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2-Methyltetrahydrofuran as a Potential Green Solvent for Lipids Extraction from Spent Coffee Grounds for Fuel Grade Hydrocarbons Production

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The present study assessed the recycling of spent coffee grounds (SCG) as a perspective source of oil which can be used as a feedstock for the production of fuel-grade hydrocarbons or Fatty Acid Methyl Esters (FAME). Traditionally, hexane is used for the recovery of lipids from lipids bearing seeds. The challenge is finding novel solvent/solvents which are derived from renewable materials but with the same or improved oil extraction efficiency than the traditional solvents such as hexane. One such solvent is 2-methyltetrahydrofuran (2-MeTHF), which is produced from renewable lignocellulosic materials. This investigation aimed to assess the capability of 2-MeTHF as a novel green solvent for the recovery of lipids from SCG employing a Soxhlet extraction system and to investigate the effectiveness of the lipid extraction process. Hexane was used as a reference solvent to measure the oil extraction capability of 2-MeTHF. The effect of the solvent-to-SCG ratio and the effect of oil recovery time on the oil yield were investigated. The SCG were characterised with regard to moisture content and particle size, and they were found to contain 66.23 wt% water, on average and a particle size of 481.22 µm on average. The lipid extraction process was carried out for 8 h using both hexane and 2-MeTHF, at a solvent-to-SCG ratio of 15:1 (% w/v), producing an oil yield of 18.99 wt% for hexane and 27.95 wt% for 2-MeTHF on average. The density of the oil extracted using 2-MeTHF was 1162.83 kg/m^3 and kinematic viscosity of 37.67 mm^2/s on average. The average free fatty acid content (FFA) of the oil extracted using 2-MeTHF was found to be 4.54 wt% and the saponification value (SV) of the oil was found to be 170.22 mg $_{KOH}$/g. These values were relatively higher than those obtained for the oil extracted using hexane.

1. Introduction

Coffee is a crop grown in more than 80 countries, with Brazil accounting for 40 % and Vietnam accounting for 20 % of the global coffee production in 2018 (Shahbandeh, 2020). Coffee is the second largest trading product after petroleum products (Efthymiopoulos et al., 2019). According to the International Coffee Association (2020), 10.16 Mt of roasted coffee were produced in the 2019/2020 season, a decrease of 2.2 % from 2018/2019. The excessive consumption of coffee beverages generates a large amount of waste referred to spent coffee grounds (Blinová et al., 2017). It is estimated that 6 Mt of coffee waste is generated from the treatment of roasted coffee beans with boiling water to make instant coffee drinks per annum (Mofijur et al., 2020). Most of this coffee waste ends up in landfills where they serve as a breeding ground for pests and contaminate groundwater as they decompose. It is estimated that for every 1 t of SCG decomposing in the landfills 682 kg of carbon dioxide is produced annually and methane which is 25 times more potent than carbon dioxide. SCG contributes a large amount of the taxpayers' money towards running and maintaining the landfills. In light of these challenges posed by the current disposal of SCG, it is sensible to collect and convert the SCG to value-added products. SCG contains 11 – 20 wt% of oil, which is depending on the oil recovery method employed, this oil can be used as substrate in the production of sustainable and green energy, i.e. FAME. Currently, 95 % of FAME is produced from renewable vegetable oils and animal fats. Producing fuels from vegetable oils, which are farmed for human consumption, have been discouraged in most parts of the world. Recovering lipids from waste material like SCG can alleviate the food versus fuel argument. The high volume of SCG produce in a year renders the SCG a readily available source of oil which can be used as a low-cost feedstock for FAME production. A recycling

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company in South Africa has predicted that 17,000 t of SCG can be used to produce 1,800 m^3 of FAME and 4,500 t of heating pellets per annum (Sapp, 2018). SCG solids that remain after the oil extraction have been recognized as a prospective substrate of sugars which can be used for the synthesis of ethanol (Fadli, 2017). The extraction of and utilisation of SCG oil for fuel grade hydrocarbons production is still a relatively new process and needs further studies to improve existing and future commercialisation.
Several studies have been conducted on lipids extraction from SCG for fuel grade hydrocarbons production, using fossil-based solvents such as hexane, isopropanol, and heptane to name a few. This renders the resulting fuel-grade hydrocarbons as a partial green fuel. The goal is to produce FAME from only renewable raw materials. This prompts the need to investigate renewable solvents that can be used to recover the valuable oil from SCG and other oil-bearing seeds. This study aims to investigate the capability of 2-MeTHF as a novel green solvent for the extraction of oil from SCG, which can be used as feedstock for FAME production. The influence of extraction parameters such as solvent-to-solids ratio and extraction duration on oil yield was studied in this study. The oil extraction process was conducted using a Soxhlet and the results obtained were compared to those found in the literature.

