

Non-distillation Oil Extraction from SCG using Ethanol and Propan-2-ol

Nomfundo Mabona, Edison Muzenda, Mansoor Mollagee, and Liberty L Mguni

Abstract—Non-distillation oil extraction is a process whereby the step required to distillate the solvent (alcohol) to recover residual oil and by-products is eliminated. This is achieved by cooling the extraction products such that oil and some by-products become immiscible and they separate from the alcohol. The effect of Spent Coffee Grounds (SCG)/solvent ratio on non-distillation oil recovery was investigated. It was observed that recovery increased with an increase in ratio for both solvents, ethanol and propanol. The effect of separation temperature was also investigated and it was observed that the highest recovery was achieved at 15 °C. Generally it was observed that propanol recovery for non-distillation extraction was higher than that of ethanol. The main fatty acids present in the SCG oil were found to be palmitic acid (C16:0), stearic acid (C 18:0) and linoleic acid (18:2). Unsaponification values obtained for non-distillation extracted oil were 6.8 and 8.3% for ethanol and propanol respectively. These values are comparable with those of refined oil.

Keywords— ethanol, non-distillation, propanol, spent coffee grounds

I. INTRODUCTION

PETROLEUM reserve depletion and global climate change have strongly encouraged the development of fuel production from a variety of feed stocks such as vegetable oils, waste cooking oil, animal fat and microalgae [1]. The use of biomass residue for biodiesel production has been considered as a solution to expensive lipid feedstock and waste disposal of these residues [2]. As biodiesel feed stock has been reported to make up to 75% of production cost, a reduction in feedstock cost will go a long way in encouraging production of biodiesel [3].

As part of lowering the production cost of biodiesel, the use of minimal energy is ideal. This can be achieved by separating the oil from the miscella without having to distillate the solvent. Thus non-distillation oil extraction is being looked into in order to achieve this goal. Non-distillation oil extraction is a process where the step required to distillate the solvent (alcohol) to recover residual oil and by-products is eliminated. This is achieved by cooling the extraction products such that oil and some by-products become immiscible and they separate from the alcohol to an extent dependent on cooling temperature [4].

Using a cooling step instead of distillation obviously

substitutes a step which requires sensible heat for one that requires latent heat of vaporization. It has been reported that energy balance shows that this process requires, theoretically, about seven-tenths as much energy as the hexane extraction process [4]. The use of ethanol and propanol dates back to the early 19th century. The Japanese have been using ethanol since 1932 and they claim that “oil and oil alone” separates when the miscella is cooled [5]. The solubility of different oils in ethanol has been investigated by a number of researchers [6, 7]. And it was reported that miscibility of oils showed dependence on reaction temperature, solvent concentration and type of oil used. Some oils such as babassu and coconut oil have shown miscibility with absolute ethanol at low temperatures between 23 and 30 °C. On another hand some oils like olive and sunflower oil only showed miscibility at high temperatures of 65 °C [8]. These oils, olive and sunflower, would be ideal for non-distillation oil extraction.

Similar work has been done for propanol, and it was observed that it generally has a lower miscibility temperature compared with ethanol for a large number of oils [9]. The lower miscibility temperature for propanol (19.9) could be due to its lower dielectric constant compared to ethanol (24.3). However, propanol has been reported to be a better solvent than ethanol for extraction of oilseeds. The major challenge for ethanol is the low ability to dissolve oil at ambient temperatures, thus extraction using ethanol requires working above atmospheric pressure to be able to increase temperature above its boiling point [8].

To the best of our knowledge, non-distillation oil extraction investigations have been limited to cotton oil seeds and soybean oil. In this work, non-distillation oil extraction using ethanol and propanol at atmospheric pressure was investigated on Spent Coffee Grounds (SCG).

II. MATERIALS AND METHODS

A. Chemicals and Reagents

Propan-2-ol (99.8%) was obtained from Rochelle chemicals whereas ethanol (>98%) was obtained from Sigma-Aldrich. All reagents were used as received.

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B. Sample collection and preparation

Waste coffee ground sample was obtained from a local coffee manufacturing company, Roast 'n Grind (filter coffee). The wet sample was dried at 104 °C for 48h.

C. Soxhlet Extraction

Soxhlet extractor was used for oil extraction. Oil was extracted from varying amounts of SCG using 150 ml solvent under reflux for 2 h. The reaction time was recorded when the first droplet of the extraction solvent recycled back into the thimble. After the extraction had been accomplished, the extracts were left overnight so to allow separation of the oil phase from aqueous phase. The oil and materials lost to the aqueous phase were recovered by distillation. The oil recovered by non-distillation was left in the oven for 6 h at 104 °C to remove any solvent from the extracted oil.

