The effect of the type of bean, processing and geographical location on the biodiesel produced from waste coffee grounds

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Abstract

Waste coffee grounds offer a viable waste feedstock for biodiesel production. Approximately 8 million tonnes of coffee are produced globally each year and contain up to 15 wt% lipid, of which the glyceride portion is predominantly made up of palmitic, stearic, oleic and linoleic acids. In this investigation the variation in the oil content, saponifiable lipids and the lipid profile according to regional location and processing or brewing techniques was assessed. A number of key fuel properties were also investigated. The oil content for fresh coffee grounds (FCG) ranged from 11- 15% across the range of coffees examined. Spent coffee grounds (SCG) had slightly reduced levels of lipid, between 7 – 13 wt%, for the coffees under investigation. The lipids contained between 0 – 40% unsaponifiable material which could not be processed to fatty acid methyl ester (FAME). For all samples, with the exception of Vietnamese coffee, the FAME profile of the resulting biodiesel was consistent; the oils contained between 35-40 % palmitic acid, 7-8 % oleic acid, 44-50 % linolenic acid and 7-8 % stearic acid, though the fuel properties were reasonably variable across the data set. The kinematic viscosity ranged between 4.0 – 5.5 $mm^2 s^{-1}$, the density ranged between 841 – 927 kg m^{-3} and the pour point between -1 – 16 °C. This variation was also observed in previous reports, suggesting that these fuel properties are not solely determined by the FAME profile but other lipid soluble biomolecules present in the coffee biodiesel.

1. Introduction

An increasing awareness of the impact of the transport sector on the environment has generated interest in developing renewable biofuels, yet concerns remain over the use of arable land to produce fuel crops which may compete with the food supply. This has driven the development of liquid fuels from waste resources, such as waste cooking oil.[1] One potential source of waste oil is from spent coffee grounds (SCG). Coffee is an important agricultural commodity; approximately 8 million tonnes are produced globally each year.[2] There are 8 major producers of coffee worldwide, with Brazil alone accounting for 35% of the total production (Figure 1). Coffee beans typically contain between 10 - 15 wt% lipids, of which 80-95% are glycerides.[3, 4] The glyceride portion of the oil can be transesterified with methanol to produce fatty acid methyl esters (FAME), known as biodiesel.[5] Potentially 1.3 billion litres of biodiesel could be added to the world fuel supply from SCG, a figure comparable to waste cooking oil.[4, 6]

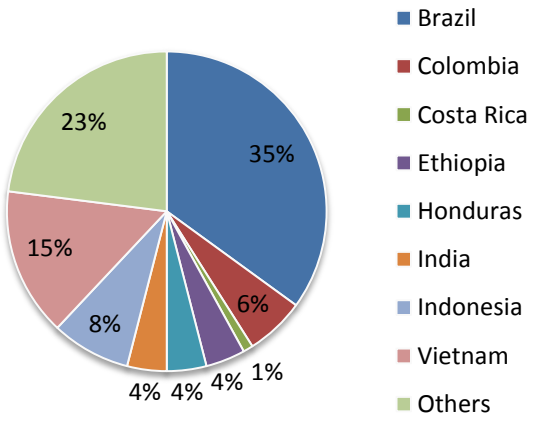

Figure 1. Total production of coffee by country, adapted from the International Coffee Organization [2]

Coffee oil can be obtained directly from the coffee bean or from the fresh or spent coffee grounds. Commercially, only two types of coffee beans are cultivated for use: *Coffea Arabica* and *Coffea canephora*, commonly referred to as Arabica and Robusta.[7] Arabica accounts for 70-75% of total production and is considered to be of superior quality due to the richer flavour developed during roasting.[8, 9] Robusta is commonly used in the freeze dried coffee industry for producing soluble coffee extracts such as 'instant coffee'. As the Robusta coffee bean contains twice the amount of caffeine as Arabica coffee beans,[10, 11] increasingly

often, blends of the two beans are sold, in order to control the strength of flavour and tailor the amount of caffeine present in the coffee.

Coffee produces more oil per hectare than soybean, with 386 kg ha^{-1} being reported in the literature as opposed to 375 kg ha^{-1}.[12] In addition to the coffee oil which could potentially be extracted from waste coffee grounds after brewing, as much as 20% of all coffee beans produced are deemed defective and offer a further source of biofuel.[13, 14] The majority of coffee is processed, roasted and then sold, but a small proportion is decaffeinated prior to roasting. There are four solvents that are used for the decaffeination process: water, ethyl acetate, supercritical CO_2 ($scCO_2$) and dichloromethane. All four methods consist of steaming the green coffee beans causing them to swell, extracting the caffeine from the beans under carefully controlled process conditions, removing the solvent residue from the beans by steam stripping and finally drying the decaffeinated coffee beans to restore their original moisture content.[15] The effect of this type of processing on the oil content or lipid profile of the resulting coffee is unknown.

Spent coffee grounds (SCG) refer to the dried solid residue produced after preparation of the coffee beverage or manufacturing of instant coffee.[7] Generally SCG are discarded as waste or used in composting. They have little commercial value, although an increased emphasis on waste reduction has increased interest into potential uses.[16, 17] Due to the heavy processing of the coffee beans prior to commercial use, extracting the oil from SCG is relatively straightforward. Soxhlet, microwave and $scCO_2$ methods have all been shown to be adequate at removing the oil over reasonable reaction times.[17-21] Al-Hamamre *et al*. demonstrated that hexane was the most suitable solvent for extraction, yielding 15 wt% oil over 30 minutes using Soxhlet apparatus.[3]

The lipid oil composition will vary depending on the source, although generally up to 80 – 90% of the oil will be made of glyceride species, including free fatty acids, with the rest of the lipids containing terpenes, sterols, and tocopherols.[22] These components are generally insoluble in the resulting biodiesel and have to be separated from the fuel prior to use. Oliveira *et al.* produced between 10 to 12 wt% oil from defective coffee beans, though the extracted oil only yielded 74% biodiesel on transesterification.[13] Similarly Al-Hamamre *et al.* produced a maximum of 86% FAME from a coffee oil produced from SCG.[3]

FAME produced from coffee oil contains palmitic, stearic, oleic and linoleic acid esters, and as such is a promising source of biodiesel.[3] However, it is unclear whether the lipid content,

lipid profile and the resulting fuel properties vary for SCGs from different regional locations, different processing and brewing methods or from the parent FCG. In this investigation representative coffees from the main growing regions were examined, including decaffeinated coffee and coffee with varying levels of Arabica beans, and were brewed under controlled conditions. The oils were extracted with heptane and analysed for their lipid content, biodiesel yield, FAME profile and key fuel properties.