2. Materials and methods

2.1 Characterisation of spent coffee grounds

The present study was conducted using three different samples (SCG1, SCG2, and SCG3) of SCG collected from local coffee shops. They were characterised in terms of moisture content on a dry basis, particle size, and oil content. The wet SCG samples were subjected to oven drying. Samples of 160 g of wet SCG were weighed using an analytical balance (Kern ALJ 220-4) per drying run, at 6.50 mm sample thickens and dried in a vacuum oven (BHO Shatter) at 110 °C. The sample was removed from the oven and weighed every 0.5 h. This was repeated until there was no observable change in the mass of the samples and this was observed to occur after 4 h of drying. The samples were kept in the oven for 5.5 h.
Determination of particle size of different SCG samples was conducted by utilising laboratory sieves with aperture sizes of 600 µm, 425 µm, 355 µm, 250 µm, and 150 µm. The screens were installed on a vibrating powder (Retsch sieve shaker) and operated at a 40 rpm vibrating frequency for 1 h. Individual sieves were weighed on a balance (METTLER PJ3000) before adding the SCG samples on the top sieve. The sieves were weighed prior and succeeding the vibration process, this was done to determine the estimated mass of the particles kept back in each sieve. Eq(1) was used to determine the portion of the SCG particles of a particular particle size range.

$$\%P = \left(\frac{\mathrm{M_2} - \mathrm{M_1}}{\mathrm{M_{total}}}\right) \times 100 \quad (1)$$

where: P is the percentage of a particular size particles, M_1 is the mass of the sieve prior shaking, M_2 is the mass of the sieve after shaking and M_{total} is the total mass of SCG used. The mean grain size for the individual SCG samples used in the present study was calculated using Eq(2).

$$D = \frac{\sum_{i=1}^{n}\left[\frac{S \times P}{100}\right]}{n} \quad (2)$$

where D is the average particle diameter size, S is the sieve aperture size, P is the portion of SCG grains that are kept back in a particular screen and n is the number of screens utilized. Samples of 35 g were deposited in a cellulose thimble and placed in a set of four Soxhlet extractors. The solvents were heated to their respective boiling points, hexane (69 °C) and 2-MeTHF (80 °C), in a distillation flask to enable refluxing. To determine the possible maximum amount of oil that could be recovered from the different SCG samples, the samples were subjected to the lipids recovery process for 8 h at a solvent-to-SCG fraction of 15:1 (0.067) for the two solvents used in this study. To investigate the effect of the solvent-to-SCG ratio (% w/v) on the extraction yield for each solvent, the ratio was varied from 20:1 (0.05), 18:1 (0.056), 15:1 (0.067), 10:1 (0.1) and 5:1 (0.2) for an extraction period of 6 h. To study the effect of the extraction period on the oil extraction efficiency of each solvent, the extraction period was varied from 1 to 8 h, while maintaining the solvent-to-SCG ratio at 15:1. A vacuum rotary evaporator system (RE-2000B) was used to separate the solvents and oil. The recovered solvent and extracted oil were quantified.

2.2 Characterisation of the spend coffee ground oil

The quantity of oil extracted from each SCG samples was determined by drying and weighing the SCG sample at 71 °C for hexane and 82 °C for 2-MeTHFfor 1 h after each extraction process. The quantity of the oil extracted in each SCG sample was determined using Eq(3) below.

$$\%\ SCG\ oil\ yield = \left(\frac{M_i - M_f}{M_i}\right) \times 100 \quad (3)$$

where M_i is the dry SCG mass before oil extraction and M_f is the mass of dry SCG succeeding oil extraction. The physicochemical properties of the oil i.e. Viscosity, density, saponification value, and acid value were determined. Kinematic viscosity was determined at determined at 40 °C using a Herzog multi range viscometer (HVM 472) and water bath, density was determined at 15 °C using a hydrometer (according to EN 14111), the acid value and the saponification value were determined using the titration method (stipulated by EN 14111). The oil quality or properties were then compared to those found in the literature.

