Waste Biomass Valor (2017) 8:1237–1245
DOI 10.1007/s12649-016-9715-x

ORIGINAL PAPER

Production of Biodiesel from Vietnamese Waste Coffee Beans: Biofuel Yield, Saturation and Stability are All Elevated Compared with Conventional Coffee Biodiesel

Rhodri W. Jenkins[1] · Emrys H. Ellis[1] · Emily J. Lewis[1] · Michael Paterson[1] · Chien Dinh Le[2] · Valeska P. Ting[1] · Christopher J. Chuck[1]

Received: 21 May 2016 / Accepted: 22 September 2016 / Published online: 27 September 2016

Abstract The suitability of biodiesel produced from spent Vietnamese coffee was examined. Previous work shows that the geographical origin of coffee beans has little effect on the composition and physical properties of the biodiesel produced Jenkins et al. [1]. Vietnamese coffee, however, is roasted in a range of fats and oils for flavour enhancement and therefore has a unique fatty acid profile. The oil yield and biodiesel properties of three Vietnamese coffees were assessed and compared to a coffee of more typical composition—Colombian—and traditional biodiesel feedstocks (rapeseed, sunflower and palm). The oil yield from fresh Vietnamese coffee was higher (12.0–14.0 %) than Colombian coffee (9.3 %), while the oil yield from spent Vietnamese coffee (9.3–10.4 %) was comparable to the Colombian coffee (9.5 %). The unsaponifiable matter was only present in low levels in the Vietnamese coffee (1.9–4.9 %) compared to Colombian coffee (30.4 % fresh, 21.4 % spent). Vietnamese coffee biodiesel was more saturated than Columbian coffee biodiesel. It was therefore more viscous and had a higher pour point than the Colombian coffee, and possessed properties more akin to palm biodiesel. Vietnamese coffee biodiesel would therefore be a suitable feedstock for use locally due to the more suitable climate and compatibility with the palm feedstock that is currently used.

Graphical Abstract Spent coffee grounds from Vietnam is demonstrated to be a suitable source of biodiesel

Keywords Bioenergy · Biofuels · Coffee waste · Vietnam · Waste valorization

Abbreviations

VCS1	Vietnamese coffee sample 1
VCS2	Vietnamese coffee sample 2
VCS3	Vietnamese coffee sample 3
CC	Colombian coffee
FAME	Fatty acid methyl ester

Introduction

Biodiesel, the fatty acid methyl esters (FAMEs) obtained *via* the transesterification of triglycerides with methanol, typically represents between 15–25 % of annual global biofuel production [2–4]. Approximately 95 % of global biodiesel is derived from edible, first generation oils such as palm, rapeseed and soybean [5]. While the technology is well developed there is simply not enough arable land to increase biofuel production to meet global need and alternative feedstocks are being urgently sought.

An alternative option for biodiesel production is the use of feedstocks which don't compete with arable land, i.e. second generation feedstocks. These come in two

Electronic supplementary material The online version of this article (doi:10.1007/s12649-016-9715-x) contains supplementary material, which is available to authorized users.

✉ Rhodri W. Jenkins
Rhodri.w.jenkins@bath.edu

[1] Department of Chemical Engineering, University of Bath, Claverton Down BA2 7AY, UK

[2] Department of Oil Refining and Petrochemistry, Hanoi University of Mining and Geology, Duc Thang, Bac Tu Liem, Hanoi, Vietnam

general forms—non-edible oils and waste oils. Non-edible oils can be grown on marginal land [6] (i.e. not suitable for growing edible plants), the most promising of which are the high oil-yielding crops *Jatropha* [7] and *Pongamia* [8]. However, regardless of whether an oil is edible or not, cultivating a feedstock specifically for biodiesel production can account for >70 % of the overall biodiesel cost [9]. Therefore, waste oils such as cooking oils and animal fats could represent a more economical route to biodiesel [10], as costs associated with the feedstock cultivation are effectively zero. Another such promising waste resource is spent (i.e. post-brew) coffee grounds, which are reported to contain between up to 20 % of saponifiable lipid, which is comparable to traditional terrestrial biodiesel feedstocks [1, 11]. Approximately 8 million tonnes of coffee grounds are produced annually [12], and it represents a relatively pure waste stream that could be used for biofuel production. A number of studies have demonstrated the suitability of coffee biodiesel as a potential fuel feedstock [13–17]. While these studies used coffee from various local areas the fatty acid profile was relatively constant, consisting of four major fatty acids; palmitic acid (C16:0, ~35 %), stearic acid (C18:0, ~8 %), oleic acid (C18:1, ~5 %) and linoleic acid (C18:2, ~44 %).

Our previous studies have similarly demonstrated that the country of origin had little effect on the lipid profile of the coffee oil produced except when the coffee was sourced from Vietnam. Vietnamese coffee oil was shown to have elevated levels of saturates in comparison to other coffee oil feedstocks [1].

Vietnam is the second largest producer globally, accounting for 15 % of global coffee production (Fig. 1). The coffee production in Vietnam is mainly concentrated in the South, with the province of Dak Lak contributing about 43 % of the national coffee produced. Vietnamese coffee is particularly famous for a niche product where the coffee beans have been eaten and partially digested by civet cats, or 'weasels' prior to brewing [18]. In this process the green beans are harvested from the dung and roasted. The digestion process breaks down some of the proteins in the coffee, resulting in a smooth, less bitter flavour. While the vast majority of Vietnamese coffee is not produced in this way, the roasting process in the region has changed in an attempt to replicate 'civet' coffee's characteristic flavour. The major difference is that the beans are roasted in salt, sugar and butter up to 240 °C [18]. This is likely the reason for the difference between the fatty acid profiles.