2. Experimental

Materials. The coffee grounds were purchased locally from a number of local supermarkets. Heptane (HPLC grade) was purchased from Fisher Chemicals, sulphuric acid (glacial), methanol (99.5%+), chloroform (99.5%+) and 1,4-dioxane (analytical grade) were obtained from Sigma Aldrich, UK and were not purified further prior to use.

General Brewing Process. Fresh coffee grounds (100g) were brewed with freshly boiled water (1 L), in a cafetière (French press) coffee maker. The mixtures were stirred to submerge all the coffee grounds, and then left to settle and brewed over exactly 5 minutes. The cafetière plunger was depressed and the resulting liquid poured off. The solid fraction was separated and the spent coffee grounds were dried in an oven at 67°C, over 24 hours to reduce the moisture content. Other brewing methods were also used, including a filter coffee machine, an 'aero-press' and an espresso maker (see supporting information).

Oil extraction. The coffee grounds were accurately weighed and suspended in fresh heptane (1:10 wt. ratio). The coffee was then stirred for 180 minutes at room temperature. The solvent was replaced with fresh heptane and the extraction undertaken for a further 180 minutes. Experimentation showed that less than 0.6 % oil was left in the grounds after this point. The solvent fractions were combined and the heptane removed *in vacuo*.

Transesterification. The oil (10g) was added to an excess of methanol (~ 50ml) and sulphuric acid (10 wt. % in relation to the oil). The reaction mixture was refluxed for 24 hours. On completion of the reaction the mixture was filtered to determine the amount of unsaponifiable material and subsequently washed three times with distilled water to remove the methanol, glycerol and acid catalyst. The glyceride to FAME yield was calculated by ^{1}H NMR to ensure that over 99% of the glyceride species had reacted.

Biodiesel analysis. The biodiesel was analysed by ^{1}H NMR and GC-MS. GC-MS analysis was carried out using the Agilent 7890A Gas Chromatograph equipped with a capillary column (60 m x 0.250 mm internal diameter) coated with DB-23 ([50%-cyanpropyl]-methylpolysiloxane) stationary phase (0.25 µm film thickness) and a He mobile phase (flow rate: 1.2 ml/min), coupled with an Agilent 5975C inert MSD with Triple Axis Detector. Approximately 50 mg of each sample was dissolved in 10 ml 1,4-dioxane and 1 µl of each solution was loaded onto the column, pre-heated to 150°C. This temperature was held for 5 minutes and then heated to 250 °C at a rate of 2 °C/min and then held for 2 minutes. The standard error for any peak was found to be less than 1.5%. NMR spectroscopic measurements were carried out at 298 K using a Bruker AV300 spectrometer, operating at 300.13 MHz for ^{1}H. Typically samples were made up of 0.05 ml of the oil or biodiesel sample dissolved in 0.5 ml $CDCl_3$. ^{1}H spectra were typically acquired using a 30 degree excitation pulse and a repetition time of 4.2 sec. 0.3 Hz line broadening was applied before Fourier transform, and spectra were referenced to the residual $CHCl_3$ peak from the solvent (δ 7.26 ppm).

Kinematic viscosities were determined in accordance with ASTM D445. A Canon-Fenske capillary kinematic viscometer was used. Temperature modulation was achieved using a refrigeration/heating unit. Samples within the viscometer were allowed to rest at 40 °C for a minimum of 5 minutes prior to viscosity measurement to allow temperature equilibration. The standard error was found to be ±0.100 mm^2s^{-1} at 40 °C. Pour points of the fuels were determined visually by cooling of 1.5 ml vials of the samples in low temperature freezers and cold rooms of specific temperatures, with periodic checking to see if the pour point had been surpassed. The samples were allowed to rest at each temperature for a minimum of 60 minutes in order to allow equilibration of temperatures. Densities were determined gravimetrically by weight 10 cm^3 ± 0.01cm^{-3} and weighing to an accuracy of ±0.0005 g.

3. Results and Discussion

Oil extraction and biodiesel conversion. While a range of techniques have been shown to be effective in extracting oil from coffee beans, Al-Hamamre *et al*. demonstrated that hexane was the most suitable, yielding 15 wt% oil over only 30 minutes with a Soxhlet set-up.[3] Accordingly, heptane was selected in this study to extract the oil from the fresh (FCG) and spent (SCG) coffee grounds, using an adapted literature method.[23] Coffee grounds have been reported to contain up to 10-15 wt% lipid, with some reports reporting lipid as high as 20

wt%.[24] However, not all of these lipids are glycerides and can be transesterified to produce biodiesel. Oliveira *et al.* determined that using Brazilian coffee up to 26% of the lipid extracted was unsaponifiable matter, which had to be removed by filtration on transesterification.

To assess the effect of geography on the lipid of the coffee bean, a range of coffees were sourced from distinct geographical locations, the lipid extracted and the unsaponifiable material measured (figure 2).