3. Results and discussion

3.1 SCG properties

The results collected from each SCG sample are summarized in Table 1 below. The SCG water contents depicted in Table 1 are indistinguishable to those outlined by Abdullah and Koc (2013), i.e., 67 wt% and were found to be in a similar range to those reported by Efthymiopoulos et al. (2019), i.e., 64.20 to 69.90 wt% for SCG obtained from retail coffee shops. The variation in SCG water content depicted in Table 1 can be attributed to different brewing methods which can drastically increase or decrease the moisture content of the resulting SCG. The high water content indicated the need for drying since it recommended that for a good oil recovery the SCG moisture content should be less 11 wt%.

Table 1: SCG characteristics for 2-MeTHF and hexane

Samples	Moisture content (wt %)	Mean particle size (µm)	Oil content (wt %)	
			2-MeTHF	Hexane
SCG1	67.75	488.70	28.20	18.13
SCG2	67.81	472.43	25.19	17.77
SCG3	67.94	490.54	26.77	17.32

The particle size distribution was found to slightly different for each sample, which could be attributed to the upstream coffee beans processing methods and the coffee beverage brewing methods used. Three 35 g samples from each sample batch were subjected to an oil extraction process using 2-MeTHF as a solvent for 8 h. It was observed that the oil yield obtained did not exceed 28.20 wt%, with the SCG getting flooded by the solvent suggesting that the SCG were getting saturated with the solvent after a prolonged extraction period.

3.2 Effect of oil extraction parameters

The dried SCG samples were mixed before investigating the effects of the oil extraction parameters. Figure 1a depicts the oil yields obtained from dry SCG mixture at different extraction periods ranging between 1 to 8 h at 1 h extraction intervals, using a constant solvent-to-SCG ratio of 15:1 (% w/v). This was done to see how the length of extraction affected the capability of oil recovery for both solvents in this investigation.

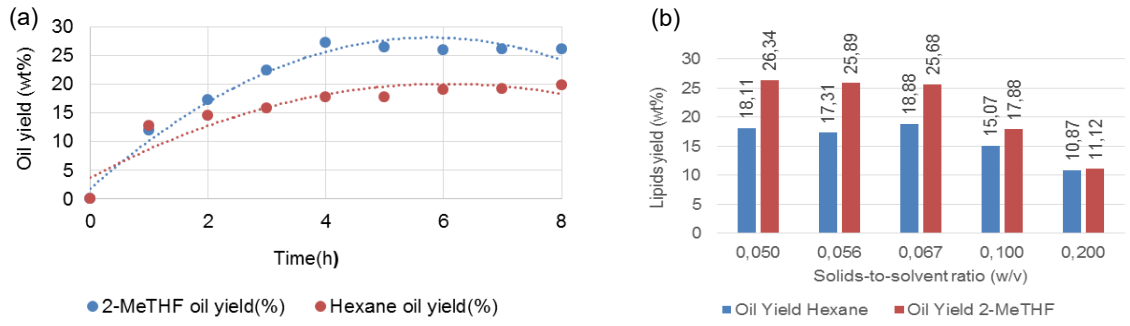

Figure 1: Illustration the effects (a) of extraction time and (b) solvent to solids ratio on the oil yield

In Figure 1a it is evident that 2-MeTHF has a higher oil extraction capability than hexane. Hexane (12.78 wt%) displayed a higher oil extraction yield than 2-MeTHF (11.79 wt%) for the 1 h extraction period. This may be attributed to the number of extraction cycles achieved by each solvent in each extraction cycle. It was observed that hexane took about 0.87 h to complete 5 extraction cycles and 2-MeTHF took about 1.20 h to complete the same number of extraction cycles. This may be the result of 2-MeTHF's high boiling point compared to hexane. The quadratic best fit line appeared to best describe the relationship between extraction period and lipids yield for both the solvents used in the present work. The maximum oil extraction of 27.26 wt% of the initial SCG sample used was achieved compared to 19.85 wt% oil extracted using hexane for the same extraction conditions. The maximum oil extraction was achieved in 4 h for 2-MeTHF and in 8 h for hexane. Figure 1a shows that there was no discernible improvement in oil recovery after 6 h of oil extraction for hexane. Suggesting that the 6 h extraction period was sufficient to recover most of the oil present in the SCG at the experimental conditions used. When compared to hexane, 2-MeTHF showed to be a more proficient solvent in recovering oil from SCG, requiring shorter extraction time to extract 8.41 wt% more oil. The 4 h extraction period for 2-MeTHF was found to be within range (3.50 - 5 h) of the optimal lipid extraction from the oil-bearing seeds (Efthymiopoulos, 2018). In Figure 1a it can be seen that increasing the extraction period for 2-MeTHF resulted in a decrease in the extracted oil. This decrease can be attributed to SCG being saturated with the solvent. This decrease in the oil extraction yield can be attributed to SCG being saturated with the solvent, preventing further oil extraction.

