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Effect of Moisture Quantity on Non-Distillation Oil Extraction from SCG using Methanol

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Abstract**—**Oil was extracted from spent coffee grounds using methanol. Methanol is not a popular solvent for oil extraction because of its toxicity but it is ideal for biodiesel production. The SCG was determined to contain 17.1 % wt% oil by extraction using hexane for 16h. The highest oil extraction 8.5 wt% was observed on a dry sample at a separation temperature of 25 ˚C representing only 50% recovery. Oil extraction was observed to depend on separation temperature and SCG water quantity. The extracted oil was characterised by a number of methods. Fourier-transform infrared spectroscopy (FTIR) results showed no difference in functional groups between hexane and methanol extracted oil. The Refractive Index (RI) results also suggested similarity in fatty acid chain length for oils extracted by these solvent. However, it was observed that oil extracted by hexane had higher amounts of FFA compared to methanol extracted oil.

Keywords**—**Non-distillation, Spent Coffee Grounds, methanol and oil extraction.

I. INTRODUCTION

INTEREST in vegetable oils as a feedstock for fuel production dates back to the Second World War and it was driven by the need for energy security [1-3]. The search for alternative solvents to extract oils from oilseeds has regained attention mainly due to risk of fire and growing environmental concerns related to the use of n-Hexane [4]. Replacing n-hexane with a bio-renewable solvent will be desirable, as bio-renewable solvents such as alcohols are good for oil extraction at elevated temperatures.

Methyl, ethyl and isopropanol alcohols are good solvents for the extraction of vegetable oils, but methyl alcohol is of little interest commercial because of its toxicity [5]. These solvents can all be produced by fermentation of bio-renewable resources. Methanol and ethanol can be produced directly by fermentation, whereas isopropanol is produced indirectly by reducing acetone obtained from corn fermentation [5]. There are a number of advantages of using alcohol, these include; reduced energy consumption up to 25% by using non-distillation process compared to hexane oil extraction process [6], high quality oil with low free fatty acids and finally it has been reported to improve industrial safety as stated above due to higher flash point compared to n-hexane (-23.3 °C) [4].

Coffee is one of the most popular beverages in the world and the residue produced after brewing coffee grounds is an oil-containing waste material which contains 12-16 wt% oil and >50 wt% moisture [7-8]. Compared to other waste sources such as cooking oil, animal fat and other biomass residues, oil from spent coffee grounds (SCG) has the additional benefits of being less expensive, higher stability in a sense that the oil does not decompose quickly (due to its high antioxidant content), has a pleasant smell and the relatively low levels of saponifiable matter makes the oil remain viscous and not congeal easily [9-11], thus making it very well suited to use in biodiesel production. Similarly to other waste sources, oil extracted from spent coffee grounds (SCG) have relatively high level of free fatty acids (FFAs) (3.65%), which is above the satisfactory limit of 0.5%-1% for one-step alkaline transesterification [12] and favours side reactions such as soap formation during transesterification reaction using base catalysts, especially when oil is extracted using hexane. The use of coffee residues for oil extraction not only offers economic benefits but also environmental benefits as their disposal usually represents a problem.

Traditionally, coffee is brewed and consumed fresh. Collection and transportation of waste coffee grounds before oil extraction would be the major challenges for biodiesel production. However, emergence of a world market for ready-to-drink or packaged coffee drinks during the last decade does not require the collection and transportation of waste coffee grounds. Processing the waste coffee ground at a nearby location where the packaged coffee drink products are produced would eliminate the requirement for collection and transportation of this waste material for oil extraction [13].

As stated above, SCG is produced with moisture content above 50wt%. It would be ideal to extract the oil without having to remove this water from SCG. This would save energy required to evaporate the water. Therefore, in this work we investigated the effect of moisture quantity on the extraction of oil from SCG using non-distillation process. The solvent used was methanol. Little interest has been shown on the use of methanol for oil extraction because of its toxicity in vegetable oil. But for biodiesel production, use of methanol would be desirable since it is the reagent used for transesterification of the oil. This will therefore mean no need to remove all methanol from oil, hence reduction in processing cost.

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II. MATERIALS AND METHODS

A. Chemicals and Reagents

Hexane (98%) and Sodium hydroxide were obtained from Sigma-Aldrich whereas ethanol (>98%) and methanol (98.8%) were obtained from Prolabo. All reagents were used as received.

B. Sample collection and preparation

Waste coffee ground sample (wet) was obtained from a local coffee manufacturing company, (filter coffee). The wet sample was dried at 104 ^{o}C for 48h, thereof in this paper is referred to as dry sample. To achieve different moisture contents for experimental purposes, distilled water was added.

