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ORIGINAL RESEARCH

Comparative analysis of palm kernel and waste cooking oils for biodiesel production as an alternative fuel to conventional diesel fuel

Manasseh T. Agbedam, Enoch K. Acquah, Anthony N. A. Prempeh, Augustine T. Tagoe, Kobina A. Ofori, Emmanuela Kwao-Boateng*

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Abstract
The steady depletion of non-renewable energy (fossil fuel) and its environmental concerns has made biodiesel one of the promising alternative fuels to meet energy demands, leading to increased production. However, using certain crops such as palm fruit (palm oil) for biofuel production contributes to food shortage in the global market. Hence, attention has been focused on the use of non-food raw materials and by-products such as vegetable waste oils. This study comparatively determined the suitability of biodiesel produced from waste cooking oil (WCO) and palm kernel oil (PKO) as alternative fuels, considering their acid value, viscosity, free fatty acid (FFA), biodiesel yield, and density. The reaction was carried out at 65 °C with a residence time of 90 mins for both oils. The PKO yielded 67.44 % biodiesel as compared to 53.82 % for WCO. At 40 °C, the viscosity of the WCO biodiesel was 38 % higher than the viscosity of the PKO; however, both met the required American Standard for Testing Materials (ASTM) and European standards for biofuels. The PKO showed the highest reduction in acid value by 98.1 %. The densities for the biodiesels were 0.90 mg/mL for WCO and 0.89 mg/mL for PKO. The PKO biodiesel showed better characteristics than WCO biodiesel, making it a better alternative and blend fuel for conventional diesel fuel. However, WCO biodiesel has the potential to fully replace petroleum diesel as it meets most of the required standards and reduces the competition between food and fuel.

Keywords: Biodiesel, Waste Cooking Oil, Palm Kernel Oil, Transesterification, Viscosity, Density

Introduction

The demand for energy due to rapid industrial growth and socio-economic development has increased exponentially. In recent decades, petroleum fuel has enormously aided in fulfilling these demands. Notwithstanding, expanding worries emanating from petroleum derivatives and the forthcoming peak oil hypothesis have diverted attention to alternative fuel sources (Kemausuor *et al*., 2013; Maggio and Cacciola, 2012; Owen *et al*., 2010). Western countries have progressively empowered alternative fuel utilization and improvement, with private and public industries in financial support for significant biofuel production development (Acheampong and Campion, 2013). An alternative fuel should be plausible, promptly accessible, ecologically accepted, and economically viable (Singh and Gu, 2010). One of the recent and most suitable renewable energy resources as an alternative fuel is biodiesel (fatty acid alkyl monoesters) derived from animal fats and vegetable oils (Sanli *et al*., 2011). Biofuels have been promoted as a promising fuel source for decreasing carbon dioxide (CO_2) outflows worldwide (Oliphant *et al*., 2018).

Biodiesel can be directly applied as fuel in internal combustion engines (Refaat *et al*., 2008). The main advantages of biodiesel, such as being a renewable resource, low emission of contaminants, and low toxicity, make it a vital substitute for diesel fuel (Romano and Sorichetti, 2011). A detailed overview of the advantages and disadvantages of using biodiesel is shown in Table 1. The primary raw materials in biodiesel are vegetable oils, animal fats, and alcohol. Non-edible and virgin edible vegetable oil have been studied for biodiesel production with great results (Gnanaprakasam *et al*., 2013).

Nonetheless, waste cooking oil can be used as raw material. The problems with the disposal of waste cooking oil cannot be overlooked. Various food vendors, companies, restaurants, and hotels dispose of waste cooking oil in water bodies and on land, causing water and land pollution. However, it has been proven that biodiesel production from waste cooking oil is feasible with reasonable economic benefits (Rahadianti *et al*., 2018).

Table 1 Advantages and Disadvantages of using biodiesel

Advantages of using biodiesel as a fuel	Disadvantages of using biodiesel as a fuel
Presents lower health risks	Fuel consumption is higher
Zero sulphur dioxide emissions	Emission of NOx is higher
Has a minimum flash point of 100°C	Lower stability compared to diesel
Can be synthesized from waste or used oil	Higher freezing point
Can be used as lubricants	Can degrade natural rubber and plastic

Source: Romano and Sorichetti (2011)

Several research methods have been conducted to synthesize biodiesel from vegetable oil and animal fats (Refaat *et al*., 2008). Transesterification is widely used in biodiesel production from vegetable oil (Udeh, 2017). Transesterification can be classified as acid-catalyzed processes, base-catalyzed processes, lipase-catalyzed processes, non-ionic base-catalyzed processes, and heterogeneously catalyzed processes. The base-catalyzed process is highly employed because it yields high conversion rates (Nasreen *et al*., 2018). Fats and oils are triglycerides, that is, fatty glycerol esters. Vegetable oils contain different types of fatty acids in different ratios (Romano and-Sorichetti, 2011).

