Improved Oxidative Stability of Biodiesel from Used Coffee Grounds

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Abstract

This study aims to investigate the oxidative stability index (OSI), fatty acid methyl ester (FAME) content, acid number, viscosity and antioxidant content of biodiesel synthesised from used *coffee arabica* grounds. Biodiesel was synthesised through Soxhlet extraction of coffee oil from used coffee grounds and then undergoing a transesterification reaction. The synthesised biodiesel was then tested for OSI, FAME content, acid number, phenolic and flavonoid contents. FTIR analysis confirmed the presence of biodiesel, and phenolic and flavonoid contents were 300.0 gallic acid equivalent mg/L and 496.7 quercetin equivalent mg/L respectively. OSI was determined to be at 7.5 min while acid number was found to be 2.41 mg KOH/g. These findings conclude that the synthesised biodiesel is unsuitable for commercial applications and can be attributed to biodiesel degradation over time as well as the lack of artificial antioxidants.

Literature Review

Food waste is a serious problem in Singapore. Approximately 744,000 tonnes of food waste were generated in 2019, of which only 18% were recycled. The remaining 607,000 tonnes of food waste were disposed of at the waste-to-energy incineration plants (National Environment Agency, n.d.). This poses serious environmental issues. 676 kg of carbon dioxide and 3.12 kg of methane, in addition to other common pollutants such as sulfur dioxide, volatile organic compounds and PM2.5, are released for every tonne of food waste incinerated. In addition, a large amount of dioxins, a serious carcinogen, is also produced from the incineration of food waste (Gao et al., 2017). Environmental pollution and threats to public health, in addition to its high operating costs and high energy inputs needed, renders incineration a problematic disposal method for food waste.

Recently, biodiesel production has emerged as an economically viable and environmentally friendlier alternative to the incineration of food waste, by using food waste to produce biodiesel which can be used to power diesel engines with few modifications

(Omidvarborna et al., 2014). Moreover, biodiesel is also a cleaner alternative to conventional diesel. Biodiesel emits 65% less greenhouse gases and 36% less fine particulate matter than conventional diesel (Ramos et al., 2016). Thus, producing biodiesel from food waste is a clean and renewable alternative to both managing food waste and offering an alternative, greener fuel to conventional diesel.

However, biodiesel is easily oxidised. Biodiesel is mainly composed of fatty acid methyl esters (FAME), which easily oxidise. Unsaturated FAME is the main factor for this oxidation, while, especially plant-based, food waste contains high concentrations of unsaturated fatty acids, which in turn leads to a higher concentration of unsaturated FAME in the produced biodiesel (Park, 2007). Oxidised biodiesel damages diesel engines severely within a short duration of usage (Waynick, 2005), and thus antioxidants are required to slow down the oxidation and extend the shelf life of biodiesel.

Waste coffee grounds are a suitable candidate for biodiesel production due to its oil content. Waste coffee grounds have a high oil content of 15% (Karmee, 2018), which allows it to be a viable feedstock for biodiesel that can offer sufficient yields. They are also highly accessible and are readily available in homes and coffee shops. In addition, waste coffee ground extracts have been found to contain a high concentration of natural antioxidants, with a phenolic content of 9.44 mg gallic acid equivalents/g and a flavonoid content of 29mg quercetin equivalents/g (Wu et al., 2019), suggesting that biodiesel synthesised from waste coffee grounds could have a longer shelf life and better oxidation stability than biodiesels synthesised from other feedstocks.

Objectives and Hypotheses

Objectives

1. To synthesise biodiesel from waste coffee grounds.
2. To study the oxidative stability index (OSI), FAME content, acid number, viscosity and antioxidant contents of the synthesised biodiesel.
3. To enhance the oxidative stability of the synthesised biodiesel with synthetic antioxidants.

Hypotheses

1. Biodiesel is able to be synthesised from waste coffee grounds.

2. Biodiesel synthesised from waste coffee grounds is higher in OSI, FAME content and antioxidant contents than commercial biodiesel.
3. The oxidative stability of synthetically enhanced biodiesel is higher than that of the synthesised biodiesel without synthetic antioxidants.

Methodology

Drying and Dehydration of Waste Coffee Grounds

The waste coffee grounds were first dried in an oven at 105°C overnight and the dried products were then ground into powder.