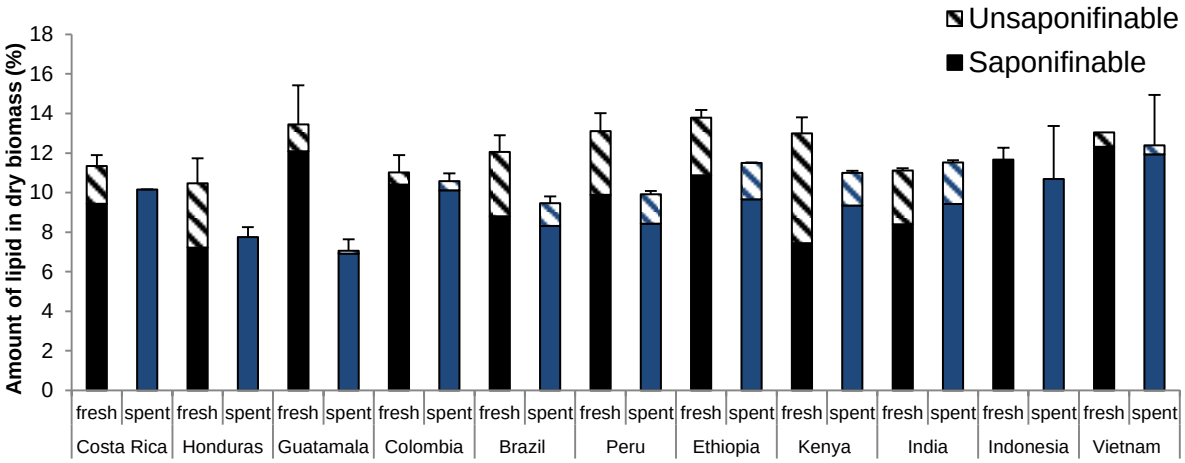

Figure 2 Oil content and FAME yield from a range of geographical locations, black bars indicate the amount of lipid extracted from FCG, the blue bars indicate the lipid extracted from SCG.

Coffee grounds (100% Arabica) from the top 11 coffee producing nations were tested in their fresh state and after using the Cafetière brewing method outlined above. All FCG oils tested contained between 11 and 14wt% lipid and on brewing around 30% of the weight of the coffee is solubilised in the water (results not shown). Irrespective of geographical location there was less oil in the SCG than the FCG. The SCG examined under these conditions contained between 7 – 13 wt% lipid, so while a majority of the oil is retained in the coffee grounds, some is lost in the brewing process.

No pattern was found to suggest that the lipid content of the coffees were determined by its country or region of origin, though this might be due to the relatively small sample set. This is not surprising as the local climatic conditions, the time of picking and the method of drying all play a large role in the composition of the coffee,[25] and these may vary within regions. For example, green coffee can by produced by either wet or dry processing methods. In wet processing the ripe berries are mechanically processed to remove the pulp and the residues

degraded by fermentation. The resulting coffee is dried, conditioned and hulled. In dry processing, entire coffee fruits are dried without removal of the pulp. These different methods are known to change the chemical composition of the beans.[26, 27]

The oil samples were transesterified with 10 wt% sulphuric acid and an excess of methanol over 24 hours. The conversion was monitored by ^{1}H NMR and over 99% FAME conversion was achieved from the saponifiable material in all cases. Upon transesterification, a dark blue-green precipitate was observed in the majority of samples tested. These non-saponifiable precipitates have been observed in previous studies, especially when using an acid catalyst.[13, 24] These precipitates are known to be formed from a range of compounds such as sterols, terpenes and organic acids. Two of the main insoluble compounds found in the esterified coffee oil are likely to be the cyclic terpenes commonly found in coffee oil: kahweol and cafestol.[28, 29] Both of these products were found to be present in the FCG and SCG oils tested (see supporting information).

Although, the amount of lipid was not determined by the place of origin of the coffee, the amount of saponifiable material present in the coffee lipid varied dramatically depending on the geographic source of the beans. This varied from below 0.1 % for coffee sourced from Indonesia to up to 40 % in the lipid sourced from Kenyan FCG. A large proportion of unsaponifiable material seemed to be removed during the brewing process as significantly less unsaponifiable material was present in the SCG than the FCG; for example the oil present in the Kenyan SCG had only 15 wt% unsaponifiable material. This means that whilst there is less total lipid present in the SCG, because some of the unsaponifiable matter is removed by brewing, in most cases the potential biodiesel yield is similar if not higher than the FCG.

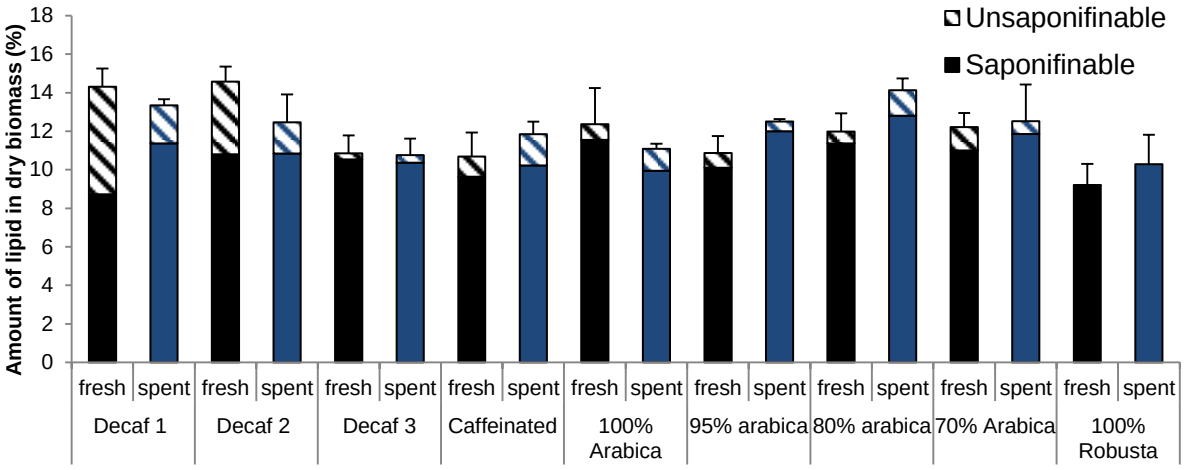

Figure 3 Oil content and FAME yield from a range of different strength blends and decaffeinated coffee. Black bars indicate the amount of lipid extracted from FCG, the blue bars indicate the lipid extracted from SCG.