*Corresponding author's email: ebosomtwi11@gmail.com
Department of Chemical Engineering, Faculty of Mechanical and Chemical Engineering, Kwame Nkrumah University of Science and Technology, Kumasi-Ghana

In biodiesel production, short-chain alcohols are used. Different types can be used, such as methanol, ethanol, and butanol. This experiment used methanol because of its high reaction rates and the ease with which excess alcohol can be recovered (Nasreen *et al*., 2018). The catalysts used in biodiesel are homogeneous alkaline catalysts, including NaOH, KOH, etc. The KOH has been found to give high kinetic reaction rates (Atadashi *et al*., 2013). Biodiesel produced from vegetable oils employs the transesterification reaction. This reaction converts triglycerides to glycerol. Other side reactions occur during the process, including saponification and hydrolysis. In the saponification reaction, free fatty acid reacts with the base to produce soap and water. This reaction is unwanted because it consumes the catalyst and makes separation difficult. Hydrolysis also occurs when water from the vegetable oil and the saponification process react with triglyceride to form free fatty acids (Gnanaprakasam *et al*., 2013).

Methods

Preparation of biodiesel

To ensure uniformity, the collected WCO was mixed into one flask and precipitated for 8 hours as a pre-treatment method. The PKO was subjected to the same pre-treatment under the same conditions. A preliminary test was carried out on the raw materials after the pre-treatment. A solution was prepared by mixing KOH (5 % of oil weight) with methanol (molar ratio of methanol to oil, 4:1). From general transesterification reaction stoichiometry, an alcohol to triglyceride (oil) ratio is expected to be 3:1 for a complete reaction as shown in Figure 1. However, in the procedure for this study, a higher ratio of 4:1 (alcohol: oil) was used to account for the higher free fatty acid content of raw materials.

This limits the excess solvent that could be present in biodiesel and glycerol. Also, a significant amount of unreacted methanol is lost when high methanol ratios are used (Aladetuyi *et al*., 2014). Equal volumes of the pre-treated raw materials were then heated separately to 60 °C. After the temperature was attained, the methanol-KOH solution was slowly added to the oils while stirring gently using a magnetic stirrer. The reaction was given a residence time of 90 minutes to ensure adequate contact time for the complete reaction for both samples.

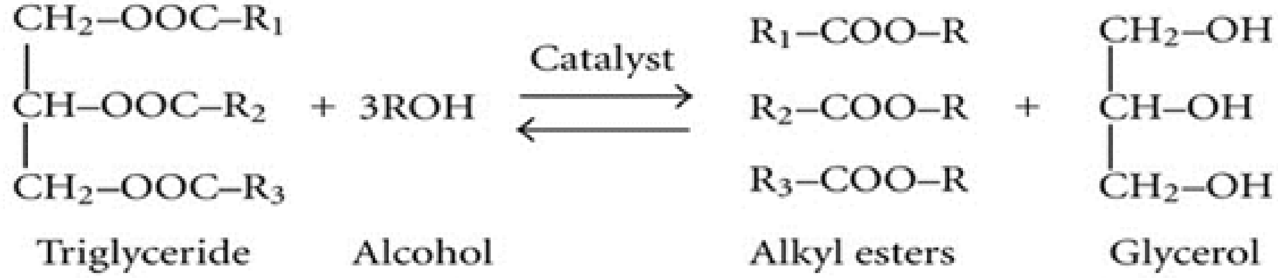

Figure 1 Reaction equation of transesterification

A bioenergy policy for Ghana was developed in 2010 (Energy Commission, 2010) to substitute petroleum fuel consumption by 20 % with biodiesel before 2030. The arrangement intends to utilize the country's colossal biomass potential and assets in present-day applications to create transport fuels and power (Kemausuor *et al*., 2013). However, using certain crops, such as palm fruits, to synthesize biodiesel may contribute to food shortage in Ghana and the global market (Energy Commission, 2010). As such, more focus has been shifted to waste oils for biodiesel production. Palm kernel oil, which is well consumed in large quantities in certain parts of Ghana, has limited consumption in some other parts. Portions of the palm kernel oil can therefore be harnessed in biodiesel production. The study compares biodiesel from waste cooking oil and palm kernel oil. The comparison was based on acid value, viscosity, FFA, biodiesel yield, and density to determine which alternative is more suitable.

