Effect of Moisture Quantity on Non-Distillation Oil Extraction from SCG Using C₁-C₃ Alcohols

Nancy R Mojapelo, Edison Muzenda, Liberty L Mguni, Ambali S Abdulkareem, and Ayo S Afolabi

Abstract—The objective of this study was to investigate the effect of moisture content and separation temperature on oil extraction from Spent Coffee Grounds (SCG). SCG is the wet residue which contains approximately 12-16 wt% oil and >50 wt% moisture. In this work SCG containing 16 wt% oil and 0-80 wt% moisture was used. The Soxhlet extraction method was used with the following solvents; methyl, ethyl and propyl alcohols. The highest oil recovery for isopropanol (10.4 %) was obtained at 60 % moisture, while for ethanol (11.2 %) at 40 % moisture and for methanol (10.8 %) it was obtained on a dry sample. The highest oil extractions were achieved at a separation temperature of 15°C. The refractive index (RI) and free fatty acid (FFA) of the extracted oil was observed to vary depending on the moisture content. Oil extracted using hexane had highest amounts of FFA as compared to the oils extracted using alcohols.

Keywords—Free Fatty Acids, Moisture content, Non-distillation, Oil extraction

I. INTRODUCTION

NON-distillation oil extraction has received little attention in the last two decades, this might be due to a well-established hexane oil extraction process. The search for alternative solvents to extract oils from oilseeds has regained attention mainly due to the risk of fire and growing environmental concerns related to the use of n-Hexane [1]. Replacing n-hexane with a bio-renewable solvent is desirable, as bio-renewable solvents such as alcohols are good for oil extraction especially at elevated temperatures [2]. Methyl, ethyl and isopropyl alcohols are good solvents for the extraction of vegetable oils, but methyl alcohol is of little interest commercially because of its toxicity. However, in our previous work we have shown the potential of using methanol [3] for oil extraction especially for biodiesel production since methanol is one of the reagents used. These solvents can all be produced by fermentation of bio-renewable resources. Methanol and ethanol can be produced directly by fermentation even though the preferred method for producing methanol is from synthesis gas. However, isopropanol is produced indirectly by reducing acetone obtained from corn fermentation.

There are a number of advantages of using alcohols including; reduced energy consumption up to 25 % by using non-distillation process compared to hexane oil extraction process [4], high quality oil with low free fatty acids and finally it has been reported to improve industrial safety due to higher flash point compared to n-hexane (-23.3 °C) [1].

Coffee is the most important agricultural commodity in the world and is second only to petroleum in global trade activity and value [5]. The remaining spent coffee grounds (SCG) after the coffee making process contains water greater than 50wt%. The residues are very toxic such that only small quantities can be used to make compost or for animal feeding such that the rest is discarded as waste [6]. The oil extracted from SCG compared to other waste sources such as cooking oil, animal fat and other biomass residues, oil from SCG has a number of benefits. These benefits include; 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 a relatively low level of saponifiable matter making the oil remain viscous and not congeal easily [7-9], thus making it very well suited to use in biodiesel production. Similar to other waste sources SCG oil has relatively high levels of free fatty acids (FFAs) (3.65 %), which is above the satisfactory limit of 0.5 %-1 % for one-step alkaline transesterification [10] and favours side reactions such as soap formation during transesterification reaction when using a base catalysts, especially when hexane is used as a solvent.

SCG is normally produced with moisture content above 50 wt%. It would be ideal to extract the oil without having to remove this water from SCG and this would save energy required to dry the SCG. Therefore, in this work we investigated the effect of moisture content on the extraction of oil from SCG using non-distillation process. The solvents discussed are methanol, ethanol and propanol.
II. MATERIALS AND METHODS

A. Chemicals and Reagents

Hexane (99 %) and ethanol (>99.5 %) were obtained from Sigma-Aldrich whereas methanol (99 %), Sodium hydroxide (99 %) and isopropanol (99.7 %) were obtained from Rochelle. All reagents were used as received in analytical grade.