A further processing stage which could affect the oil content is decaffeination, as the use of solvents to remove the caffeine could potentially remove other lipids. To test this, three examples of decaffeinated FCG were selected and the lipid extracted (figure 3). No difference between the decaffeinated samples selected and the other coffees used in this study was found. The total lipid ranged from 12 -14 %, with a slightly reduced lipid level in the SCG. It seems that modern decaffeination techniques do not affect the lipid content substantially. The amount of unsaponifiable matter left in the FCG and SCG is also elevated and similar to the other coffees tested, this suggests that the decaffeination process is highly selective for caffeine over alternative biomolecules.

Robusta beans are commonly mixed with Arabica to control the caffeine content and the taste. There is some indication in the literature that Robusta beans have lower levels of lipid in than Arabica.[30, 31] To determine what influence of the composition of the coffee grounds has on the oil content, the lipid was extracted from a range of FCG and SCG samples (figure 3). The coffees selected were made from beans blended from a range of geographical locations and correspond with coffee 'strength' from mild to very strong tasting. The coffees selected were 100% Arabica (mild), 95% Arabica 5% Robusta, 80% Arabica 20% Robusta, 70% Arabica 30% Robusta and 100% Robusta (strong). The total oil recovered from FCGs and SCGs, composed of varying proportions of Arabica and Robusta, ranged from 9.5% to 13.2% and 11.0% to 14.0%, respectively. The 100% Robusta coffee examined in this study did have reduced lipid content relative to the 100% Arabica coffee, although the lipid

contained little unsaponifiable matter. This effect was not as pronounced for the blends of beans, suggesting that the oil yield is not heavily dependent on the composition of the coffee and both types of beans are suitable for biodiesel production.

Coffee is brewed in a variety of ways around the world. The influence of a range of methods was therefore tested to determine if the brewing process affects the lipid content. A Colombian coffee used in the previous extractions was also used in an espresso machine, an aero-press coffee maker and in a filter coffee maker (figure 5). Full details on the type, and method, of brewing are given in the supporting information.

The highest level of lipid recovered from fresh Columbian coffee grounds was 13.5%; for the different brewing methods the oil yield ranged from 10.3% to 13.3%. Filter coffee grounds had the highest oil yield, whilst Aero-press coffee grounds had the lowest. These results suggest the method of brewing has a significant influence on the oil content in the SCG. SCG obtained by the filtered method had an oil content of 8.1%, 15.4% and 28.7% higher than SCG obtained by Cafetière, Espresso and Aero-press, respectively. The FCG and SCG from the filter coffee were not found to be significantly different. The two systems that use pressure to brew the coffee, the Cafetière and Aero press makers, were not significantly different from one another but both were found to be significantly different than the filter coffee. This is presumably due to the conditions employed in the different brewing processes. For filtered coffee the grounds are enclosed in a filter and hot water is poured over them, the filter may retain the majority of the extracted oils in the waste coffee grounds resulting in a higher oil content in the SCG.[28] Whilst the higher pressures employed in the other methods compresses the coffee grounds more effectively, resulting in superior extraction of the oils and more retention of unsaponifiable lipids.

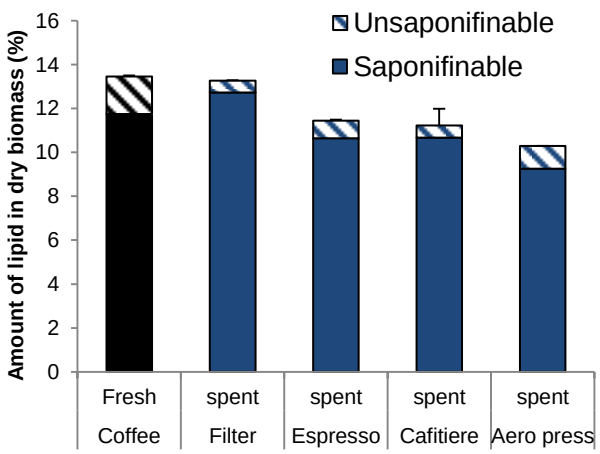

Figure 4. Oil extracted from the same type of coffee subjected to a number of brewing methods, black bars indicate the amount of lipid extracted from FCG, the blue bars indicate the lipid extracted from SCG. The filled area shows the level of saponifiable matter and the striped area, the unsaponifiable lipid.

	Costa Rica		*Honduras*		*Ethiopia*		*Indonesia*		*Kenya*		*Columbia*		*Brazil*		*Vietnam*	
Type	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*
16:0	36.9	35.4	37.2	35.4	36.4	36.4	36.8	36.9	38.1	41.4	36.5	36.7	36.7	37.1	41.0	40.4
18:0	6.7	6.7	7.3	6.7	7.4	7.4	7.4	7.5	7.4	8.2	7.0	7.6	8.2	8.5	12.1	13.5
18:1	6.6	6.7	6.8	6.7	7.4	7.4	6.6	6.6	6.7	7.1	6.7	7.9	8.2	8.3	23.1	24.0
18:2	48.5	49.9	47.4	49.9	46.4	46.4	46.5	46.2	45.3	42.2	47.1	45.1	45.6	44.7	22.9	22.0
18:3	Tr.	Tr.	Tr.	Tr.	1.4	1.4	1.4	1.4	1.4	Tr.	1.4	1.5	Tr.	Tr.	Tr.	Tr.
20:0	1.2	1.2	1.3	1.2	1.0	1.0	1.4	1.4	1.1	1.2	1.2	1.3	1.3	1.4	0.9	0.0