Biodiesel, however, is not a perfect drop-in biofuel in terms of its physical properties. One of the main issues of biodiesel are its poor oxidative stability, due to the relatively facile abstraction of the bisallylic protons present in polyunsaturated fatty acids [19]. The high temperature processing conditions that coffee beans and grounds are subjected to, i.e. roasting and brewing, may partially degrade the composition of the fatty acids present and will significantly reduce the level of natural antioxidants in the coffee [20]. Another issue with biodiesel is its cold flow properties—the high levels of saturated fatty acids in the lipid feedstock can lead to high cold filter plugging points which would inhibit its use in colder climate areas [8]. This effect can be ameliorated by the use of other alcohols for the triglyceride transesterification to fatty acid alkyl esters [21], however methanol is largely used due to its relatively low cost. The higher level of saturates level present in Vietnamese coffee oil, therefore, could cause the biodiesel produced from it to fall out of fuel specification.

In this study, the Vietnamese coffee biodiesel from three different sources was assessed. This was to determine their FAME profiles, physical fuel properties and ultimately their suitability as feedstocks for biodiesel production. The Vietnamese coffee biodiesels were compared to a typical coffee biodiesel in terms of FAME profile (Columbian, as determined in our previous work [1]) and traditional biodiesel commercial feedstocks (rapeseed, palm and sunflower).

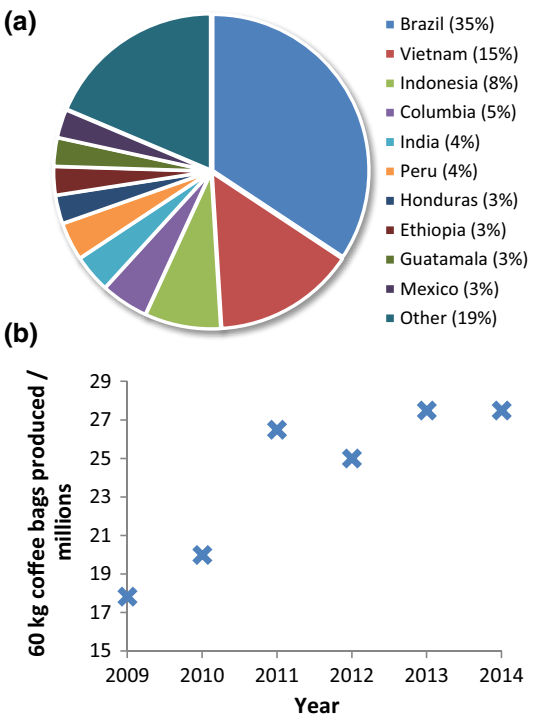

Fig. 1 **a** Total production of green coffee beans in 2012, adapted from data from the UN Food and Agricultural Organization [35], and; **b** Annual coffee production in Vietnam, adapted from data from the International Coffee Organization [36]

Materials and Methods

Materials

The Vietnamese coffee grounds were purchased *via* an online retailer (Weasel Coffees, www.weaselcoffees.com). Three different Vietnamese coffees were investigated, originally purchased from Weasel Coffees. These were Vietnamese coffee sample 1, sold under the brand name "Mr. Phong" (VCS1), Vietnamese coffee sample 2 sold as "Masterpiece coffee" (VCS2) and Vietnamese coffee sample 3 sold as "Café Blend" (VCS3). As a comparison, an alternative coffee of Colombian origin was purchased from a local high-street coffee shop. Rapeseed, sunflower and palm oil were purchased from local retailers. Hexane [high-performance liquid chromatography (HPLC)-grade], sulfuric acid (glacial), methanol (99.5 %+), chloroform (99.5 %+), d-chloroform (99.9 %+) and ethyl acetate (analytical grade) were purchased from Sigma Aldrich, UK and were not purified prior to use.

Methods

Brewing

Freshly boiled water (1 L) was added to a French press coffee maker, before the immediate addition of fresh coffee grounds (100 g). The mixture was manually agitated until all the coffee grounds were submerged. The mixture was brewed for exactly 5 min before the plunger was depressed and the liquid fraction was poured off. The solid fraction (spent coffee grounds) was separated *via* gravity filtration, and dried in an oven at 65 °C for 24 h to remove the water.

Lipid Extraction

Lipid extraction was carried out according to an adapted method given by Jenkins et al. [1] Coffee grounds were accurately weighed and added to a suitably sized borosilicate glass vessel, before the addition of hexane according to the following equation:

$$\text{Volume of hexane (mL)} = 10 \times \text{mass of coffee grounds (g)} \quad (1)$$

The mixture was stirred for 3 h, before being filtered and washed further with hexane (100 mL). The hexane was then removed *in vacuo* to yield a clear brown oil.

Biodiesel Production (Transesterification)

The coffee oil (5 g) was accurately measured and added to an excess of methanol (~50 mL) and sulfuric acid (10 wt% in relation to the oil). The mixture was then refluxed for 24 h. Upon completion, the reaction mixture was filtered to determine the amount of unsaponifiable material produced. To this, distilled water (100 mL) and chloroform (100 mL) were added to solubilize the polar and non-polar components and aid in phase separation. The organic layer was then washed a further three times with distilled water (100 mL) to remove any unreacted methanol, acid catalyst and glycerol. The chloroform was then removed *in vacuo* to yield a clear brown oil. The resulting oil was then analysed *via* nuclear magnetic resonance (^{1}H NMR), according to previous studies [22], to ensure >99 % of the glyceride species had reacted.