B. Sample collection and preparation

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

C. Soxhlet extraction

A Soxhlet extractor was used for oil extraction. Oil was extracted from 25g of Spent Coffee Grounds using 150 ml solvent (i.e alcohols) under reflux. The contact time was 2 hours and 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 as 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 remaining 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 [11].

\[ \% \text{crude oil extracted} = \frac{W_2 - W_1}{W_3} \times 100 \]  

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. For comparison purposes oil was extracted using hexane. SCG oil content was determined by Soxhlet extracting 25g of SCG using 150 ml of hexane under reflux for 16 h. The oil was recovered by evaporation of hexane and oil content was determined using the equation above.

D. Analysis of SCG extracts and oil produced

The SCG extracts using methanol, ethanol and isopropanol were analyzed 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). The oven program used was by Adam et al. [12]. The secondary column (2 D) used was a Rxi®-17 Sil MS (2 meter, 0.15 mm ID, 0.25 µm df). The samples were analyzed before separating the solvent and extracts. FTIR spectra of oils extracted using different solvents were recorded using a Bruker Tensor 27 ATR in the range of 4000-400 cm⁻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 content was determined by a proximate standard analysis [13], while refractive indexes (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 several substances mainly fatty acids in the extracted oil. The major substances observed are presented in GC image in Fig. 1 and compound list is presented in table I for all the extraction solvents showing typical compounds found in all alcohol extracted oils. The solvent was observed to elute along 300s on the primary column. The oil was determined to be 16 % of the spent coffee grounds using the hexane extraction method and this is in the range found by other researchers [5], [6].

![Image](361x414 to 527x539)

**Fig. 1** 2D-GC image of SCG extracts the x-axis represents retention time of primary column while y-axis is retention time of secondary column.

**TABLE I**

<table>
<thead>
<tr>
<th>PEAK LIST FOR METHANOL EXTRACTS [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention time (s)</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>1344, 2.330</td>
</tr>
<tr>
<td>1304, 2.425</td>
</tr>
<tr>
<td>1440, 2.565</td>
</tr>
<tr>
<td>1104, 2.250</td>
</tr>
<tr>
<td>276, 3.280</td>
</tr>
<tr>
<td>364, 1.405</td>
</tr>
<tr>
<td>1208, 3.460</td>
</tr>
</tbody>
</table>

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. This was achieved by extracting oil from SCG at different moisture contents and then recovering the oil using non-distillation method at these separation temperatures; 15 °C, 25 °C and 45 °C. Fig. 2 shows that there was a decrease in oil extraction with the increase in water content. From the same graph it was observed that increasing water content beyond 40 % resulted...
in little amount of oil recovered at 25 °C and no oil recovery at all at 45 °C separation temperature. The reason for the decrease in oil recovery with an increase in water content might be as suggested by Johnson and Lusas [14] that alcohols are good solvents given they remain anhydrous. This fall in activity might also be due to an increase in dielectric constant beyond the optimum value [15], hence hydrolysis of oil to produce FFA. It was also observed that oil recovery increased with decrease in separation temperature. This increase is consistent with our expectations as oil solubility decreases with decrease in temperature [16]-[18] hence more oil was recovered by non-distillation at lower temperatures.

C. Effect of water quantity and separation temperature on SCG oil recovered using Propanol

Propanol has a similar trend to the one observed when using ethanol as the extraction solvent, shown in Fig. 4, but in this case the oil recovery increased with moisture content until 60% and thereafter no oil was extracted at 80% moisture content. It was also observed that oil extracted increased with decrease in separation temperature as discussed above.

D. Comparison of the SCG oil produced

The oil extraction trends for ethanol and propanol were observed to be similar while methanol had a different behavior. The amount of oil extracted with ethanol and isopropanol were observed to increase with increase in water content until 40 and 60% respectively. However, the oil extracted by methanol only decreased with increase in water content. With the belief that there is an optimum dielectric constant as suggested by some researchers [14] [19], dielectric constants were calculated for all solvents at different water concentrations and are presented in table 2 below. The dielectric constants for pure solvents were obtained from work by other researchers [20].