	Peru		*Guatemala*		*India*		*100% Arabica*		*100% Robusta*		*95% Arabica*		*80% Arabica*		*70% Arabica*	
Type	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*
16:0	37.3	41.3	37.0	38.8	37.6	36.8	36.1	36.0	35.4	35.7	36.3	36.5	36.2	36.3	36.8	37.0
18:0	7.4	8.2	6.8	6.9	8.4	8.3	8.1	8.1	7.5	7.6	8.1	8.3	7.8	8.0	7.9	8.0
18:1	6.5	6.7	6.8	6.3	8.0	8.4	7.0	7.0	11.5	11.5	7.6	7.8	7.9	8.0	8.3	8.3
18:2	46.1	42.2	48.2	46.7	43.3	43.8	46.1	46.1	44.5	44.0	45.3	46.1	46.6	46.3	45.6	45.3
18:3	1.4	Tr.	Tr.	Tr.	1.4	1.3	1.4	1.4	Tr.	Tr.	1.4	Tr.	Tr.	Tr.	Tr.	Tr.
20:0	1.3	1.5	1.2	1.2	1.3	1.3	1.4	1.4	1.2	1.2	1.3	1.4	1.4	1.4	1.4	1.4

	De-caffeinated 1		*De-caffeinated 2*		*De-caffeinated 3*		*Colombian FCG*	*Cafetière (Colombian)*	*Filter coffee (Colombian)*	*Aero-press (Colombian)*	*Espresso (Colombian)*
Type	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*FCG*	*SCG*	*SCG*	*SCG*	*SCG*
16:0	36.9	37.4	42.0	40.7	36.5	36.8	36.5	36.7	37.0	37.3	36.5
18:0	7.4	7.5	7.5	7.9	8.4	8.3	7.0	7.6	7.6	7.8	7.7
18:1	7.0	7.2	6.6	6.7	8.2	8.4	6.7	7.9	8.0	8.2	8.0
18:2	46.2	45.4	43.9	43.4	44.3	43.8	47.1	45.1	44.7	45.3	45.1
18:3	1.2	1.3	Tr.	Tr.	1.3	1.3	1.4	1.5	1.5	Tr.	1.5
20:0	1.3	1.3	Tr.	1.2	1.3	1.3	1.2	1.3	1.3	1.3	1.3

Table 1 Weight percent FAME of the biodiesel produced from the coffee samples, FCG = fresh coffee grounds, SCG = spent coffee grounds, Tr = trace, less than 0.5%. The standard deviation for any peak was found to be less than 1% using this method.

Biodiesel properties. The composition of the resulting biodiesel was analysed by GC-MS (Table 1). The fuel properties, and therefore the suitability of an oil for biodiesel production

are highly reliant on the FAME profile.[32] Previous studies on the lipid content of the coffee oil show that the profile is relatively simple, with four major fatty acids; linolenic acid (40-46%),palmitic acid (32-51%), oleic (0-9%) and stearic acid (7 – 8%).[4, 13, 14, 24]

All the coffee oils, with just one exception, had a very similar fatty acid profile, irrespective of the growing conditions, type of bean or brewing method. This is in contrast to terrestrial crops oils[33] and in complete contrast to microbial oils, where the FAME profile can change dramatically when subjected to alternative environmental conditions.[34, 35]

The GC-MS analysis demonstrates that the FAME profile does not change on brewing the coffee, and the polyunsaturated esters are not degraded to any significant extent. This suggests that the resulting coffee oil is reasonably stable. This is in line with previous studies, for example Kondamudi *et al.* found that biodiesel produced from waste coffee grounds had a Rancimat score of 3.05.[4] Though it should be noted that the oxidative stability is more closely related to the method of roasting the bean than any other factor.[31]

While the FAME profile does not change on brewing, the amount of total biodiesel produced from SCG is slightly lower than for FCG. This would suggest that defective beans will produce higher yields of biofuel than waste coffee. However, caffeine is a xanthine based alkaloid and as such contains nitrogen. Caffeine is present in all the oils extracted from FCG, though was not observed in any of the SCG biodiesel (see supporting information). It is preferable to remove nitrogen containing compounds, as their presence can have serious implications for the effective operation of the vehicle by increasing harmful NO_x emissions.[36] For example 130 mg of caffeine in 100 g coffee sample, could lead to the production of around 150 mg / km of excess NO_x, if it was present in the final fuel and fully combusted. This value is almost double the Euro 6 standard.Therefore these results indicate that biodiesel derived from SCG could potentially have better emissions than the comparable biodiesel produced from fresh defective beans.

Only a handful of studies have investigated the fuel properties of coffee derived biodiesel. For example Kondamundi *et al.* investigated the composition and properties of biodiesel produced from oil extracted from SCG derived from a commercial coffee shop. The FAME profile was found to contain 59% saturated esters and 40% linoleic acid, the resulting biodiesel had a viscosity of 5.8 mm^2s^{-1} at 40 °C, a cloud point of 11 °C and a pour point of 2 °C.[4] Oliveira *et. al.* determined that two types of fresh Brazilian bean, one deemed defective and the other suitable for coffee production, produced fuels with variable properties. The

kinematic viscosity of the biodiesel produced from the defective beans was 3.1 mm^2s^{-1} at 40 °C, meanwhile the biodiesel from the non-defective beans was 4.9 mm^2s^{-1} at 40 °C. The densities of the biodiesel samples also varied being 894.1 and 892.5 kg m^{-3} respectively.

The density of biodiesel is an important parameter as it directly affects fuel performance, since fuel injection is operated on a volume metering system.[37] Biodiesel fuels are generally denser and less compressible than diesel fuels regardless of the feedstock, and while there is no limit in the ASTM standards, the density is limited to between 860 – 900 kg m^{-3} by EN 14214. The density of a majority of the fuels produced from the different geographical locations fell within the European standard (Figure 5). The density of the biodiesel produced from the fresh and spent coffee oil obtained from coffee grounds ranged from 844 kg m^{-3} to 927 kg m^{-3}. While there is a lot of deviation across the sample set, the density of the biodiesel produced from the SCG are generally similar to that of the FCG, for the same type of coffee. There is no clear pattern between regional area, the type of bean or whether the coffee has been decaffeinated (figure 6).