Materials and Methods

Materials

Waste cooking oil was obtained from several households and street vendors across Oforikrom Municipality for this study. On the other hand, the PKO was purchased from Kejetia, a local market within the Kumasi Metropolis, while all the chemicals and reagents, viz. KOH, methanol, and phenolphthalein, used were provided by the Department of Chemical Engineering, KNUST. Additionally, the distilled water used in the study was obtained from the same Department. The methanol was used as alcohol for the transesterification reaction, while the KOH served as the base catalyst for the reaction.

Table 2 The experimental conditions for WCO and PKO biodiesel production

Experimental Conditions	WCO	PKO
Reaction temperature (°C)	**65**	**65**
Reaction time (mins)	90	90
Quantity of raw material (g)	481	481
Ethanol to oil ratio	4:01	4:01
Catalyst loading (w/w in %)	8	8
Quantity of biodiesel obtained (g)	259.14	324.38
Quantity of glycerol produced (g)	270	189
Yield of Biodiesel (%)	53.82	67.44

Production

The experimental conditions followed for optimum production and purification of biodiesel from these raw materials are shown in Table 2.

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Phase separation
This involved separating the layer in the mixture containing glycerol from the ester layer (biodiesel). The mixture was allowed to stand for one and a half hours. Two separate layers consisting of biodiesel (upper layer) and glycerol (bottom layer) for each sample were observed due to the differences in their densities.

Purification of biodiesel
Using hot distilled water at a temperature of 70 °C (Rahadianti *et al*., 2018), the impure biodiesel was washed till a yellowish colour of the biodiesel was seen in a separating funnel. The biodiesel was washed to remove unreacted methanol, traces of soap, and any contaminants in the biodiesel. The biodiesel was then heated to 110 °C for 30 minutes in a water bath on a hotplate to remove moisture. After the purification, the biodiesel samples were subjected to qualitative and quantitative analysis.

% of oil weight) was used based on preliminary tests done on the raw materials. The percentage yield (PY) obtained was calculated using Eqn. (1). The PKO transesterification produced more biodiesel than the WKO at a yield of approximately 67 %.

$$PY = \frac{Quantity\ of\ Biodiesel\ produced\ (mass)}{Quantity\ of\ Raw\ Material(mass)} \times 100\% \quad (1)$$

Biodiesel parameters comparison
The biodiesels produced in this study are intended to replace or compatibly blend with conventional diesel fuels thoroughly. Therefore, it is appropriate to compare these biodiesels' properties to conventional diesel types. ASTM D6751 (ASTM, 2002) and EN 14214:2012 (BS EN 14214:2012, 2012) give the threshold for biodiesel properties. Table 4 highlights conventional diesel and biodiesel's set limits and desirable properties.

Table 3 Characteristics of raw materials (WCO and PKO)

Parameter	Waste Cooking Oil	Palm Kernel Oil	Unit	Method
Density(40°C)	0.96	0.96	g/mL	Measurement
Viscosity(40°C)	28.23	26.89	cSt	Measurement
Free Fatty Acid	0.70	11.07	%	Titration
Acid Value	1.40	21.99	mgKOH/g	Titration

Results and Discussion
Analysis of raw materials
The raw materials specifications (characterization) and test methods were done according to ASTM D6751-12 standard. Table 3 compares the raw oil characteristics of WCO and PKO.

WCO and PKO
From Table 3, the density of both raw materials was approximately the same. Density is an important parameter influencing the conversion of volume flowrate into mass biodiesel flowrate (NguyenThi *et al*., 2018). Undeniably, the viscosity of the WCO (28.23) at 40 °C was higher than the PKO (26.89) since the WCO, which had been reused several times, contained several compounds that turned to impact its properties. The high viscosity of WCO is one of the reasons it is not directly used as a blend stock for diesel engines (Anisah *et al*., 2019); thus, the need for transesterification to bring the levels within permissible limits.