Oxidative Stability Testing

The biodiesel sample (10 mL) was held at 110 °C for 6 h with a constant airflow bubbled through at a rate of 6.67 $cm^3\ s^{-1}$. 0.5 mL aliquots were taken hourly for a total of 6 h, before analysis *via* ^{1}H NMR.

Biodiesel Analysis

Composition Analysis The FAME profile of the biodiesel was analysed using an Agilent 5977B gas chromatograph mass spectrometer (GC/MS), equipped with a capillary column (60 m × 0.250 mm internal diameter) coated with a DB-23 ([50 % cyanpropyl]-methylpolysiloxane) stationary phase (0.25 μm film thickness) and a He mobile phase (flow rate of 1.2 mL min^{-1}). Approximately 50 mg of the sample was dissolved into 10 mL of ethyl acetate, and 1 μL of each solution was loaded onto the column and preheated to 150 °C. This temperature was held for 5 min, then the sample was heated to 250 °C at a rate of 2 °C min^{-1}, and held for 2 min. NMR spectroscopic measurements were carried out at 25 °C using a Bruker AV300 spectrometer, operating at 400 MHz. Spectra were referenced to the residual $CHCl_3$ peak from the solvent (δ, 7.26 ppm).

Bulk Physical Property Analysis 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 min prior to viscosity measurement to allow for temperature equilibration. The standard error was found to be ±0.100 $mm^2\ s^{-1}$ at 40 °C. Pour points of the fuels were determined visually by cooling of 1.5 mL vials of the samples in a low-temperature freezer, 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 min to

allow for temperature equilibration. Densities were determined gravimetrically by accurately weighting 10 ± 0.01 cm^{-3} of sample to an accuracy of ± 0.0005 g. A Grant IKA C1 Calorimeter compact bomb calorimeter was used for all energy density analyses, in accordance to DIN 51900.

Results and Discussion

Sample Sets

Each type of coffee had a unique combination of coffee beans or is roasted using a distinctive method. VCS1 and VCS2 contained a mixture of Robusta and Arabica beans with 10 % of domesticated weasel coffee. The beans were sourced from the Buon Ma Thuot region in the province of Dak Lak. In addition, VCS2 were roasted using a traditional method coating the beans in a mixture of butter and chocolate. VCS3 contained purely peaberry robusta beans and, as such, had a higher caffeine content than VCS1 or VCS2. The extraction efficiency, chemical composition, and properties of the biodiesel obtained was compared to that of coffee beans of more typical composition (Colombian coffee [CC1]), as well as common biodiesel feedstocks (rapeseed, sunflower and palm oils).

Lipid Extraction

Hexane has been demonstrated to be the most suitable solvent for extraction of the oil [14] and was used in this study. Upon extraction of both fresh and spent coffee grounds, the average yield of coffee oil from fresh Vietnamese coffee grounds ranged from 12.0–14.0 wt% (Fig. 2). Extracting spent Vietnamese coffee grounds yielded slightly less oil (9.3–10.3 wt%) presumably as small amounts of the lipid were solubilised in the hot brewing process. The overall loss of coffee oil was minimal (between 2 and 3 %). These oil yields were consistent with those in the literature [16]. Little difference was seen between lipid yields of VCS1, VCS2 and VCS3.

The coffee of Colombian origin (CC1), however, showed lower levels of extracted coffee, with 9.3 wt% for fresh and 9.5 wt% for spent. This is likely due to the process of Vietnamese coffee roasting which adds oils and fats and therefore increases the overall available lipid for extraction [18]. Roasting the beans in oil and butter leads to a significant amount of oil on the surface of the resultant grounds, rather than within the grounds themselves. This would result in the greater lipid yields from the fresh coffee grounds. Loss of this excess surface lipid in the brewing process would also explain the reduction in oil yield from Vietnamese coffee after brewing, while very little

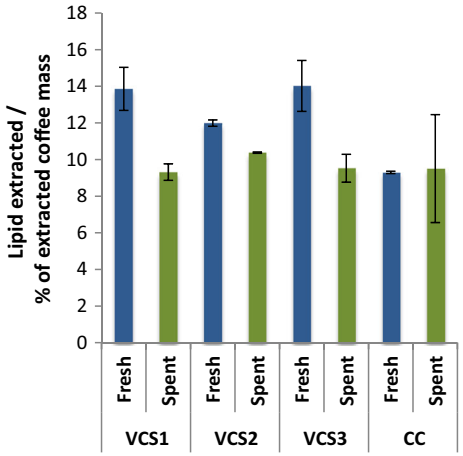

Fig. 2 Lipid extraction (by percentage of extracted coffee mass) of different coffees

difference is seen between the fresh and spent Colombian coffee. This was also consistent with observations of the oils when purified *in vacuo* and allowed to cool to room temperature. A portion of each Vietnamese coffee oil solidified leading to a two-phase product, likely caused by the saturates present in butter and cocoa lipids, while the CC1 oil remained as a liquid (see supporting information).

Transesterification/Unsaponifiables

After extraction, the coffee oil was transesterified using an excess of methanol and sulfuric acid as a catalyst. This method produced a blue-black solid unsaponifiable material [1]. The unsaponifiable material was separated from the reaction mixture through gravity filtration once the reaction period was complete, the biodiesel was isolated using hexane and washed with distilled water to remove any traces of unreacted material, co-products and catalyst, before being dried *in vacuo* (Fig. 3). The CC1 oil contained significantly more unsaponifiable material (30.3 wt% fresh; 21.39 wt% spent) than the Vietnamese coffee samples (2.2–4.9 wt% fresh; 1.8–4.8 wt% spent). While this will in part be due to the presence of non-coffee lipids in the Vietnamese coffee samples, leading to a reduction in the proportion of unsaponifiable lipids present, it might also be a characteristic of Vietnamese coffee in general. For both coffee types, however, brewing led to a reduction in unsaponifiable material as presumably much of this material is extracted in the brewing process.