Extraction of Oil

Oil was extracted from dried coffee waste through Soxhlet extraction. Hexane was used as a solvent in a 1:6 m/v solute-solvent ratio. A Soxhlet extractor containing the dried coffee waste was attached to a round bottom flask containing the hexane. The hexane was heated at 200°C for 2 hours. This allows the hexane to evaporate and then condense at the top of the Soxhlet extractor where it drops into the food waste container. The dissolved oil compounds are then collected in the round bottom flask. A rotary evaporator was then used to separate the hexane and oil compounds.

Synthesis of Biodiesel

The extracted coffee oil was then converted into biodiesel with a transesterification reaction. 99% methanol and 2M sulfuric acid was added and mixed in a 3:1 v/v ratio, and then added to the extracted oil in a 3:1 v/v ratio. This mixture was stirred at 100 RPM with a magnetic stirrer for 2 hours. After 2 hours, deionised water was added to dissolve glycerol and the sulfuric acid catalyst. Fatty esters were then separated out using a separating funnel.

Fatty Acid Methyl Ester (FAME) Content Studies

FTIR analysis was carried on biodiesel samples. 0.5mm KBr cells were used as windows while cyclohexane was used as dilution and cleaning. Calibrations were then achieved with 1, 2, 4, 6 and 10g/L of FAME in cyclohexane. FAME contents were then determined by integration of the signals at 1745 cm^{-1}.

Disruptions. FTIR analysis was able to be carried out, however the exact concentration of FAME determined through the integration of signals was unable to be determined.

Antioxidant Studies

Phenolic Content Studies

0.2ml of biodiesel sample was mixed with 0.2ml ferroin indicator and 0.6ml of deionised water. After 5 minutes, 1ml of 8% w/v sodium carbonate solution was added, and made up to 3ml with deionised water. The mixture was kept in the dark for 30 minutes before centrifuging. Absorbance values were then determined with a UV-vis spectrophotometer at 765nm. 0mg L^{-1}, 100mg L^{-1}, 200mg L^{-1}, 300mg L^{-1}, 400mg L^{-1} and 500mg L^{-1} gallic acid solutions were used to determine the standard curve.

Flavonoid Content Studies

0.6ml of biodiesel sample was mixed with 0.6ml of 2% aluminium chloride solution. After mixing, the solution was incubated for 60 minutes at room temperature. Absorbance values were then determined with a UV-VIS spectrophotometer at 420nm. 0mg L^{-1}, 40mg L^{-1}, 80mg L^{-1}, 120mg L^{-1}, 160mg L^{-1} and 200mg L^{-1} quercetin solutions were used to determine the standard curve.

Oxidative Stability Index (OSI) Studies

2ml of biodiesel sample was heated while air was bubbled through. The oxidised volatiles were then transferred to a water trap. The pH of the water trap was measured and the induction period endpoint (IPE) was determined by a rapid decrease of pH. OSI was then determined by the time taken to reach IPE.

Acid Number Studies

Ethanol was used as a titration solvent while thymolphthalein was used as indicator. 2g of biodiesel sample was added to 10ml of titration solvent and 8 drops of indicator solution. The resulting mixture was titrated with 0.02M KOH in isopropanol. The thymolphthalein indicator changes from colourless to blue at pH 9.3-10.5. Acid number was then determined with the following equation:

$$\text{acid value}\left(\frac{\text{KOH/mg}}{\text{sample/g}}\right) = \left(\frac{\text{volume KOH/mL} \times \text{N KOH/mmol mL}^{-1} \times 56.1/\text{mg mmol}^{-1}}{\text{sample weight/g}}\right)$$

Viscosity Studies

A ball bearing was dropped into a measuring cylinder of the biodiesel sample heated to 40°C. The time taken for the ball bearing to drop between specified points on the measuring cylinder was recorded. Viscosity was then determined by the following equation:

$$\frac{2(\rho_s - \rho_l)gr^2}{9v}$$

where ρ_s is the density of the ball bearing, ρ_l is the density of the sample, g is the acceleration due to gravity, r is the radius of the sphere and v is the velocity of the sphere.

Disruptions. Viscosity studies were not carried out due to time and material constraints.

Material and Synthetic Antioxidant Studies

To simulate the effects of storage material and synthetic antioxidants on the oxidation of biodiesel, a 4cm by 6cm piece of metal, copper or zinc, will be placed in 250ml of biodiesel sample. 1000 ppm of synthetic antioxidants tert-butylhydroquinone (TBHQ) and butylated hydroxytoluene (BHT) will also be added to biodiesel samples. The biodiesel samples will be stored in a glass container at room temperature. OSI, FAME content, acid number and viscosity tests will be carried out every 30 days for 90 days.