C. Soxhlet extraction

Soxhlet extractor was used for oil extraction. Oil was extracted from 25g of spent coffee grounds using 150 ml solvent under reflux. The reaction time was 2h, it 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 recovered by non-distillation was left in the oven for 6 h at 104 ˚C to remove any solvent from the extracted oil. The amount of crude oil was determined from the original sample weight and the weight of the extraction cup before and after the extraction, i.e., by directly weighing the extracted crude oil [14].

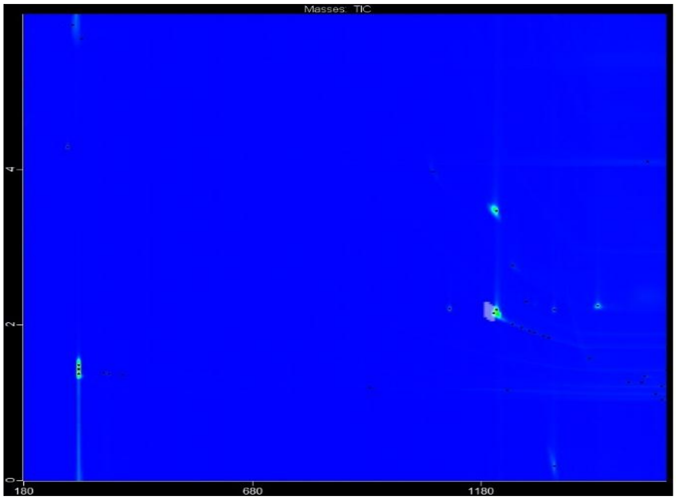
$$\%\, crude\ oil\ extrated = \frac{w_2 - w_1}{w_3} \times 100$$

Where W_1 = weight of the extraction cup, W_2 = weight of the extraction cup + extract, W_3 = weight of the spent coffee ground sample.

D. Analysis of SCG extracts and oil produced

The SCG extracts using methanol and hexane were analyzed using Gas Chromatography–Mass Spectrometry (GC-MS) 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.* [15]. 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 analyzed before separating the solvent and oil phase. The amount of oil in SCG was determined by extracting oil from SCG using hexane for 16h. FTIR spectra of oils extracted using methanol and hexane were recorded using a Bruker Tensor 27 ATR in the range of 4000-400cm^{-1} to determine its main functional groups. The free fatty acid (FFA) content and refractive index of the produced oil were also determined. The FFA was determined by a proximate standard analysis [16], while refractive indices (RI) were determined using a refractometer, Mettler Toledo 30PX.

III. RESULTS AND DISCUSSION



The analysis results of the GC-MS on the SCG extracts show that there were a number of substances mainly fatty acids. The major substances observed are presented in contour image in figure 1 and compound list is presented in table1. From the figure above the solvent was observed to elute along 300s on the primary column. The oil content in SCG was determined to be 17.1wt% by extraction using hexane for 16 h. This value is comparable with the reported range [8].

TABLE I
PEAK LIST FOR METHANOL EXTRACTS

Retention time (s)	Compound	Peak area
304,1.5150	1,5-Heptadiene-3-yne	$2.7*10^{7}$
1344, 2.330	4, 4-Ethylenedioxy-pentanenitrile	$2.3*10^{7}$
1304, 2.425	Cyclopentaneundecanoic acid, methyl ester	$2.21*10^{7}$
1440, 2.565	Eicosanoic acid, methyl ester	$2.19*10^{7}$
1104, 2.250	Hexadecanoic acid, methyl ester	$2.17*10^{7}$
276, 3.280	Trichloromethane	$1.96*10^{7}$
364, 1.405	o-Xylene	$1.40*10^{7}$
1208, 3.460	Caffeine	$5.62*10^{6}$

A. Effect of water quantity and separation temperature on oil recovery using methanol

The effect of water quantity and separation temperature on oil recovery was investigated by extracting oil from SCG at different moisture contents and then recovering the oil using non-distillation method at different separation temperatures; 25˚C and 45˚C. Figure 2 shows that there was a decrease in oil extraction with an increase in water content. From the same graph it was also observed that increasing water content beyond 40% resulted in little amount of oil being recovered at 25˚C and no oil recovery at 45˚C separation temperature. The decrease in oil extraction with increase in water content is consistent with work by Johnson and Lusas [17] were they reported that alcohols are good extraction solvents given they remain anhydrous. This fall in activity with increase in water could be due to a decrease in the methanol concentration with increase in water quantity. It was also observed that oil extraction decreased with increase in separation temperature. This decrease is consistent with our expectations as oil solubility decreases with decrease in temperature [18-20] hence more oil was recovered by non-distillation at lower temperatures.