The lack of unsaponifiable material in Vietnamese coffee is supported by the ^{1}H NMR analysis of the oils extracted (see supporting information). Typical unsaponifiable sterols present in coffee oil are kahweol and cafestol [23], which are observed in the ^{1}H NMR of the CC1 oil, though entirely lacking in the spectra of the three Vietnamese coffee oils.

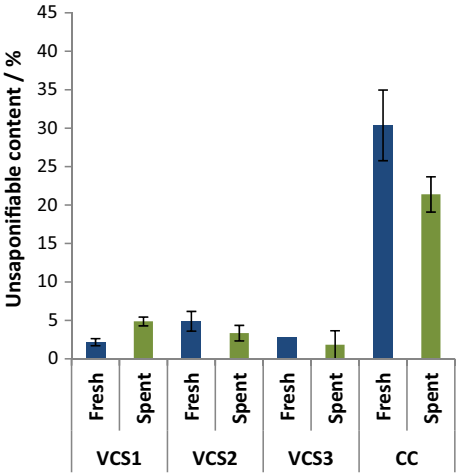

Fig. 3 Unsaponifiable content (by percentage of the mass of coffee oil transesterified) of the different coffees assessed

FAME Profile

The FAME profile of a biodiesel determines the physical properties of the fuel produced [2]. The FAME profile of the coffee biodiesel was analysed by GC–MS and compared to more common biodiesel feedstocks (Table 1). As expected, the CC1 FAME profile varied little from previously reported values containing methyl palmitate (C16:0, 37 %), methyl linoleate (C18:2, 46 %), methyl stearate (C18:0, 8 %) and methyl oleate (C18:1, 8 %) as well as small amounts (~1 %) of methyl linolenate (C18:3) and methyl arachidate (C20:0) [1].

The three Vietnamese coffee biodiesels, however, possessed significantly different FAME profiles to the other coffee biodiesels, with significantly higher amounts of methyl oleate (C18:1, 24.7–26.5%), and lower amounts of methyl linoleate (C18:2, 23.1–26.3 %). The lack of variation between the three Vietnamese coffees shows that the different processing methods used within Vietnam have little effect on the overall fatty acid profile. Also present in the Vietnamese coffee biodiesel were small amounts (2.3–5.3 %) of methyl laurate (C12:0), typically found in butter and vegetable oils [24]. The greater proportions of saturated and monounsaturated FAMEs, as well as the lower levels of polyunsaturated FAMEs will have a significant impact on the physical properties of the oil and subsequent biodiesel produced.

Fuel Properties

To assess the suitability of Vietnamese coffee biodiesel, a number of fuel properties were examined and compared to biodiesel produced from rapeseed, sunflower and palm oils. These have largely differing FAME profiles. Palm biodiesel had fairly equal proportions of saturates (50.7 %) and unsaturates (49.4 %), while rapeseed and sunflower possessed much higher amounts of total unsaturates, with 92.6 and 89.6 % respectively.

Kinematic Viscosity

The kinematic viscosity is a measure of flow resistance, and is one of the most important aspects of a fuel as it affects its handling, pumping and atomisation [25]. The international standards for biodiesel specification state that the viscosity of biodiesel (at 40 °C) must be between 3.5 and 5.0 $mm^2\ s^{-1}$ in the EU (EN 14214) [26], or between 1.9 and 6.0 $mm^2\ s^{-1}$ in the US (ASTM D6751) [27]. The three Vietnamese coffees all exhibited similar viscosities to one another with the fresh samples having a viscosity between 3.30 and 3.96 $mm^2\ s^{-1}$ which rose to 4.23–4.32 $mm^2\ s^{-1}$ for the spent coffee fuels (Fig. 4). Presumably this is due to the extraction of small amounts of water-soluble biomolecules during the brewing process, which interupt the stacking of the linear fatty acid chains. The viscosity of the Colombian coffee biodiesel decreased slightly upon brewing (from 3.70 to 3.36 $mm^2\ s^{-1}$). The significantly lower viscosity of the spent CC1 biodiesel, however, is likely due to the higher proportion of polyunsaturates present [28]. Rapeseed and sunflower biodiesels had similar viscosities of 3.83 and 3.86 $mm^2\ s^{-1}$ while due to the higher saturated profile the palm biodiesel had a far high viscosity (4.35 $mm^2\ s^{-1}$). The viscosity of the Vietnamese coffee biodiesel was far more similar to the palm-derived biodiesel than other biodiesels examined.

Despite the wide variation in viscosity, all biodiesels produced fell within the US standard for biodiesel, and most fell within the EU standard. The exceptions, fresh VCS2 and spent CC1, exhibited viscosities of 3.30 and 3.36 $mm^2\ s^{-1,}$ respectively, which falls below the EU standard minimum of 3.5 $mm^2\ s^{-1}$. While this is narrowly out of specification it should be noted that the European standard for diesel (EN 590) which can include up to 7 % of biodiesel outlines the required viscosity be within 2.0 and 4.5 $mm^2\ s^{-1}$ [29].