Table 1

Combinations of Samples Created

	Copper	Zinc	Control
TBHQ	Copper + TBHQ	Zinc + TBHQ	TBHQ Only
BHT	Copper + BHT	Zinc + BHT	BHT Only
Control	Copper Only	Zinc Only	Pure Biodiesel

Disruptions. Material and synthetic antioxidant studies were not carried out due to a lack of time.

Results and Discussion

FAME Content Studies

Figure 1

FTIR Characterisation of Biodiesel from Waste Coffee Grounds

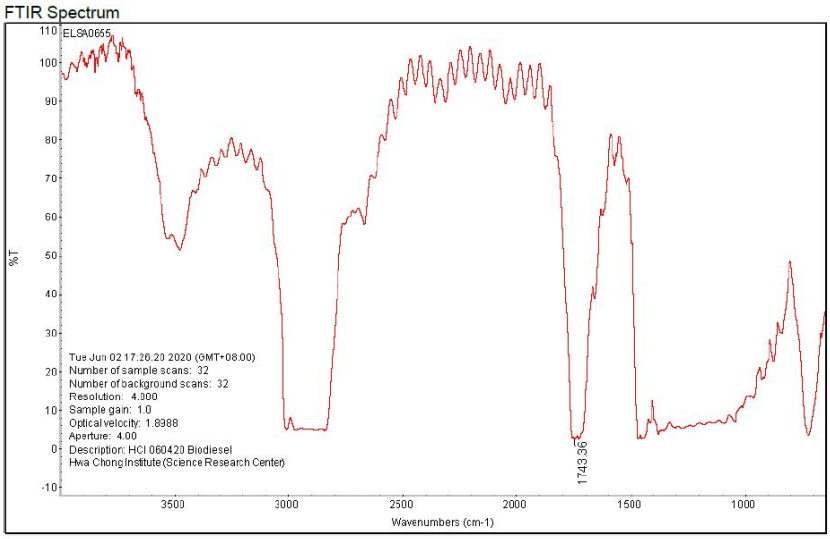
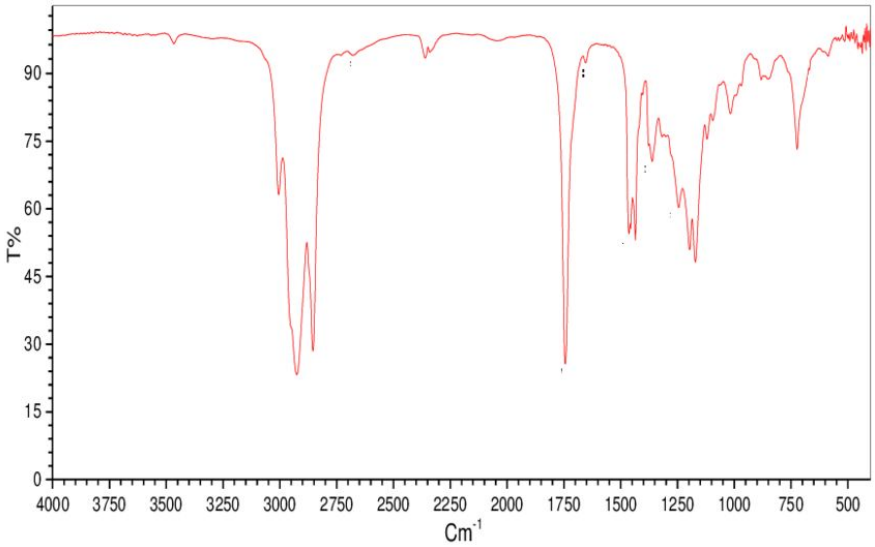


Figure 2

FTIR Characterisation of Commercial Biodiesel (Abderrhmane et al., 2016)