Dielectric constants for alcohol-water mixtures were calculated using the method used by Tir et al. [19]. From the results it was observed that the fall in oil extraction took place when the dielectric constant increased above 31. These results suggest that the optimum dielectric constant was around 31 meaning an increase in polarity of extraction solvent before reaching this value enhance destruction of lipids associated with cell membranes or with lipoproteins hence increase in oil extraction. However, a further increase in polarity above this value lead to hydrolysis of extracted lipids hence a drop in oil extracted as discussed above.

\[
\begin{array}{cccc}
\text{Water %} & \text{Methanol} & \text{Ethanol} & \text{Propanol} \\
0 & 31 & 26 & 19 \\
20 & 33 & 28 & 21 \\
40 & 36 & 31 & 25 \\
60 & 41 & 37 & 31 \\
80 & 51 & 47 & 43 \\
\end{array}
\]
The FTIR results for the crude oil extracted by hexane and the alcohols are presented in Fig. 5. From the figure, it was observed that there is no difference in the functional groups observed for all the samples. The functional groups observed were the methyl, methylene, amine and carbonyl groups. The methyl group is shown by the presence of these bands; 2923 cm⁻¹ for the C-H stretch and 1464 cm⁻¹ for C-H bend. The C-H bend, C-H stretch and rocking were observed at 721, 1464 and 2853 cm⁻¹ respectively for methylene group. Other bands observed were for carbonyl group at 1744 cm⁻¹ and secondary amine C-O stretch at 1161 cm⁻¹. There was a broad absorbance between 2953 and 3512 cm⁻¹ attributed to -OH from water. All these bands are consistent with those observed for other oils [21], except for the –OH observed in this work.

![FTIR spectra for oils extracted using hexane (a), methanol (b), ethanol(c) and propanol (d)](image)

Fig. 5 FTIR spectra for oils extracted using hexane (a), methanol (b), ethanol(c) and propanol (d)

The oil produced by the three extraction solvents was analyzed to determine its FFA content and refractive index (RI). It was observed from Fig. 6 that increasing the amount of moisture content increased the FFA content in the oil. The increase in FFA with the increase in water quantity could be due to the presence of water which increases the solvent dielectric constant hence encourages extraction of polar substances i.e. FFA. Hexane extracted oil had the highest FFA content (4.4 %) compared to the oil extracted using alcohols. This is consistent with work reported by Seth et al. [1] were they extracted oil from Soybean. The low value of FFA content in oil extracted by the alcohols compared to oil extracted by hexane was suggested to be due to FFA tendency to concentrate in light alcohol rich phase, hence lower concentration on the oil. Methanol had the highest FFA compared to propanol and ethanol for dry and 20 % moisture containing samples; this could be due to high dielectric constant as observed in table II. The FFA values in this work are lower than those reported by Hartman et al. [22] before refining, this suggests that non-distillation process produces oil of better quality and/or SCG oil used had different properties due to different treatment methods of raw materials, boiling, drip-filtering or percolating, which leads to different concentration of substances in the SCG [23].

![FFA obtained for different extraction solvents](image)

Fig. 6 FFA obtained for different extraction solvents

Generally, there is a close relationship between RI of oil and its molecular weight and to a minor degree its unsaturation [24]. The influence of solvent type and moisture content on the refractive index of SCG oils are shown in Fig. 7. It was observed that RI was gradually increasing when water content was increased up to 40%, for ethanol and propanol extracted oils. However, a steeper increase was observed at 60% moisture. This increase could be due to hydrolysis of lipids and these results are consistent with extraction results and FFA results. The RI value for hexane (1.4734) extracted oil was comparable with the RI of oil extracted using all the alcohols.

![RI obtained for different extraction solvents](image)

Fig. 7 RI obtained for different extraction solvents

IV. CONCLUSION

The results suggest that propanol might make a more cost effective solvent since it could extract more oil at higher water content (60 %). The results also suggest that extracting in the presence of water increases FFA content for all solvents. It should however be noted that the FFA content in these water containing SCG is still lower compared to FFA content on oil extracted using hexane on a dry sample.

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REFERENCES