D. Analysis of SCG extracts and oil produced

The SCG extracts using propanol and ethanol were analysed using Gas Chromatography–Mass Spectrometry to determine the materials extracted. The primary column (1 D) used was a Stabilwax ®-DA (30 meter, 0.25mm ID, 0.25µm). Helium gas was used as a carrier gas flowing at a rate of 1ml/min. Samples were injected at a split ratio of 100:1. The oven program used was from Adam *et al.* [10]. The secondary column (2 D) used was a Rxi®- 17 Sil MS (2 meter, 0.15 mm ID, 0.25 µm df). Modulator was enabled at a modulation period of 6s. The acquisition rate was 200 spectra/ second. The samples were analysed before evaporating the solvents and after transesterification of the oil. The unsaponification value was determined by an approximate standard analysis method [11].

E. Oil transesterification

A one step approach was used, where SCG oils extracted using different solvents were reacted with sodium methoxide. The sodium methoxide was prepared by mixing 4g NaOH with 350 ml methanol. The reaction was carried out at a molar reaction ratio of 1:6 (oil: methanol). The stirring speed was kept constant at 250 rpm at a reaction temperature of 40°C for 2h. After 2h, the product was heated at 65°C to remove methanol. The products that remained after drying were glycerol, unreacted oil and methyl esters. These products separate into two phases: glycerol as the bottom phase and oil and methyl esters as the top phase. The top phase was used to determine the fatty acids produce using GC-MS.

III. RESULTS AND DISCUSSION

Ethanol and propanol were used to extract SCG oil from SCG using non-distillation extraction. The analysis results of the GC MS on the SCG extracts show that there were a number of substances extracted including: free fatty acids, cyclo-compounds and benzene compounds. The major substances observed are shown in figure 1 below. The major

peaks are; caffeine (1212, 3.470), 1,4-Dioxane (1542, 4.105), Octadecadienoic acid (1434, 2.250), Hexadecanoic acid (1212, 2.205), 2-p-Nitrobenzoyl-1,3,5-tribenzyl-à-d-ribose (300, 1.435), Trichloromethane (276, 4.285), p-Xylene (366, 1.375), oleic acid (1206, 2.155) and the solvent was observed to elute along 300s on the primary column. The use of secondary column was key, since it allowed separation in the second dimension as shown below. The substances observed are common in nature and have been observed in coffee with the exception of trichloromethane which is used to extract caffeine from coffee [12, 14]. The high amounts of Free Fatty Acids extracted might be due to high dielectric constant of extracting solvents hence extraction of compounds with high dielectric constants [15].

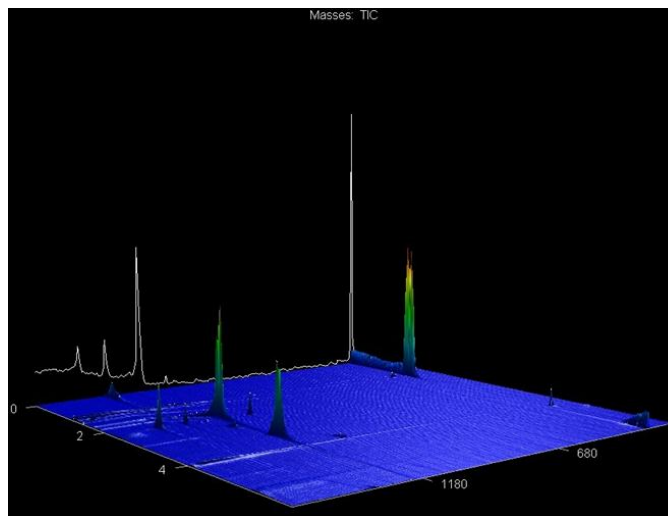


Fig. 1: Major SCG extracts analysed using GC MS

A. Effect of SCG/Propanol ratio on recovery

In this investigation, different solid: solvent ratios were used. Only the solid amounts were varied while keeping the solvent amount constant at 150 ml. The solids used were varied from 5g to 30 g. At a ratio of 5g SCG to 150ml solvent, no SCG oil was observed for non-distillation extraction. The failure to recover any SCG oil could be due to small amounts of oil produced at this ratio resulting in difficulty to observe the meniscus separating these two phases and/or all the amount of oil produced was miscible with the solvent. Increasing the amount of SCG from 10g to 30 g lead to an increase in the SCG oil recovered using this procedure of non-distillation extraction. The steady increase in oil recovery with increase in SCG amount could be due to a decrease in the percentage of oil lost into the solvent as SCG/propanol ratio increased and/or an increase in oil extracted as SCG/propanol ratio increased. The lost oil was then recovered by distillation of the aqueous phase. The results show that some of the SCG oil and other extracted material remained dissolved in the solvent at room temperature.