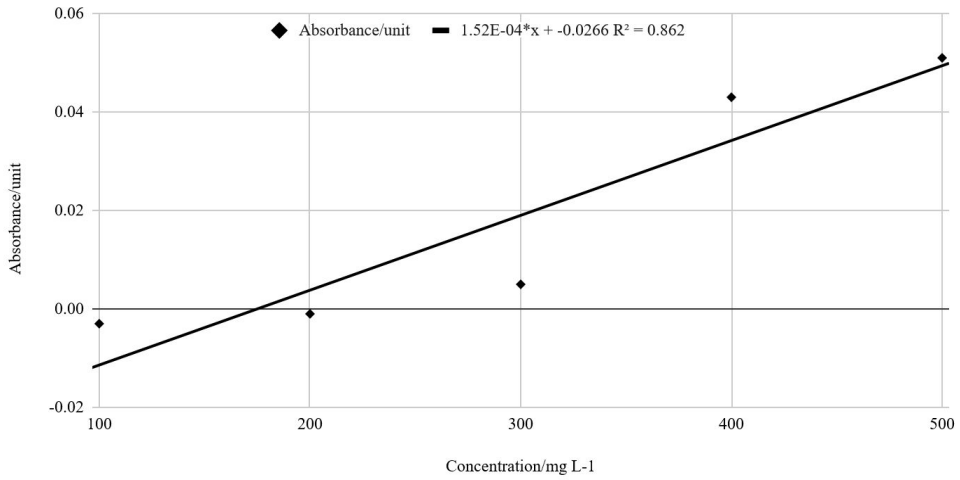
A peak can be observed around 1745 cm^{-1}, confirming the presence of FAME. However, the concentration of FAME could not be determined.

Antioxidant Content Studies

Phenolic Content Studies

Figure 3

Gallic Acid Standard Calibration Curve

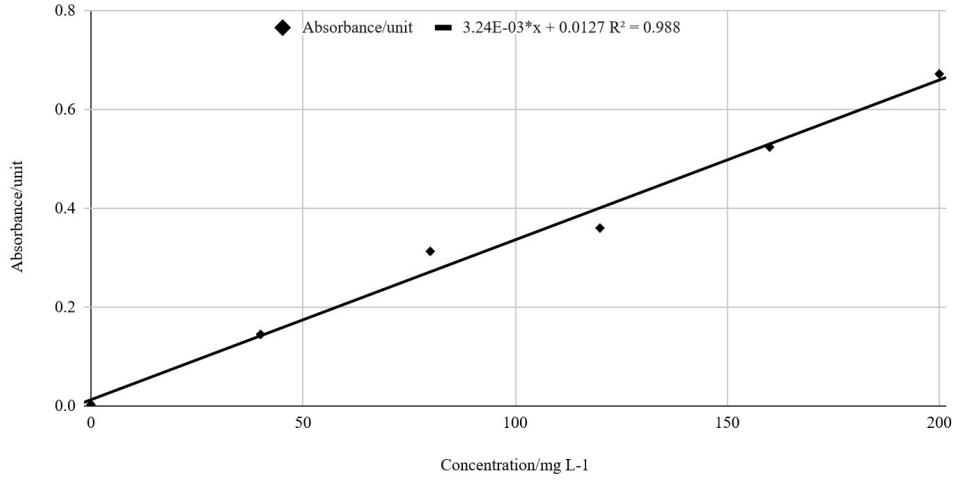


Using the gallic acid standard curve, the phenolic content in the biodiesel is calculated by substituting the equation of the standard curve for the absorbance value.

Flavonoid Content Studies

Figure 4

Quercetin Standard Calibration Curve



Using the quercetin standard curve, the flavonoid content in the biodiesel is calculated by substituting the equation of the standard curve for the absorbance value.

Table 2

Mean Antioxidant Contents and Standard Deviation

Biodiesel Feedstock	Gallic Acid Equivalent/mg L^{-1}		Quercetin Equivalent/mg L^{-1}	
	Mean	Standard Deviation	Mean	Standard Deviation
Waste Coffee Grounds	300.0	170.3	496.7	336.3
Scenedesmus obliquus (Ferreira et al., 2019)	249	n.a.	167	n.a.