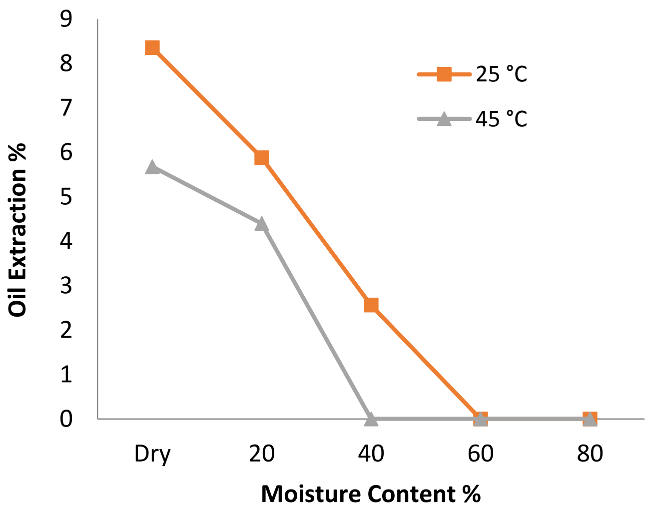


Fig. 2: Effect of water quantity and separation temperature on oil recovery using methanol

B. Spent Coffee Grounds oil analysis

The FTIR results for the crude oil extracted by hexane and methanol are presented in Figure 3 below. It was observed that there is no difference in the functional groups observed for the two samples. The functional groups observed were the methyl, methylene, amine and carbonyl groups. The methyl group is shown by the presence of these bands; 2853 cm^{-1} for the C-H stretch and 1464 cm^{-1} for C-H bend. Also C-H bend, C-H stretch and C-H rocking were observed at 721, 1464 and 2923 cm^{-1} respectively for methylene group. Other bands observed were for carbonyl group at 1744 cm^{-1} and secondary amine C-N stretch at 1161 cm^{-1}. Finally there was a broad absorbance between 2953 and 3512 cm^{-1} attributed to -OH from water.

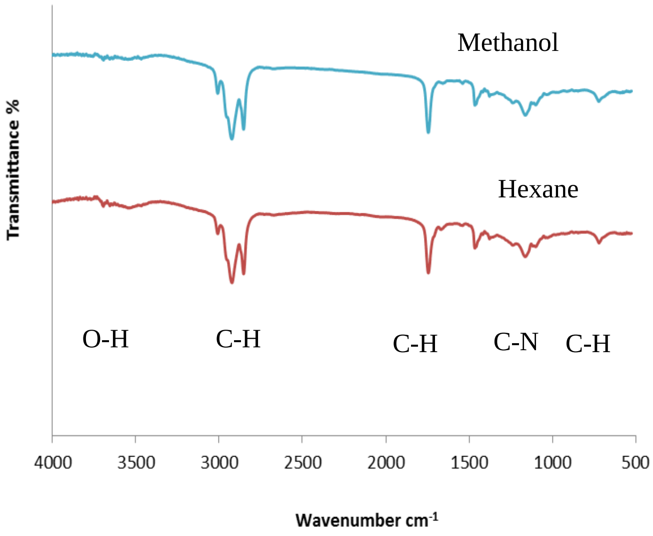


Fig. 3: FTIR spectra for oils extracted using methanol and hexane.

The oil produced by different extraction solvents was also analyzed to determine its FFA content and refractive index (RI). From the results given in table 2 below it was concluded that the coffee oil extracted by hexane and methanol had similar fatty acid chain length as suggested by comparable RI values. The FFA content was analyzed for oil extracted using hexane (dry sample), and methanol (dry and 20 wt% water). SCG oil from 60wt% water containing sample could not be analysed because of little oil recovered. Hexane extracted oil had the highest FFA content compared to methanol extracted samples. This is consistent with work reported by Seth *et al.* [4]. The lower value of FFA in oil extracted by methanol compared to oil extracted by hexane is due to that, FFA has a tendency to concentrate in light alcohol rich phase hence lower concentration on the oil. The FFA values in this work are lower than those reported by Hartman *et al.* [21] before refining this suggest that non-distillation extraction produces oil of better quality. From the result in table 2 below it was also observed that oil from dry SCG had a lower percentage of FFA than oil from a sample at 20wt% water. The higher FFA at 20wt% could be due to the presence of water which encourages extraction of polar substances i.e. free fatty acids.

TABLE II

EXTRACTS FFA AND RI FOR METHANOL AND HEXANE EXTRACTED SCG

Oil sample	% FFA	RI
Dry	2.48	1.4782.48
20	3.14	1.4773.14
Hexane	4.37	1.4774.37

IV. CONCLUSION

The oil extraction results have shown dependence on moisture content and separation temperature. The results suggest that methanol will make a good extraction solvent in the absence of water. The analysis results of the oil extracted suggests a dependence of FFA quantity on moisture content of SCG. The results not only suggested that oil extraction decreased with water quantity in SCG but that FFA quantities increased with water quantity. The FFA values obtained also suggest that for SCG oil in this work to be usable in alkaline transesterification reaction they will require further processing so that FFA content can be in the acceptable arrange to avoid soap formation.

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