To establish which solvent worked better and to investigate the influence of the solvent-to-SCG ratio on oil recovery proficiency, the extraction time was fixed at 5.50 h, after observing that an extraction period greater than 6 h reduced the extraction yield for 2-MeTHF.The solid-to-solvent ratio was varied as depicted in Figure 1b. In Figure 2b it is evident that despite the solvent-to-solid ratio used, 2-MeTHF has a better oil extraction compared to hexane. For 2-MeTHF the maximum lipid extraction of 26.34 wt% was obtained using the solvent-to-SCG ratio of 20:1 (% w/v). For hexane, a maximum of 18.88 wt% was achieved using the solvent-to-SCG ratio of 0.067 and 15:1 (% w/v) instead of 20:1 (% w/v). These observations contrast the general trend of low solvent-to-SCG ratio giving a high lipids extraction yield, and could be attributed to the presence of relatively high moisture in the SCG samples used which usually inhibits the lipids extraction process as reported by Najdanovic-Visaket al. (2017).

3.3 Lipids quality

Figure 2 depicts the oil extracted from the SCG mixture using the two solvents. There is a visible difference in the color of the samples. The sample in Figure 2b, the darker sample is the oil extracted using 2-MeTHFand the brighter sample in Figure 2b is the oil extracted using hexane. When the oil samples were heated to elevated temperatures between 100 and 110 °C to remove water and traces of the solvents from the oil, a dark gummy residue was observed at the bottom of the flask for the oil extracted with 2-MeTHF.This material was not observed when the oil extracted using hexane was subjected to similar elevated temperatures. Temperatures between 100 and 200 °C have been reported to weaken the coffee cell wall structure and increase the solubility of color bodies such as arabinogalactans and mannans (Campos-Vega et al., 2015). The origin and up-stream coffee processing methods used coupled with the high boiling and polarity of 2-MeTHF may have contributed to the weakening and recovering of polar molecules such as SCG cell wall and inbound oil (Campos-Vega et al., 2015), improving the overall oil extraction.

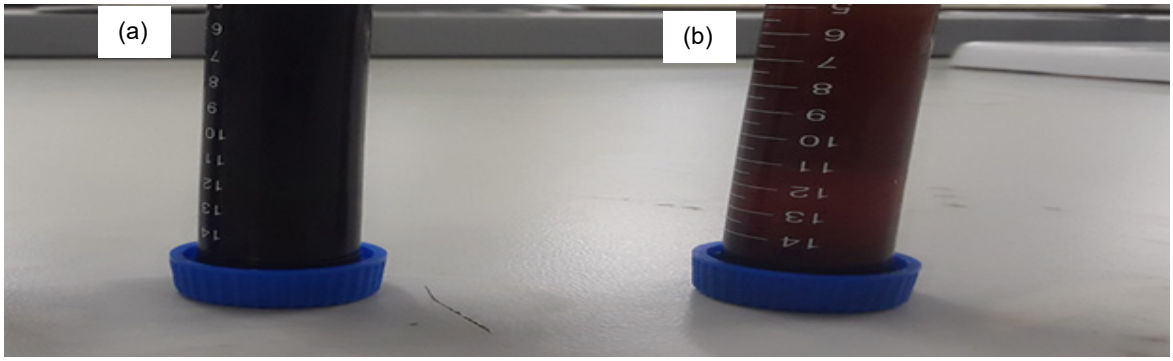

Figure 2: Illustration colour differences between (a) SCG oil extracted using 2-MeTHF (b) SCG oil extracted using hexane.

Table 2 depicts the characteristics of the crude oil extracted during these tests. The density and the kinematic viscosity of the oil provide the liquid properties of the extracted oil. The density, i.e., 1162.83 kg/m^3 of the oil extracted using 2-MeTHF was moderately similar to those reported by Al-Hamamre et al. (2012), i.e.1180.40 kg/m^3. The high oil density can be attributed to the aforementioned gummy material observed in the oil. The kinematic viscosity of the oil extracted using 2-MeTHF was 52.25 mm^2/s. This result was moderately higher compared to those reported by Muhammad et al. (2019), i.e.,43.82 mm^2/s and relatively lower compared to those reported by Abdullah and Koc (2013), i.e., 62.0 mm^2/s.