Pour Point

The pour point of a fuel is the lowest temperature at which the fuel flows before gelling. Operating an engine below a fuel's pour point therefore causes major operability issues [28]. Biodiesel typically has a higher pour point than its petrodiesel counterpart, and therefore cannot be used in high blends at low temperatures.

Little difference was observed between the Vietnamese and Colombian derived coffee biodiesels, though the pour points of the biodiesel obtained from fresh and spent

Vietnamese and Colombian coffee exhibited some variation, between 3.0 and 7.5 °C (Fig. 5). There is no clear trend between the effect of brewing, or the different treatment techniques of the Vietnamese coffees. Again, however, the Vietnamese coffee biodiesel was far more similar to palm oil biodiesel (9.5 °C) than either rapeseed (−15.5 °C) or sunflower (−5 °C). The slightly reduced pour points between the coffee and palm fuels could be due to the presence of alternative biomolecules which inhibit sufficient stacking of the fatty acid chains, or the higher proportion of polyunsaturates in the coffee biodiesel.

While the pour points of the biodiesel derived from coffee are not suitable for use in cold climates, they are suitable for warmer climates and could be used locally in Vietnam, as well as other regions that rely on palm biodiesel currently.

Energy Density

The energy density, or calorific value, is the energy obtainable from a fuel *via* combustion per unit mass, and therefore fuels of varying energy density alter the vehicle range achievable. Biodiesel typically possesses a lower energy density than traditional hydrocarbon based fuels (roughly 10–12 % lower) due to the presence of oxygen in its molecular structure [30]. While there is no specific

Table 1 Mass percent FAME present in the biodiesel produced from extracted coffee oils, and common biodiesel feedstocks used for comparisons in structure and physical properties in this study

FAME	Coffee oil biodiesel								Comparisons		
	VCS1		VCS2		VCS3		CC1		Palm (%)	Rapeseed (%)	Sunflower (%)
	Fresh (%)	Spent (%)	Fresh (%)	Spent (%)	Fresh (%)	Spent (%)	Fresh (%)	Spent (%)			
12:0	4.6	4.6	4.8	5.3	2.3	4.6	0.0	0.0	0.0	0.0	0.0
16:0	38.4	37.8	39.0	38.4	39.9	38.2	35.0	35.0	44.4	5.1	6.6
18:0	5.8	5.5	5.6	5.5	5.8	5.5	7.3	7.0	4.6	1.7	3.8
18:1	25.5	25.9	25.1	26.6	24.7	25.3	8.6	8.5	39.8	64.1	28.5
18:2	24.4	24.9	24.2	23.1	26.3	25.1	45.1	45.5	10.6	20.0	60.9
18:3	0.3	0.2	0.3	0.1	0.9	0.1	1.5	1.6	0.3	8.5	0.2
20:0	1.0	1.1	0.9	1.0	0.1	1.2	2.5	2.3	0.4	0.6	0.0
Saturates	49.8	49.0	50.3	50.2	48.1	49.5	44.8	44.3	49.4	7.4	10.4
Monounsaturates	25.5	25.9	25.1	26.6	24.7	25.3	8.6	8.5	39.8	64.1	28.5
Polyunsaturates	24.7	25.1	24.5	23.2	27.2	25.2	46.6	47.1	10.9	28.5	61.1
Total unsaturates	50.2	51.0	49.6	49.8	51.9	50.5	55.2	55.6	50.7	92.6	89.6

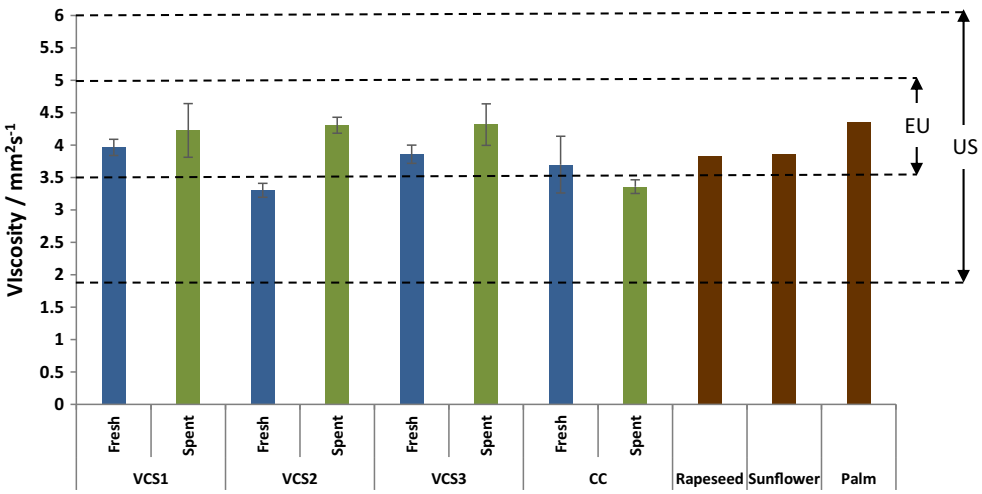

Fig. 4 Kinematic viscosity (at 40 °C) of the FAME produced from different coffee sources (both fresh and spent), and traditional biodiesel sources, showing the allowed ranges for biodiesel in both EU and US fuel specifications

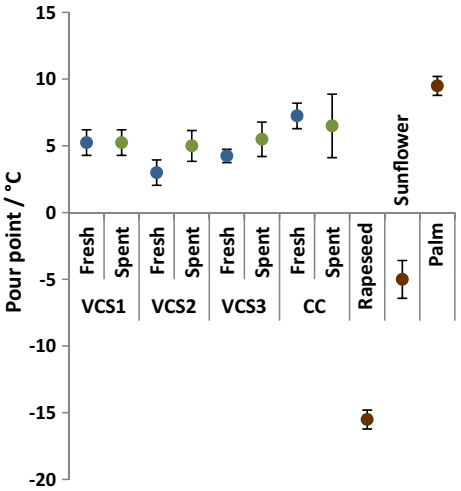

Fig. 5 Pour point of the FAME produced from different coffee sources (both fresh and spent), and traditional biodiesel sources

energy density requirement outlined in either European or US standards, a higher energy density is desirable and petrodiesel has a typical energy density of 45 MJ kg^{-1}.