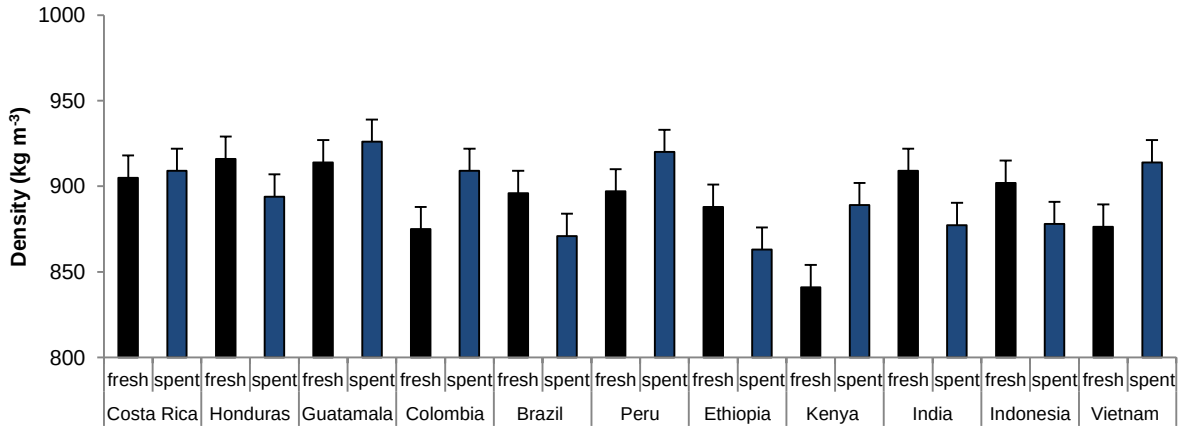

Figure 5. Densities of the FAME produced from coffee sourced from a range of geographical locations, black bars indicate FCG, the blue bars indicate SCG.

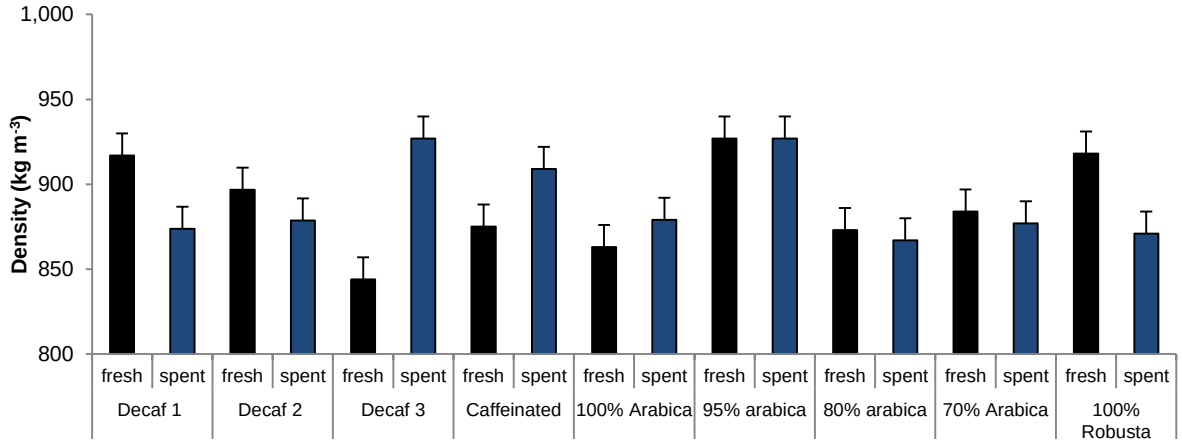

Figure 6. Densities of the FAME produced from coffee sourced from a range of different strength coffees including decaffeinated coffee. Black bars indicate FCG, the blue bars indicate SCG.

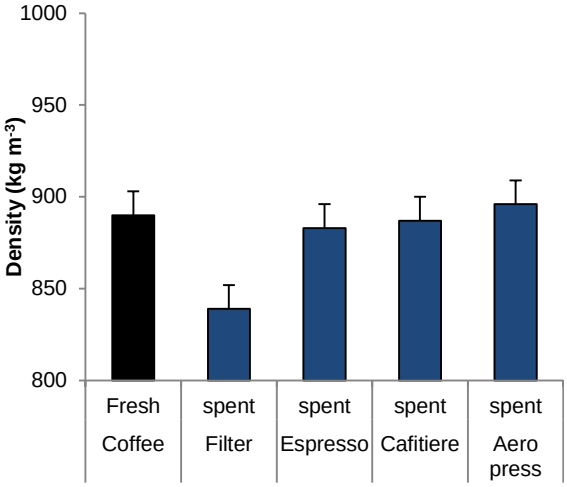

Figure 7. Densities of the FAME produced from the same type of coffee subjected to a number of brewing methods, black bars indicate from FCG, the blue bars indicate from SCG.

The density of the biodiesel for the Colombian FCG and SCG made from the espresso, cafetière and aeropress methods was highly similar, though this was reduced for the filter SCG (figure 7). This suggests that whatever is being removed on brewing the coffee with these pressurised systems has little effect on the density of the resulting fuel.

The kinematic viscosity of the biodiesel is also an important parameter as it affects the way the fuel flows through the engine and the atomization on injection. The ASTM standards for biodiesel state that the kinematic viscosity must lie between 1.9 and 6.0 $mm^2\ s^{-1}$ at 40 °C. EN 14214 is more restrictive and biodiesel sold in the EU must have a kinematic viscosity of between 3.5 – 5.0 $mm^2\ s^{-1}$ at 40 °C. All the coffee biodiesel samples were analysed using a

kinematic viscometer at 40 °C (Figures 8 - 10). The biodiesel produced from the different regions generally lies between 3.5 and 5 mm^2 s^{-1} and is comfortably within both European and American standards, as well as being similar to the previously published Brazilian coffee FAME.[13] The only outlier is the Kenyan coffee, which has a viscosity of 5.89 mm^2 s^{-1} which is only reduced slightly in the SCG biodiesel.