The acid value (AV) and the saponification value (SV) are the chemical properties of the extracted oil. These chemical properties determine the quality of the extracted oil. AV corresponds to the FFA content of the oil and is defines as the amount of KOH required to neutralize the free acid within the oil. The SV of the oil extracted using 2-MeTHF was found to be 184.11 mg$_{KOH}$/g. This result was moderately higher compared to those reported by (Muhammad et al., 2019), i.e., 176.40 mg$_{KOH}$/g. FFA content of the oil extracted using 2-MeTHF was 5.53 wt%. This result is similar to that reported by Vardon et al. (2013), i.e. 5.60 wt%. This result is 4 times higher than the one obtained for the 2-MeTHF oil. This can be linked to the coffee beans' origin, the oil's water content, and the upstream processing method employed (Jenkins et al., 2014).

Table 2: Characteristics of SCG oil extracted using 2-MeTHF and hexane

Solvent	Density (kg/m^3) @ 15°C	Viscosity (mm^2/s) @ 40°C	FFA (wt%)	SV (mg$_{KOH}$/g)
2-MeTHF	1162.83	52.24	5.53	184.11
Hexane	919.12	23.10	3.55	165.32

The density and viscosity of the oil extracted using hexane are comparable to those previously reported by Caetano et al. (2012), i.e.917 kg/m^3 and 22.23 mm^2/s. The saponification value (SV) of the lipids was similar to that reported by Haile (2014), i.e., 67.28 mg$_{KOH}$/g and the FFA value was similar to that reported by as Al-Hamamre et al. (2012), i.e., 3.65 wt%. The quality of the oil extracted using hexane was similar to those found in most literature, (Efthymiopoulos al., 2019).

The quality of the oil extracted using 2-MeTHF was somewhat inferior to the quality of the extracted using hexane. The density of the oil extracted using 2-MeTHF was found to be 1.27 times higher than the density of the oil extracted using hexane. This variation in the densities maybe attributed to the gummy material observed in the oil extracted with 2-MeTHF. This observation was also made by Al-Hamamre et al. (2012), it was observed that oil extracted from SCG with polar solvents such as ethanol, acetone and isopropanol, had gummy material on it and had a higher SV compared to oil extracted with non-polar solvents like hexane or heptane. The gummy substance might be composed up of carbohydrates, proteins, and other components generated by fatty acid complexes, which would explain the lipids' high SV and FFA concentration. Tiny particles were evident in the oil extracted using 2-MeTHF, which were removed by small screens under vacuum pressure. The mass of the oil did not considerably reduce when the particles were removed.

4. Conclusion

The Soxhlet extraction technique yielded the maximum oil recovery when the extraction time was between 3.5 and 4.5 h. Oil yields were significantly reduced for the extraction periods of < 2 h, indicating that this extraction period was not appropriate for the oil extraction with either solvent employed in this study. It was also observed that extending the extraction duration increases the oil output significantly. When it came to the influence of the solvent-to-SCG ratio on extraction efficiency, reducing the ratio from 5:1 (% w/v) to 20:1 (%w/v) resulted in a higher lipid yield. SCG was observed to become saturated with solvent, especially 2-MeTHF at a low solids-to-solvent ratio for extraction periods > 5.5 h. Both solvents were saturated with lipids at a high SCG-to-solvent ratio when subjected to the extraction process for longer than 3 h.To fully characterise the SCG oil extracted with 2-MeTHF, the iodine value (IV) needs to be determined. The iodine value of the oil gives an indication of the total wax present in the oil and gives an insight on the degree of saturation of the oil. The amount of wax present in the oil affects the quality the fuel grade hydrocarbons produced from the oil. The low iodine value of the oil corresponds to low NO_x emissions when the FAME produced from the oil is combusted. The crude oil extracted using 2-MeTHF was significantly higher than that of hexane at the same solids-to-solvent ratio and extraction time, signifying that not only glycerides and FFA were extracted. Identifying the other compounds extracted would be beneficial in understanding the nature of the SCG oil. The high FFA concentration on the SCG oil implies that obtaining FAME from it will need a two-step esterification procedure.

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