The energy densities of the biodiesel obtained from fresh and spent Vietnamese and Colombian coffee showed some significant variation, with most falling between 35.0 to 38.0 MJ kg^{-1} (Fig. 6), with the exception of VCS2 fresh coffee biodiesel, which possesses a significantly lower energy density (32.0 MJ kg^{-1}). All the spent coffee biodiesel was similar to the other standard rapeseed, palm and sunflower biodiesels, with just the fresh coffee biodiesel differing significantly. Again, this is most likely due to the presence of alternative oxygenated biomolecules that are removed on brewing.

Nitrogen Content

Caffeine is a xanthine based alkaloid containing four nitrogen atoms. Caffeine was found to be present (via ^{1}H NMR) in all the biodiesels extracted from the fresh coffees, whether Vietnamese or Colombian, though was not observed in biodiesel derived from the spent coffees (See supplementary information). The presence of nitrogen-containing compounds may, upon combustion, produce harmful mono-nitrogen oxides (NO_x) which are potent greenhouses gases and contribute to ozone and smog formation [31].

The amount of caffeine present can be calculated from the ^{1}H NMR spectroscopy, using the integration values for the FAME methoxy group (δ 3.6 ppm) and the shift for the aromatic proton in caffeine's structure (δ 7.45 ppm) [1]. For the VCS1 fresh coffee oil, the approximate amount of caffeine present is 2.5 mol%. Caffeine would therefore account for 1.6 % of the weight of the fuel, or 21.5 g L^{-1}.

Current European standards quote the emission limits of a car in g km^{-1}. Assuming an average fuel consumption of a diesel car of 4.5 litres per 100 km (combined fuel consumption of a 2015 Ford Focus 1.6 L TDCi), 0.045 litres of fuel would be combusted each km, in which 0.648 g of caffeine would be present. Assuming complete combustion of the caffeine, and that an even amount of NO and NO_2 are produced, this would equate to 0.507 g of NO_x per km. The current European legislation on emissions, Euro 6, allows only 0.080 g km^{-1} NO_x. Irrespective of the level of NO_x produced from atmospheric nitrogen, caffeinated fuels would not be permissible in the EU. It is therefore necessary for coffee biodiesel to be solely produced from used coffee grounds and not from rejected beans or FCG.

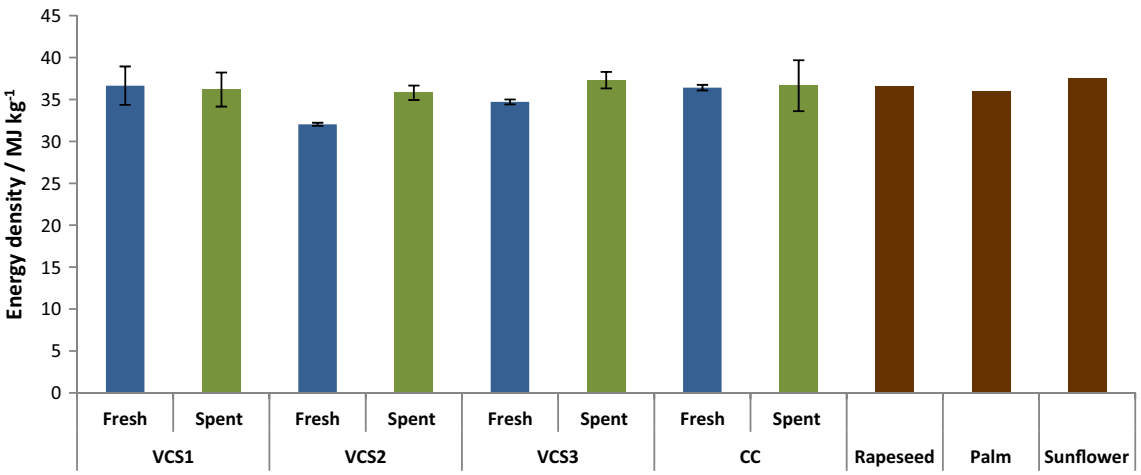

Fig. 6 Energy densities of the FAME produced from different coffee sources (both fresh and spent), along with traditional biodiesel sources

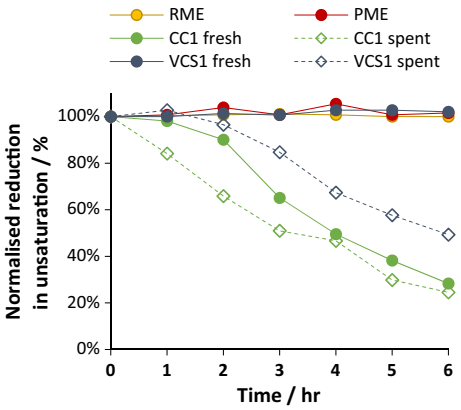

Fig. 7 Normalised reduction in unsaturation (as found in Chuck et al. [32]) calculated from the ^{1}H NMR of the biodiesel samples held at 110 °C under a constant airflow

Oxidative Stability

Oxidative stability is a key factor to consider when storing biodiesel. If the oxidative stability of the biodiesel is poor it will degrade during storage. This can lead to solid deposits and the formation of contaminants including alcohols and acids, and these in turn can have a damaging effect on the engine of a vehicle [32]. Research has shown that biodiesel is less stable than regular diesel due to an increased proportion of unsaturated molecules [33]. The stability of the biodiesel can be affected by many different parameters, including the composition, oxygen content and the presence of antioxidants. The composition of the biodiesel is one the most important factors, as different bond types will be more prone to oxidation than others. The methylene group situated at allyic positions to the double bonds will be the first to be oxidised, and these will further trigger the cyclic reaction due to the formation of hydroperoxide ions [32].