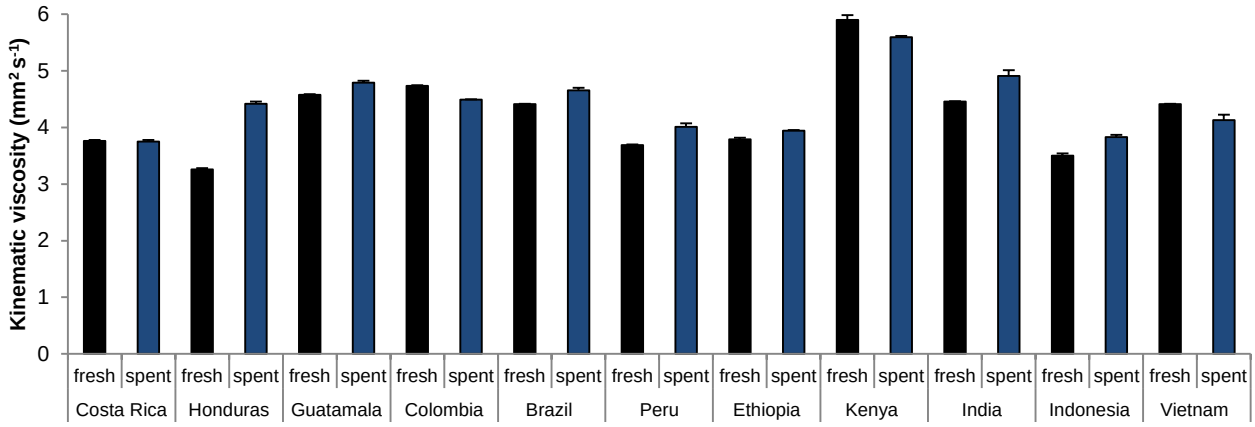

Figure 8. Kinematic viscosity of the FAME produced from coffee sourced from a range of geographical locations, black bars indicate the biodiesel was produced from FCG, the blue bars indicate from SCG.

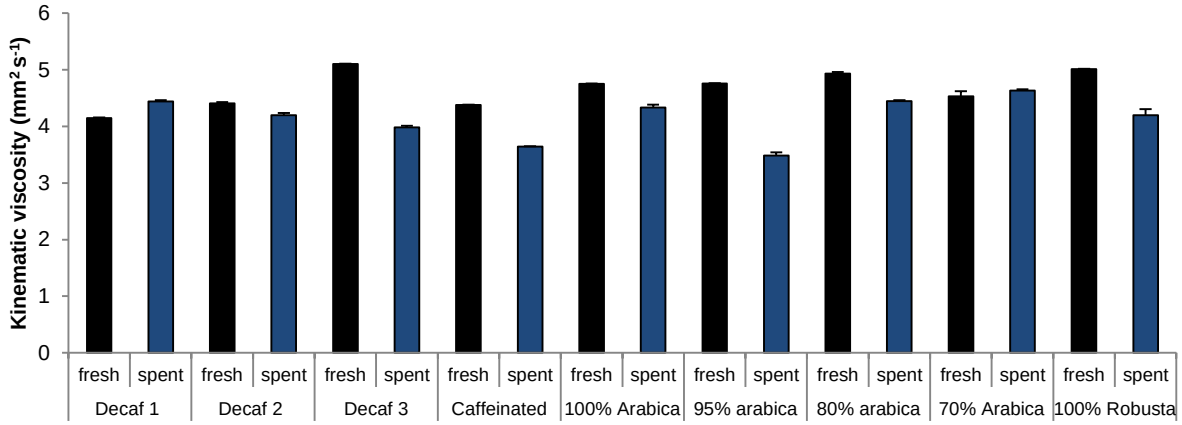

Figure 9. Kinematic viscosity of the FAME produced from coffee sourced from a range of different strength coffees including decaffeinated coffee. Black bars indicate FCG, the blue bars indicate SCG.

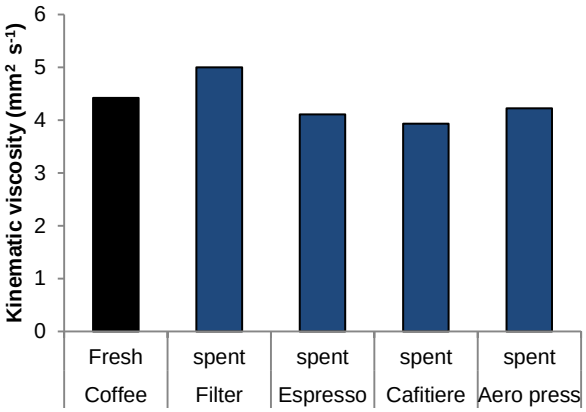

Figure 10. Kinematic viscosity of the FAME producedfrom the same type of coffee subjected to a number of brewing methods, black bars indicate from FCG, the blue bars indicate from SCG.

The viscosity of the biodiesel produced from the decaffeinated coffee and from the varying proportions of Arabica and Robusta all range between 3.5 and 5.0 mm^2s^{-1}, and are also comfortably within the EU and US fuel standards. Interestingly the viscosity of the biodiesel increases slightly when the grounds have been put into a filter coffee maker. The harsher methods, such as using the cafetière or espresso machine reduce the viscosity slightly. This demonstrates that different compounds which affect the viscosity are being removed under the different conditions. This effect is large, and goes someway to explaining the discrepancy between the similar FAME profiles having variable fuel properties.