Synthesis
In this study, biodiesel production was done using optimum conditions recommended in the study conducted by Rahadianti *et al*. (2018), namely, a temperature of 65 °C and a reaction time of 90 minutes. According to Rahadianti *et al*. (2018), the use of these optimum conditions resulted in an improved yield and quality of biodiesel. A methanol-to-oil ratio of 4:1 KOH (5

EN 14214:2012 was used as the standard for the discussion in this study.

Density
The density values were measured at 40 °C and atmospheric pressure. The results obtained from the biodiesel analysis are demonstrated in Figure 2 and show that the density of WCO biodiesel was approximately 1.2 % greater than the density of

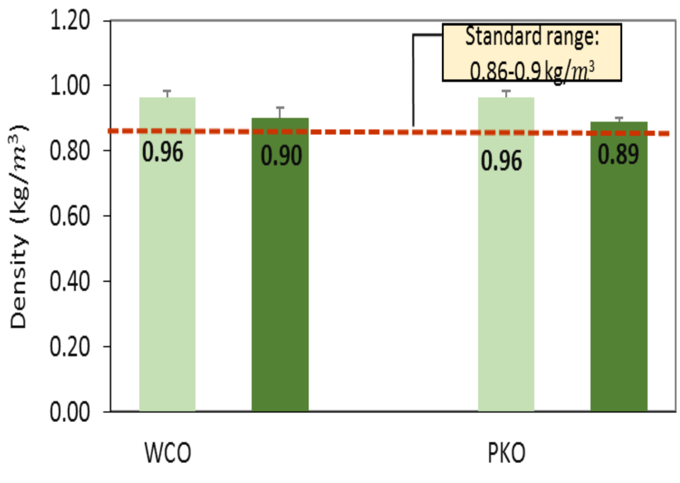

Figure 2 Density comparison of WCO and PKO and the biodiesels with the standard

Table 4 Set limits and desirable properties of conventional diesel and biodiesel

Property	Set limit (ASTM D975) (Conventional Petroleum diesel)	ASTM D6751-12 (Biodiesel)	EN 14214:2012 (Biodiesel)
Density (g/cm^3)	0.82-0.87 at 15 °C	0.88 at 40 °C	0.86-0.9 at 40 °C
Viscosity at 40 °C (mm^2/s or cSt)	2-4.5	1.9-6.0	3.5-5.0
Acid number (mgKOH/g)	-	≤ 0.5	≤ 0.5

the PKO biodiesel. Density, defined as the amount of biodiesel per unit volume, may be affected by many factors, including the biodiesel's water content, which amounts to 0.99 g/ml (Rahadianti *et al.*, 2018) and fatty acid composition (Worldwide Fuel Charter Committee, 2009). After the transesterification reaction, the presence of unconverted triglyceride molecules may have amounted to the significantly higher density in WCO biodiesel. Biodiesel ignites and combusts better when the density value is low. Therefore, PKO biodiesel would be more desirable than WCO biodiesel, as reported by (Rahadianti *et al.*, 2018). Comparing the specific gravities to European (EN 14214:2012) standards of biodiesel (0.860 – 0.900 g/ml) (Hannu Jääskeläinen, 2009), PKO and WCO biodiesel fall within the range with a density of 0.889 and 0.900g/ml respectively. PKO and WCO density values had reduced by 2.3 and 2.5 %, respectively, compared to the initial specific gravities. Figure 2 compares the marginal difference of each biodiesel from the maximum density required by the EN standard.

Viscosity

From the concept of biodiesel viscosity (a measure of a fluid's resistance to flow or its shear resistance) (Rahadianti *et al.*, 2018), the higher the viscosity, the more complex the flow of the biodiesel. The quality of biodiesel in an air–fuel mixture in a combustion engine cylinder relies upon the size and homogeneity of the fuel beads in the wake of being infused, which is affected by the viscosity of the fuel (Hoang, 2021). The viscosity of the prepared biodiesel was determined at a temperature of 40 °C and 100 °C. At 40 °C, the viscosity of the WCO biodiesel was 38 % higher than the viscosity of the PKO as seen in Figure 3. Higher viscosities affect injector lubrication by forming large droplets on injection, resulting in inefficient fuel combustion. Therefore, PKO biodiesel would combust efficiently when introduced into a fuel engine as compared to WCO. However, the viscosity values of both biodiesels fall within the range stipulated by both ASTM and European standards. The viscosity of the PKO had reduced by 83 % after the transesterification reaction, while WCO showed 87 % reduction.