All of the samples were held at 110 °C under a constant airflow and the mixture sampled regularly. The samples were analysed by ^{1}H NMR and the decrease in the number of bisallyic, olefinic and allyic groups present in the biodiesel was assessed according to literature methods (Fig. 7) [19]. There was little degradation observed over this time period for the fresh Vietnamese coffee samples, however the spent Vietnamese coffee biodiesel had significantly degraded over the 6 h period. It seems likely that the proportion of antioxidants was reduced significantly upon brewing. Coffee is known to contain many different antioxidants including, chlorogenic acids, caffeine, niacin and tocopherols, most of which are removed during the brewing process [34]. In comparison, both the fresh and spent Colombian coffee started to degrade under these accelerated conditions. The fresh coffee biodiesel started to degrade after 2 h whereas the spent coffee degraded immediately. This demonstrates that the spent coffee biodiesel is more unstable than the fresh, though the standard Colombian coffee had a far lower stability than the Vietnamese biodiesel. This is presumably due to the lower proportions of polyunsaturates in the Vietnamese coffee samples, though the unique roasting method of Vietnamese coffee may introduce other antioxidants into the biodiesel, which could increase its stability,

All of the standard biodiesel samples were stable throughout this testing. Although the rapeseed contains a very large proportion of unsaturated molecules (96 %) the majority of these are in the form of 18:1 (69 %), the most stable form of unsaturation. Palm oil has a larger proportion of saturation (49 %), which is likely to be the cause of its stability especially where (40 %) is 18:1. However, this elevated stability is presumably due to the level of antioxidants in the lipid, and it seems likely that coffee biodiesel would need additional additives to increase the stability to an acceptable level.

Conclusions

Three representative samples of Vietnamese coffee was assessed for its suitability as a biodiesel feedstock in terms of its lipid content, as well as the physical fuel properties of the biodiesel produced. Vietnamese coffee is roasted very differently from coffee elsewhere in the world, using butter and oil to enhance certain flavours. The level of oil extracted was slightly higher for the samples of Vietnamese coffee than for the alternative coffee (Colombian), and the level of unsaponifiable material produced after transesterification was lower for the Vietnamese coffee oil samples than the Columbian. The FAME profile of the Vietnamese was significantly different from the Colombian (which included an increase in the amount of monounsaturates, and a decrease in polyunsatures), while also including a small number of shorter fatty acids not typically found in coffee oil, but found in the fats Vietnamese coffee is roasted in. These saturates had a large effect on the fuel properties, leading the Vietnamese coffee biodiesel samples to possess higher viscosity and lower pour points than the Columbian coffee biodiesel. Furthermore, the Vietnamese coffee biodiesel to be was far more similar to palm biodiesel than any other type of commercial biodiesel. The Vietnamese coffee was also found to be more oxidatively stable than the Columbian coffee biodiesel, with the fresh sample maintaining its unsaturation throughout the oxidative stability test, comparable with the commercial biodiesel samples. Brewing the coffee, however, does decrease the stability. Three different samples of Vietnamese coffee were assessed and no significant difference was found between them, suggesting that waste

coffee biodiesel sourced from Vietnam could have consistent and predictable fuel properties. Vietnamese coffee, therefore, is a potential source of biodiesel that could be utilised locally, though extensive further testing of the fuel is required before commercial production and availability.

Acknowledgments The authors would like to thank the RAEng for partially funding this work through a Newton Fellowship grant (NRCP/1415/176) and to Roger and Sue Whorrod for funding the external fellowship held by CJC.

Compliance with Ethical Standards

Conflict of interest The authors have declared no conflict of interest.

Human and Animal Rights No animals or humans were harmed as a result of this research.