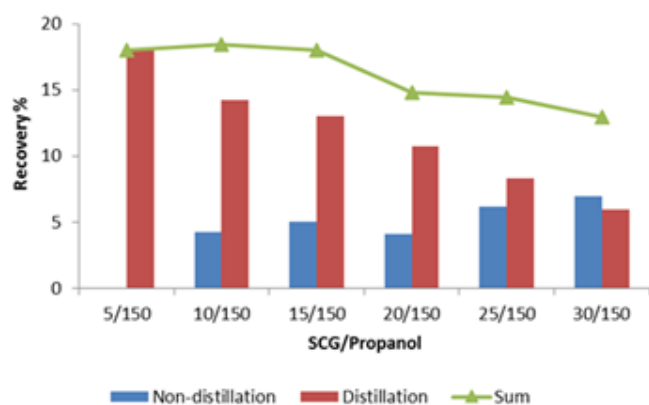


Fig. 2: Effect of SCG/Propanol ratio on recovery

It was observed that non-distillation extracts looked light in colour more like oils, while distillation extracts look very dark; suggesting that they contain a number of contaminants as such they may need intensive purification efforts before use. On the other hand, the light coloured SCG oil recovered using non-distillation process may require less purification in order to meet standards required. Generally, the sums of extracts (non-distillation and distillation extraction) were observed to decrease with an increase of SCG/propanol ratio. This suggests that in this range of SCG/Solvent ratio total extractable materials amounts are affected by SCG/solvent ratio. This might be due to a decrease in solvent available to extract extractable materials.

B. Effect of SCG/Ethanol ratio on recovery

A similar trend was observed for ethanol where recovery using non-distillation extraction was observed to increase with SCG/ethanol ratio. From figure 3, it is observed that in the range of 5/150 – 15/150 ratios no SCG oil was recovered using the non-distillation process. This could be that only small amount of SCG oil might have been extracted as discussed above. However, above 15/150 ratio, oil extraction was observed. The recovery of SCG oil increased from 4.2 – 6.2 % as the SCG/ethanol ratio increased from 20/150 to 30/150. As suggested above, this could be due to a decrease in the percentage of oil lost to the solvent as SCG/ethanol ratio increased and/or as a result of increase in SCG oil extraction as SCG/ethanol ratio increases. The overall recovery of extracted material was observed to be around 7.4%. The constant overall extraction recovery suggests that changing the SCG/solvent ratio in this range does not affect the amount of extractable material extracted when using ethanol contrary to when using propanol.

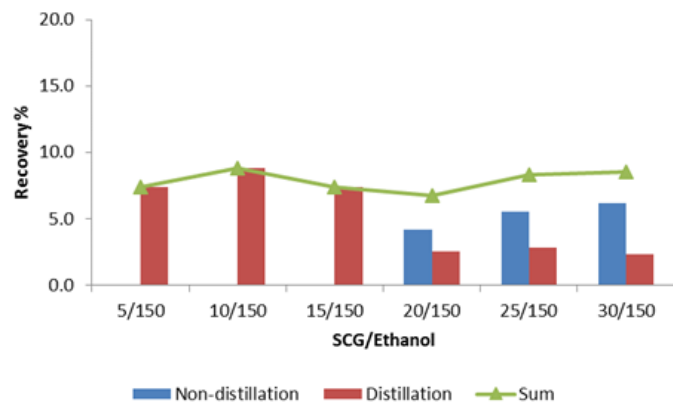


Fig. 3: Effect of SCG/Ethanol ratio on recovery

As mentioned before, materials which were not recovered using the non-distillation process were recovered by distillation. In figure 3 it was also observed that in the range of 5/150 – 15/150 ratios, there was no significant change in distillation recovery. However, there was a decrease in distillation extracts in the range of 20/150 - 30/150 ratios. This is as expected, since some of the extracted material was recovered using non-distillation process in this ratio range hence, less material reporting to distillation recovery process.

C. Effect of separation temperature for propanol

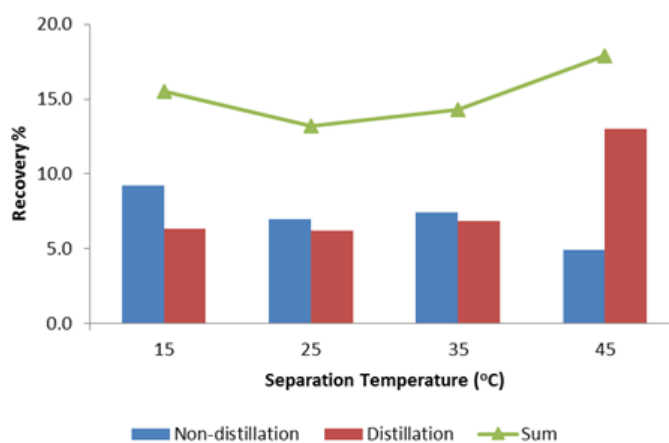


Fig. 4: Effect of separation temperature for propanol.