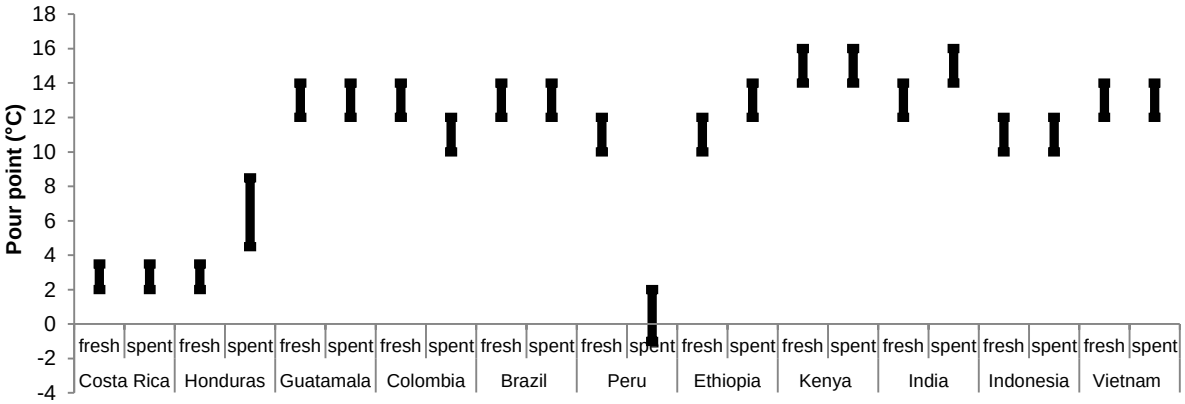

Figure 11. Pour points of the FAME produced from coffee sourced from a range of geographical locations, black bars indicate FCG, the blue bars indicate SCG.

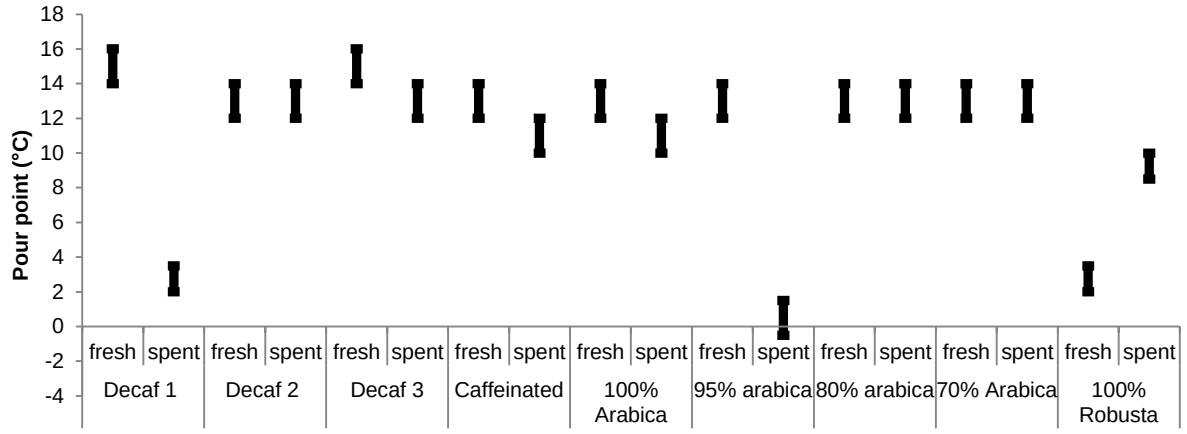

Figure 12. Pour points of the FAME produced from coffee sourced from a range of different strength coffees including decaffeinated coffee. Black bars indicate FCG, the blue bars indicate SCG.

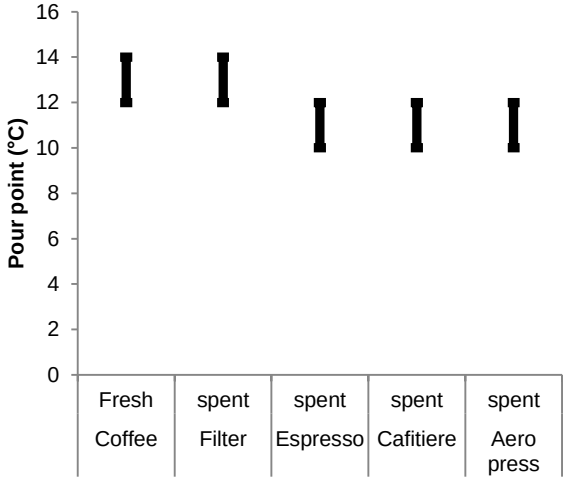

Figure 13. Pour points of the FAME producedfrom the same type of coffee subjected to a number of alternative brewing methods, black bars indicate from FCG, the blue bars indicate from SCG.

The pour point of biodiesel from fresh and spent coffee oil obtained from all the samples tested ranged from between -1.0 °C to 16 °C (Figures 11-13). Though there is no clear trend, generally across the sample set the SCG have a similar or lower pour point to biodiesel produced from FCG. The coffee biodiesels produced have roughly 50% saturated esters. Based on this, it would be expected that the biodiesel would have a similar pour point to palm oil, which is between 10-16 °C.[32] While most samples are comparable, some have sub-zero pour points. This could be due to further biomolecules in the biodiesel disrupting the stacking between the saturated esters. Brewing the coffee with a technique that uses pressure (the Aero-press, cafetière or espresso maker) did not change the pour point substantially over the FCG.

4. Conclusions

Waste coffee grounds contain between 7 – 14 % lipids with a significant glyceride portion that can be transesterified into biodiesel. The amount of lipid in the coffee does vary from coffee type though this cannot simplistically attributed to geographic region or the type of bean. The amount of unsaponifiable lipid also varies and can be as high as 40% in some oils. The unsaponifiable lipid is generally less prevalent in the spent coffee than it is in the fresh; this means that similar biodiesel production levels are achieved for both the fresh and the spent coffee grounds. The FAME profile produced hardly varies irrespective of the region or processing, and contains high levels of palmitic and linolenic acid and lower levels of stearic and oleic acid. Biodiesel produced from SCG does not contain caffeine unlike the FCG biodiesel which could potentially lead to increased NO_x emissions. Some of the key fuel properties were also reasonably variable across the samples analysed with the kinematic viscosity being between 3.5 – 5.5 $mm^2\ s^{-1}$, the density being between 841 – 927 kg m^{-3} and the pour point being between -1 – 16 °C. However, all the biodiesel produced would be suitable for use in both the USA and Europe when blended to the recommended level.

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