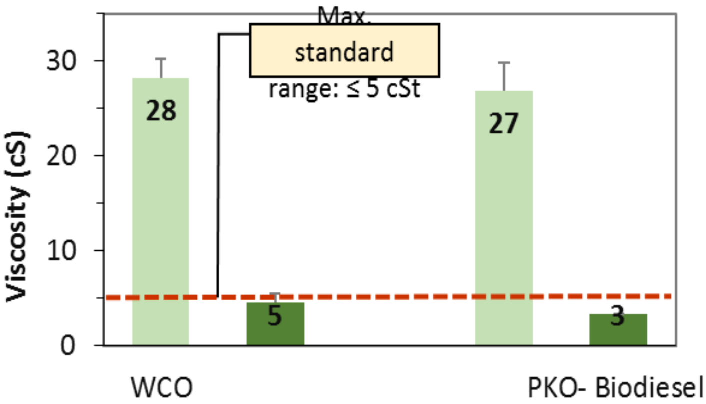

Figure 3 Viscosities of WCO and PKO biodiesel compared with standard thresholds

Acid value and FFA

Acid values represent the amount of potassium hydroxide in milligrams needed to neutralize the quantity of free fatty acid present in fat or oil. The higher the free fatty acids, the higher the acid value (Aladetuyi *et al.*, 2014). According to Rahadianti *et al.* (2018), high acid value reduces the oil's quality, reducing its reaction rate. In the presence of water molecules, oil can be converted to free fatty acid in a hydrolysis reaction, damaging the quality of the oil (Witono *et al.*, 2014).

In Figure 4, the acid value of WCO and PKO biodiesel was measured to be 0.5386 mg KOH/g and 0.3647 mg KOH/g, respectively. These values represent a significant reduction in free fatty acid in the raw materials. The reductions indicate that the free fatty acids in oils had been converted into esters (biodiesel) in the transesterification process. The lower acid value of PKO biodiesel makes the quality of the biodiesel synthesized better than that of WCO. There was also a 98.1 % reduction in acid value in the PKO compared to 61.6 % in WCO. This represented a higher conversion rate for the PKO reaction than the WCO transesterification reaction. Comparing the measured values to the ASTM and European standard requirements (≤ 0.5 mgKOH/g), the acid value of WCO biodiesel is slightly higher (by 0.0386 mgKOH/g). This indicates that WCO biodiesel would be more corrosive to fuel engines than PKO biodiesel due to the high amount of free fatty acid present.

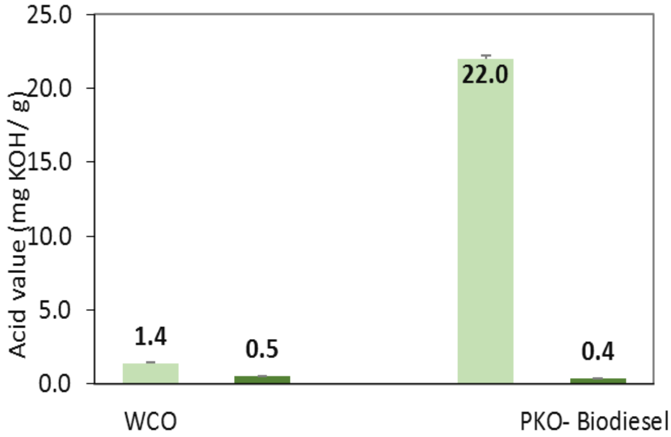

Figure 4 Acid value of PKO and WCO before and after transesterification

Conclusions

This study compared biodiesel produced from PKO and WCO to determine which of them is best suited as an alternative/blending fuel. The PKO yielded more biodiesel than WCO with a higher conversion ratio. The viscosity, density, and acid value of the PKO biodiesel produced was within both ASTM and European standard ranges. The results show PKO can be fully utilized to replace petroleum fuel successfully. However, the viscosity and acid value of WCO, 3.294 cSt and 0.3647 mgKOH/g respectively, exceeded the ASTM and European standards. The FFA of the PKO showed a significant reduction in the amount of free fatty acid in PKO biodiesel compared to WCO biodiesel.

Overall, it can be concluded that, the PKO produced biodiesel had more quality characteristics of a standard biodiesel suitable for blending with conventional diesel than WCO biodiesel. However, further investigation can be conducted by varying the reaction and experimental conditions, such as catalyst-to-oil ratio, temperature, etc., to increase biodiesel yield.

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Conflict of Interest Declaration

The authors declare that there is no conflict of interest on their part.

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