From figure 4 above, it was observed that oil recovery using non-distillation extraction decreased with an increase in temperature. This might be due to a decrease in miscibility of solvent and oil at low temperatures. This is consistent with work done by other researchers on a number of oils [6-8]. It was also observed on the same figure that as temperature increased more materials were recovered using distillation. This is as expected since less oil was recovered at high temperatures hence some SCG oil was reporting to lost materials. Finally the total recovered materials were observed to be around 15%.

D. Effect of separation temperature for ethanol

A similar trend was observed for ethanol, figure 5 below, where non-distillation SCG oil was observed to decrease with increasing temperature. As explained above the decrease in oil recovery was due to an increase in miscibility of oil with increase in temperature. Distillation recoveries were observed also to increase with temperature. The sum of recoveries was observed to be around 11% lower than that observed for propanol. This is contrary to expected results since propanol has a lower dielectric constant compared to ethanol, it would be expected that propanol be more miscible with the oil hence lower recovery. This suggests that propanol make up for poor immiscibility by higher extraction [8, 9]. This is consistent with all other results were total extracted materials are higher for propanol than ethanol.

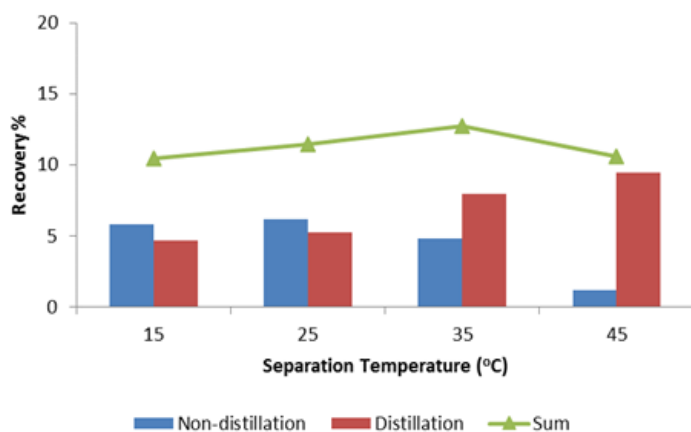


Fig. 5: Effect of separation temperature on ethanol

E. Oil quality

The main fatty acids produced from SCG oil are palmitic acid (C16:0), stearic acid (C 18:0) and linoleic acid (C 18:2) with the following order of quantity: palmitic > linoleic acid > stearic acid as shown in figure 6 below. The fatty acids from SCG oils in this work are comparable with those reported by other researchers [16, 17]. The unsaponification value for non-distillation oils extracted using ethanol and propanol were 6.8 and 8.3 % respectively. The two unsaponification values are comparable with values for refined oil [18, 19] this suggests that non-distillation process produces oil of good quality.

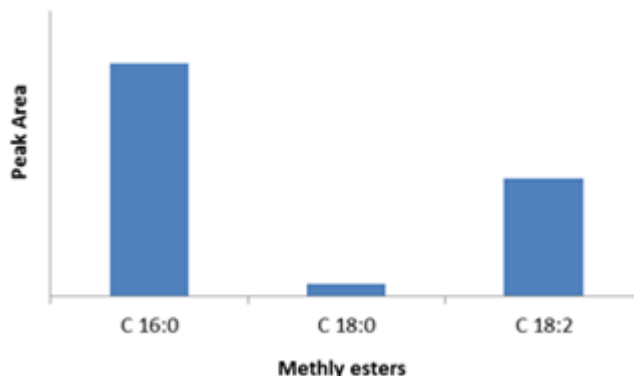


Fig. 6: Major methyl ester produced from SCG oil.

IV. CONCLUSION

SCG oil recovery was observed to increase with increase in SCG to solvent ratio and it was also observed that oil separation improved with a decrease in separation temperature. Highest non-distillation recovery was obtained at 15 °C for both solvents; however, it is expensive to cool the system to this temperature. Therefore, 25 °C would be more acceptable from an economical perspective. Propanol showed better recovery of SCG oil for non-distillation oil extraction than for ethanol, this is believed to be due to better extracting capabilities of propanol. Observation on the quality of SCG oil produced by non-distillation and extracts recovered by distillation, suggest that distillation extracts will need more intensive process to purify them. Total extracted materials for ethanol showed dependence on SCG/solvent ratio while no dependence was observed for propanol. Finally the main fatty acids observed from oil extracted from the SCG oil are palmitic acid (C16:0), stearic acid (C 18:0) and linoleic acid (C 18:2) with the following order of quantity: palmitic > linoleic acid > stearic acid.

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