comparably shorter timeframe. Interestingly with this set of experiments, the energy consumption of the system dropped for the 95 °C and 105 °C extractions – an appealing, albeit

uncorrelated result (Table 1). The ‘drop’ in energy consumption continues across the following set of experiments as well, where it was observed that less energy was required to extract more oil at 95 °C using 140 mL solvent compared with the extractions at 85 °C using 120 mL solvent. Reasoning behind these uncorrelated results may lie with traces of water in the extraction mixture as the temperatures when energy consumption decreased were around the boiling point of water. Although the SCG had undergone drying before oil extraction, traces of water are likely to remain in the SCG and importantly are likely trapped deep in the SCG matrices. Upon the approach to the boiling temperature of water, the ‘trapped’ traces of moisture will vaporise and ‘burst’ or ‘break out’ of the SCG matrices [37]. Firstly this would aid the solvent’s penetrative powers, making more oil contactable by the solvent and therefore allowing for more oil to be extracted. Secondly this mechanism, would promote more efficient heat transfer in the SCG as the water vapour, in bursting out of the SCG matrices acts as a turbulent medium, allowing for the lower dielectric components in the extraction mixture to be heated more quickly therefore requiring less energy to successfully extract the oil [37]. Unlike other extraction methods for this application, which require drying, a certain water content in the SCG may play a part in optimising the efficiency of the extraction also saving energy on drying.

Varying the solvent volume allowed yielded the most oil across all experiments – 11.54% (Table 1). The 37.7% increase in oil (100 mL to 160 mL of solvent) came at the cost of an energy consumption increase of 33% (Figure 4, Table 1). The increase in energy consumption for this set of experiments supports, in concurrence with the lack of literature regarding the heating of hexane by microwaves, that absorption of the microwave irradiation is partially derived from something other than hexane. This conclusion also supports the argument that traces of water remaining in the SCG may add to the rapid heating of the extraction mixture with a decrease in energy consumption. Unlike Soxhlet apparatus, which makes use of continuous distillation of the solvent, promoting the greatest concentration gradient of the oil in the SCG and hexane, the microwave apparatus has no such mechanism. As a result, increasing solvent volume acted significantly in producing more oil. Changing solvent volume directly increases the concentration gradient as described in equation 2. The increased concentration gradient will provide faster mass diffusion for longer, and the increased solvent volume reaches its saturation point slower, ultimately producing more oil [36].

It should be mentioned that during the MAE the SCG remaining after extraction has occurred remain saturated with hexane. This indicates that not all the solvent was recoverable and that oil would also be present in the remaining hexane. Nevertheless, even though SE extraction

solvent percentage recoveries were greater, using the MAE method lost less solvent per gram of oil produced (Table 2). It was seen that although no hexane (and oil) was lost during the MAE, hexane was lost during the separation process, and at a greater percentage (of the original solvent volume) than with Soxhlet extraction. However, per gram of oil produced, the MAE lost considerably less solvent as compared with the SE.

The GC result of the oil showed the peaks of FFA and two significant peaks: hexadecanoic acid and linoleic acid. The HPLC results showed that the majority of the oil was made-up of TAGs. Peaks MAG DAG and TAG appeared clustered and due to the solvents selected, peaks from plasticisers were also detected. This is probably a result of using ethyl acetate with PEEK plastic tubing. It is suggested that the method developed requires further solvent gradient optimisation.

Conclusion

The developed MAE method proved to be more efficient, in yielding more oil whilst requiring a fraction of the time and losing less solvent than the conventional SE method. The MAE also benefitted from water content in the SCG, previously thought to hinder such a process.

More specifically, the best extraction produced 11.54 wt% of oil equating to just under 12% of the dry SCG mass. The water moisture of the supplied SCG was 55.3%. With reference to the extraction method varying temperature, raising the operating temperature to within 5 °C of the boiling point of water lowered the energy consumption of the process and produced more oil when compared with an 85 °C extraction. It was proposed that this result occurs because of minute traces of water, left behind after drying. This moisture remained deep within the SCG particle matrix, and when vaporised breaks apart the molecules of SCG. This mechanism compliments the penetration of the hexane solvent into the SCG particles but additionally accelerates the heat exchanged from the most dielectric responsive particles in the SCG/hexane mixture to the remainder of the mixture. Under this assumption, there is room to investigate the optimal water content in the SCG before oil extraction occurs as the evaporation of the water aids the oil extraction.