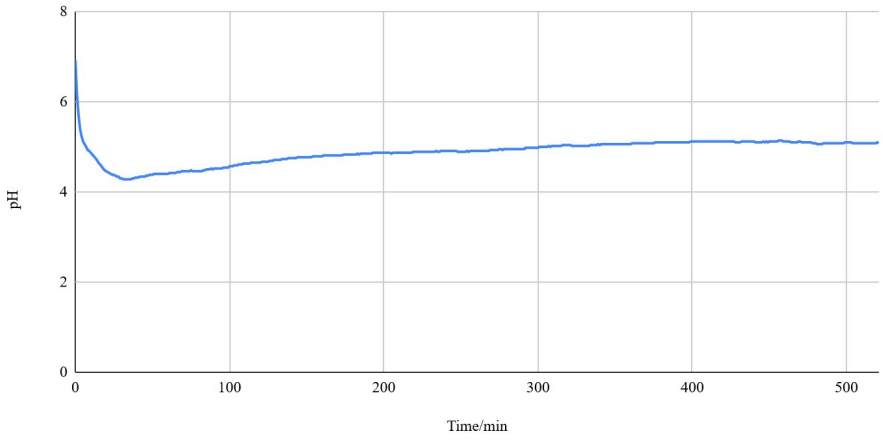
Biodiesel synthesised from waste coffee grounds contains a higher concentration of antioxidants than that synthesised from other feedstocks with lower antioxidant content. This is likely due to the high antioxidant content of waste coffee grounds, which is 22.29 mmol/100g (Carlsen et al., 2010).

However, biodiesel from waste coffee grounds could not be compared with biodiesel synthesised from banana peels (originally intended to be done by groupmates in Bugil High School, South Korea), and thus without statistical tests, the higher antioxidant content in the biodiesel cannot be concluded to be caused by the higher antioxidant content in the feedstock. High standard deviations were observed for both phenolic and flavonoid contents, decreasing the reliability of the final results.

Oxidative Stability Index (OSI) and Acid Number Studies

Figure 5

Graph of pH against time of sample 1



The induction period endpoint (IPE) was determined when the greatest decrease in pH was measured during the experiment.

Table 3

Mean Oxidative Stability Index, Acid Number Compared Against EN14214 Biodiesel Standards

Biodiesel	Oxidative Stability Index/min		Acid Number/mg KOH g^{-1}	
	Mean	Standard Deviation	Mean	Standard Deviation
Waste Coffee Grounds	7.5	8.96	2.41	0.504
EN14214 Standards	>480	n.a.	<0.50	n.a.
B100 Biodiesel without Antioxidants after 3 months of simulated storage (Christensen & McCormick, 2014)	6	n.a.	n.a.	n.a.

Biodiesel synthesised from waste coffee grounds has poor oxidative stability, as indicated by the low OSI and high acid number, both of which do not meet EN14214 standards for biodiesel. One possible reason is the high concentration of unsaturated FAME in the biodiesel. Coffee oil has a high concentration of unsaturated fatty acids, between 41.86% and 56% w/w, with linoleic acid concentration between 32.41% and 44.2% w/w (Efthymiopoulos et al., 2019; Somnuk, Eawlex & Prateepchaikul, 2017). EN14214 limits the concentration of linoleic acid methyl esters to a maximum of 12% w/w. The high concentration of unsaturated FAME leads to a lower oxidative stability (Christensen & McCormick, 2014).

A long storage time between synthesis and characterisation is also a possible reason. Table 3 shows that commercial biodiesel without added synthetic antioxidants had its oxidative stability decrease to 0.1 hours after 3 months of simulated storage. The tested biodiesel from waste coffee grounds was stored for over 3 months before characterisation could be conducted. Therefore, the measured OSI and acid number are consistent with prior research.

Conclusion

Biodiesel can be synthesised from waste coffee grounds. However, the other hypotheses cannot be confirmed due to a lack of data. The results suggest that the antioxidant content of biodiesel from waste coffee grounds could be higher than that of biodiesel from other feedstocks, however it cannot be conclusively determined. The oxidative stability of the synthesised biodiesel cannot be determined accurately due to a long delay in conducting characterisation after its synthesis. Nonetheless, it can be concluded that biodiesel from waste coffee grounds, similarly to commercial biodiesel, would require the addition of synthetic antioxidants to be able to be stored for a reasonable duration, due to fast oxidation and degradation.

The pandemic has led to restrictions in data collection, since time constraints limited the number of experiments conducted and also left inadequate time to troubleshoot problems with other experiments.

Future Work

The calibration curve in antioxidant studies could be refined to obtain a higher accuracy and reliability, and tests not conducted due to the pandemic, such as the viscosity and material studies, could be conducted in the future. The iodine number and glycerine content could also be determined as alternative indicators of oxidative stability. Antioxidant and material studies can also be conducted with different proportion blends of synthesised biodiesel and commercial diesel, which more closely resembles biodiesel usage in cars. Proton NMR can be used to quantify biodiesel instead of FTIR as well.

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