References

1. Jenkins, R.W., Stageman, N.E., Fortune, C.M., Chuck, C.J.: Effect of the type of bean, processing, and geographical location on the biodiesel produced from waste coffee grounds. Energy Fuels **28**(2), 1166–1174 (2014)
2. Knothe, G., Krahl, J., Van Gerpen, J.: The Biodiesel Handbook. Elsevier, Amsterdam (2015)
3. Food and Agriculture Organization of the United Nations: The State of Food and Agriculture—Biofuels: Prospects, Risks and Opportunities (2008)
4. REN21: Renewables 2014 Global Status Report. Paris (2014)
5. Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T., Masjuki, H., Mekhilef, S.: A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renew. Sustain. Energy Rev. **16**(4), 2070–2093 (2012)
6. Verma, P., Sharma, M.: Review of process parameters for biodiesel production from different feedstocks. Renew. Sustain. Energy Rev. **62**, 1063–1071 (2016)
7. Tiwari, A.K., Kumar, A., Raheman, H.: Biodiesel production from jatropha oil (Jatropha curcas) with high free fatty acids: an optimized process. Biomass Bioenergy **31**(8), 569–575 (2007)
8. Dwivedi, G., Sharma, M.P.: Investigation and improvement in cold flow properties of Pongamia biodiesel. Waste Biomass Valoriz. **6**(1), 73–79 (2015)
9. Chhetri, A.B., Watts, K.C., Islam, M.R.: Waste cooking oil as an alternate feedstock for biodiesel production. Energies **1**(1), 3–18 (2008)
10. Banković-Ilić, I.B., Stojković, I.J., Stamenković, O.S., Veljkovic, V.B., Hung, Y.-T.: Waste animal fats as feedstocks for biodiesel production. Renew. Sustain. Energy Rev. **32**, 238–254 (2014)
11. Karmakar, A., Karmakar, S., Mukherjee, S.: Properties of various plants and animals feedstocks for biodiesel production. Bioresour. Technol. **101**(19), 7201–7210 (2010)
12. Obruca, S., Benesova, P., Kucera, D., Petrik, S., Marova, I.: Biotechnological conversion of spent coffee grounds into polyhydroxyalkanoates and carotenoids. New Biotechnol. **32**(6), 569–574 (2015)
13. Oliveira, L.S., Franca, A.S., Camargos, R.R., Ferraz, V.P.: Coffee oil as a potential feedstock for biodiesel production. Bioresour. Technol. **99**(8), 3244–3250 (2008)
14. Al-Hamamre, Z., Foerster, S., Hartmann, F., Kröger, M., Kaltschmitt, M.: Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing. Fuel **96**, 70–76 (2012)
15. Kwon, E.E., Yi, H., Jeon, Y.J.: Sequential co-production of biodiesel and bioethanol with spent coffee grounds. Bioresour. Technol. **136**, 475–480 (2013)
16. Vardon, D.R., Moser, B.R., Zheng, W., Witkin, K., Evangelista, R.L., Strathmann, T.J., Rajagopalan, K., Sharma, B.K.: Complete utilization of spent coffee grounds to produce biodiesel, bio-oil, and biochar. ACS Sustain. Chem. Eng **1**(10), 1286–1294 (2013)
17. Caetano, N.S., Silva, V.F., Melo, A.C., Martins, A.A., Mata, T.M.: Spent coffee grounds for biodiesel production and other applications. Clean Technol. Environ. Policy **16**(7), 1423–1430 (2014)
18. Thout, B.M.: Coffee in Vietnam: it's the shit. Economist (2012)
19. Chuck, C.J., Bannister, C.D., Jenkins, R.W., Lowe, J.P., Davidson, M.G.: A comparison of analytical techniques and the products formed during the decomposition of biodiesel under accelerated conditions. Fuel **96**, 426–433 (2012)
20. Budryn, G., Nebesny, E., Żyżelewicz, D., Oracz, J., Miśkiewicz, K., Rosicka-Kaczmarek, J.: Influence of roasting conditions on fatty acids and oxidative changes of Robusta coffee oil. Eur. J. Lipid Sci. Technol. **114**(9), 1052–1061 (2012)
21. Verma, P., Sharma, M., Dwivedi, G.: Impact of alcohol on biodiesel production and properties. Renew. Sustain. Energy Rev. **56**, 319–333 (2016)
22. Anderson, L.A., Franz, A.K.: Real-time monitoring of transesterification by 1H NMR spectroscopy: catalyst comparison and improved calculation for biodiesel conversion. Energy Fuels **26**(10), 6404–6410 (2012)
23. D'Amelio, N., De Angelis, E., Navarini, L., Schievano, E., Mammi, S.: Green coffee oil analysis by high-resolution nuclear magnetic resonance spectroscopy. Talanta **110**, 118–127 (2013)
24. Holland, E., Gaevey, M., Pieeoe, H., Messer, A., Aechibald, J., Dunbar, C.: Determination of fatty acids in butter fat. J. Agr. Res. **24**, 365 (1923)
25. Totten, G.E., Westbrook, S.R., Shah, R.J.: Fuels and lubricants handbook: technology, properties, performance, and testing. ASTM Int. **1**, (2003)
26. EN 14214: Automotive fuels—Fatty acid methyl esters (FAME) for diesel engines—Requirements and test methods
27. ASTM D6751: Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels. ASTM Int. (2008)
28. Knothe, G.: Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process. Technol. **86**(10), 1059–1070 (2005)
29. EN 590: Automotive fuels—Diesel—Requirements and test methods
30. Beith, R.: Small and Micro Combined Heat and Power (CHP) Systems: Advanced Design, Performance, Materials and Applications. Elsevier Science, Amsterdam (2011)
31. van Dop, H., Fabian, P., Güsten, H., Hales, J.M., Wint, A.: Air Pollution. Springer, Berlin, Heidelberg (2013)
32. Chuck, C.J., Jenkins, R.W., Bannister, C.D., Han, L., Lowe, J.P.: Design and preliminary results of an NMR tube reactor to study the oxidative degradation of fatty acid methyl ester. Biomass Bioenergy **47**, 188–194 (2012)
33. Bannister, C., Chuck, C., Bounds, M., Hawley, J.: Oxidative stability of biodiesel fuel. Proc. Inst. Mech. Eng. Part D: J. Automob. Eng. **225**(1), 99–114 (2011)
34. Chu, Y.-F.: Coffee: Emerging Health Effects and Disease Prevention, vol. 59. Wiley, Hoboken (2012)
35. Food and Agriculture Organization of the United Nations: FAOSTAT—Green Coffee World Production Quantity (2012)
36. International Coffee Organization: Trade Statistics (Total Production exporting countries) (2015)