The extracted oil was analysed by GC and HPLC and the results showed the majority of the oil was made-up of TAGs. SCG are a diverse parent material for many products that currently depend on fossil fuels for manufacture. The possible valorisation routes can enable the production of biofuels, chemicals and solid fuels all potentially sustainable in nature if the coffee itself is grown without replacing carbon sinks.

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Fargione, J., Hill, J., Tilman, D., Polasky, S. and Hawthorne, P. (2008). Land Clearing and the Biofuel Carbon Debt. *Science*, 319 (5867) 1235-1238.
2. Giroto, F., Pivato, A., Cossu, R., Nkeng, G.E., Lavagnolo, M.C., (2017). The broad spectrum of possibilities for spent coffee grounds valorisation. *J. Mater. Cycles Waste Manage.* 1–7.
3. Coffee: World Markets and Trade. (2019). United States Department of Agriculture, Available at: <https://apps.fas.usda.gov/psdonline/circulars/coffee.pdf> [Accessed 15 July 2019].
4. Barkenbus, C. and Zimmerman, A. (1927). Kentucky coffee nut tree seed oil. *Journal of the American Chemical Society*, 49 (8) 2061-2064.
5. Haile, M. (2014). Integrated valorization of spent coffee grounds to biofuels. *Biofuel Res. J.*, 2, 65-69.
6. Kondamudi, N., Mohapatra, S. and Misra, M. (2008). Spent Coffee Grounds as a Versatile Source of Green Energy. *J. Agric. Food Chem.*, 56 (24) 11757-11760.
7. Kwon, E., Yi, H. and Jeon, Y. (2013). Sequential co-production of biodiesel and bioethanol with spent coffee grounds. *Bioresour. Technol.*, 136, pp.475-480.
8. Sheldon, R. (2014). Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chem.*, 16 (3) 950-963.
9. Yanagimoto, K., Ochi, H., Lee, K. and Shibamoto, T. (2004). Antioxidative Activities of Fractions Obtained from Brewed Coffee. *J. Agric. Food Chem.*, 52(3), pp.592-596.
10. Campo, P., Zhao, Y., Suidan, M., Venosa, A. and Sorial, G. (2007). Biodegradation kinetics and toxicity of vegetable oil triacylglycerols under aerobic conditions. *Chemosphere*, 68 (11), 2054-2062.

11. De Melo, M., Barbosa, H., Passos, C. and Silva, C. (2014). Supercritical fluid extraction of spent coffee grounds: Measurement of extraction curves, oil characterization and economic analysis. *The Journal of Supercritical Fluids*, 86, pp.150-159.
12. Agwaramgbo, L., Lathan, N., Edwards, S. and Nunez, S. (2013). Assessing Lead Removal from Contaminated Water Using Solid Biomaterials: Charcoal, Coffee, Tea, Fishbone, and Caffeine. *Journal of Environmental Protection*, 04 (07) 741-745.
13. Tokimoto, T., Kawasaki, N., Nakamura, T., Akutagawa, J. and Tanada, S. (2005). Removal of lead ions in drinking water by coffee grounds as vegetable biomass. *Journal of Colloid and Interface Science*, 281(1) 56-61.
14. Ogata, F., Tominaga, H., Yabutani, H. and Kawasaki, N. (2011). Removal of Fluoride Ions from Water by Adsorption onto Carbonaceous Materials Produced from Coffee Grounds. *Journal of Oleo Science*, 60 (12) 619-625.
15. Plaza, M., González, A., Pevida, C., Pis, J. and Rubiera, F. (2012). Valorisation of spent coffee grounds as CO₂ adsorbents for postcombustion capture applications. *Applied Energy*, 99, 272-279.
16. Hirata, M., Kawasaki, N., Nakamura, T., Matsumoto, K., Kabayama, M., Tamura, T. and Tanada, S. (2002). Adsorption of Dyes onto Carbonaceous Materials Produced from Coffee Grounds by Microwave Treatment. *Journal of Colloid and Interface Science*, 254 (1), 17-22.
17. Zein, S.H., Asenso, B., Skoulou, V. K. (2017), Nanocarbons from Acid pre-treated Waste Coffee Grounds using Microwave Radiation, *Materials Letter*, 193 (2017) 46–49
18. Sendzikiene, E., Makareviciene, V., Janulis, P. and Kitrys, S. (2004). Kinetics of free fatty acids esterification with methanol in the production of biodiesel fuel. *European Journal of Lipid Science and Technology*, 106 (12) 831-836.
19. Vardon, D., Moser, B., Zheng, W., Witkin, K., Evangelista, R., Strathmann, T., Rajagopalan, K. and Sharma, B. (2013). Complete Utilization of Spent Coffee Grounds To Produce Biodiesel, Bio-Oil, and Biochar. *ACS Sustainable Chemistry & Engineering*, 1(10), pp.1286-1294.
20. Luque de Castro, M. and Priego-Capote, F. (2010). Soxhlet extraction: Past and present panacea. *Journal of Chromatography A*, 1217 (16) 2383-2389.
21. Atabani, A., Silitonga, A., Ong, H., Mahlia, T., Masjuki, H., Badruddin, I. and Fayaz, H. (2013). Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid

- compositions, biodiesel production, characteristics, engine performance and emissions production. *Renewable and Sustainable Energy Reviews*, 18, 211-245.
22. Araújo, J. and Sandi, D. (2007). Extraction of coffee diterpenes and coffee oil using supercritical carbon dioxide. *Food Chemistry*, 101 (3) 1087-1094.
 23. Halim, R., Gladman, B., Danquah, M. and Webley, P. (2011). Oil extraction from microalgae for biodiesel production. *Bioresource Technology*, 102 (1) 178-185.
 24. Hawthorne, S., Grabanski, C., Martin, E. and Miller, D. (2000). Comparisons of Soxhlet extraction, pressurized liquid extraction, supercritical fluid extraction and subcritical water extraction for environmental solids: recovery, selectivity and effects on sample matrix. *Journal of Chromatography A*, 892(1-2), pp.421-433.
 25. Rajaei, A., Barzegar, M. and Yamini, Y. (2004). Supercritical fluid extraction of tea seed oil and its comparison with solvent extraction. *European Food Research and Technology*, 220 (3-4) 401-405.
 26. McHugh, M.A. and Krukonis, V.J. (1994) *Supercritical Fluid Extraction: Principles and Practice*. 2nd Edition, Butterworth-Heinemann, Boston.
 27. Calixto, F., Fernandes, J., Couto, R., Hernández, E., Najdanovic-Visak, V. and Simões, P. (2011). Synthesis of fatty acid methyl esters via direct transesterification with methanol/carbon dioxide mixtures from spent coffee grounds feedstock. *Green Chemistry*, 13 (5) 1196.
 28. Stanisavljević, I., Lazić, M. and Veljković, V. (2007). Ultrasonic extraction of oil from tobacco (*Nicotiana tabacum* L.) seeds. *Ultrasonics Sonochemistry*, 14 (5) 646-652.
 29. Luque-García, J. and Luque de Castro, M. (2004). Ultrasound-assisted Soxhlet extraction: an expeditive approach for solid sample treatment. *Journal of Chromatography A*, 1034(1-2), pp.237-242.
 30. Szentmihályi, K., Vinkler, P., Lakatos, B., Illés, V. and Then, M. (2002). Rose hip (*Rosa canina* L.) oil obtained from waste hip seeds by different extraction methods. *Bioresource Technology*, 82(2) 195-201.
 31. Vinatoru, M (2001). An overview of the ultrasonically assisted extraction of bioactive principles from herbs. *Ultrasonics Sonochemistry*, 8, 303-313
 32. Giergielewicz-Możajska, H., Dąbrowski, L & Namieśnik, J (2001) Accelerated Solvent Extraction (ASE) in the Analysis of Environmental Solid Samples — Some Aspects of Theory and Practice, *Critical Reviews in Analytical Chemistry*, 31(3) 149-165

33. Cravotto, G., Boffa, L., Mantegna, S., Perego, P., Avogadro, M. and Cintas, P. (2008). Improved extraction of vegetable oils under high-intensity ultrasound and/or microwaves. *Ultrasonics Sonochemistry*, 15 (5) 898-902.
34. Burton, R., Fan, X. and Austic, G. (2010). Evaluation of Two-Step Reaction and Enzyme Catalysis Approaches for Biodiesel Production from Spent Coffee Grounds. *International Journal of Green Energy*, 7 (5), 530-536.
35. Gross, G., Jaccaud, E. and Huggett, A. (1997). Analysis of the content of the diterpenes cafestol and kahweol in coffee brews. *Food and Chemical Toxicology*, 35 (6) 547-554
36. Mingos, D. and Baghurst, D. (1991). Tilden Lecture. Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chemical Society Reviews*, 20 (1) 1.
37. Letellier M. and Budzinski H. (1999) Microwave assisted extraction of organic compounds. *Analisis*, 27, 259-271