USE OF WATERMELON AND ORANGE FRUIT PEEL DERIVED ECO-FRIENDLY CATALYST FOR BIODIESEL SYNTHESIS

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Abstract

Biodiesel is an alternative eco-friendly fuel synthesized by transesterification. Conventional catalysts used for transesterification, such as potassium hydroxide, are corrosive, expensive and produce a lot of wastewater. This study aimed to obtain eco-friendly catalysts from orange peel and watermelon peel. The two types of fruit peels were carbonized at 700°C to obtain ash which was subsequently extracted with water to obtain the catalysts. The masses of the fruit peel derived catalysts were varied during the transesterification to determine the optimum mass. Using ^{1}H NMR (Nuclear Magnetic Resonance), the percentage conversion of oil to biodiesel was determined and compared to that of potassium hydroxide. The quality of biodiesel produced was also evaluated in terms of density, total percentage of glycerol and heat of combustion. Results showed that the catalyst derived from the orange and watermelon fruit peels contained mainly potassium carbonate and potassium hydrogencarbonate. The percentage conversion of oil to biodiesel by orange peel derived catalyst is greater than that by watermelon peel derived catalyst. The orange fruit peel-derived catalyst at 3.5% was also comparable to potassium hydroxide catalyst in terms of oil to biodiesel conversion, total glycerol content and density. Furthermore, the quality of biodiesel obtained by the orange fruit peel-derived catalyst at 3.5% was determined to be within European Standards (EN 14215) and therefore has great potential for commercial use. Orange peel derived catalyst is a promising eco-friendly alternative to conventional potassium hydroxide as the use of it in transesterification reduces food wastes and conserve resources.

1. Introduction

Energy allows mankind to further economic growth and development, as well as to maintain a high standard of living (Atabani et al, 2012). Currently, it is notable that a majority of our energy demand is satisfied by the burning of fossil fuels, with renewable energies contributing only 15% of Earth's energy supply. Fossil fuels will continue to be depleted rapidly for the foreseeable future (Narasimharao et al., 2007). Hence there is a need to explore alternative fuel, one of which is biodiesel.

Biodiesel is a diesel type fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel is a suitable replacement for petro-diesel as

it is biodegradable, renewable, low in toxicity and emission of harmful carbon emissions (Knothe, 2010). Many types of catalysts can be used for biodiesel synthesis, the most commonly used catalyst being sodium hydroxide or potassium hydroxide (Marchetti, Miguel, & Errazu, 2005). However, the use of such strong alkalis as catalyst have drawbacks such as production of large volumes of wastewater due to soap formation, difficulty in removing the basic catalysts after the reaction, and impossibility of recycling (Viriya-empikul et al., 2010). Acids can also be used as catalysts instead of bases but they have slow reaction rates, require high temperatures, high molar ratio of oil to alcohol, difficult separation of the catalyst and severe environmental and corrosion associated issues (Sharma et al., 2010).

Plants contain alkali metals such as potassium, calcium, sodium and magnesium in the form of various salts. Among these minerals, potassium is the most abundant mineral (Morais et al., 2017). When the plant matter is subject to heat and combusted in the presence of air, the metals are oxidized to metal oxides. Carbon dioxide produced during the burning of carbonaceous matter reacts with potassium oxide to produce potassium carbonate. Other minor product formed during burning, in the presence of water vapour, is potassium hydrogencarbonate (Kumar, 2013). These reactions can be expressed as:

$$K_2O + CO_2 \rightarrow K_2CO_3 \qquad \ldots(1)$$
$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3 \ldots(2)$$
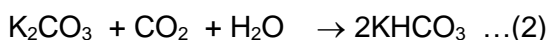
Potassium carbonate and potassium hydrogencarbonate are weaker alkalis than potassium hydroxide, the conventional catalyst used for the transesterification. As such, they are likely to form less soap during transesterification and are promising alternatives to potassium hydroxide.

1.1 Objectives

This study aims to extract potassium carbonate and potassium hydrogencarbonate from orange and watermelon peels, both of which are waste. As much as 809800 tonnes of food waste was generated in Singapore in 2017, with only 16% of it being recycled (Koh, 2019). The percentages of potassium carbonate and potassium hydrogencarbonate in the fruit peel ash were determined using double indicator titration. Finally, transesterification was carried out using the extracted potassium carbonate and hydrogencarbonate as catalyst. Optimum mass of catalyst which led to greatest percentage conversion of oil to biodiesel was determined for each type of fruit peel derived catalyst. The quality of the biodiesel in terms of density, total glycerol content and heat of combustion was evaluated and compared with that of potassium hydroxide.

1.2 Hypotheses

This study hypothesizes that potassium carbonate and potassium hydrogencarbonate can be obtained from orange and watermelon peels.

Catalysts derived from orange and watermelon peel are comparable with potassium hydroxide, a conventional catalyst, in terms of percentage conversion of oil to biodiesel and quality of biodiesel.

2. Materials and Methods

2.1 Materials

Methanol was procured from Labscan. Orange peel and watermelon peel were collected from school canteen. Sunflower oil was purchased from local supermarket.

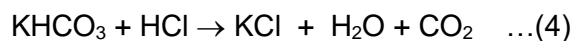### 2.2 Extraction of potassium carbonate and potassium hydrogencarbonate from fruit peels

The watermelon and orange peels were cut, washed with deionised water and dried in an oven at 60°C until constant mass. The dried peels were then calcined at 700°C for 3 hours to obtain a white ash. The fruit peel ash was mixed with deionised water at a ratio of 1:20 parts by weight. The mixture was stirred, heated for 1 hour and filtered. The residue was washed with deionized water to minimize loss of soluble potassium carbonate and potassium hydrogencarbonate. The filtrate collected was subsequently evaporated to dryness over a hot plate until a white solid (catalyst) was formed.

2.3 Analysis of potassium carbonate and hydrogencarbonate in fruit peel derived catalysts

2.5g of catalyst was dissolved in deionized water and made up to 250ml using a volumetric flask. The composition of potassium carbonate and hydrogencarbonate was determined using the double indicator method. In the first titration, 25.0 ml of the solution prepared was titrated with 0.02 mol dm^{-3} HCl using thymol blue indicator until it turned from blue to green (pH 8.3). The volume of HCl required was recorded as V_1 cm^3, and it is the volume required to convert all potassium carbonate to potassium hydrogencarbonate. The reaction is shown in equation (3).

$$K_2CO_3 + HCl \rightarrow KHCO_3 + KCl \qquad …(3)$$

Another aliquot of 25.0 ml of catalyst solution was titrated with methyl orange until it turned from yellow to orange (pH $\approx$ 4). The volume of HCl required was recorded as V_2 cm^3, and it is the volume required to neutralize all the potassium hydrogencarbonate and potassium carbonate.

$KHCO_3 + HCl \rightarrow KCl + H_2O + CO_2$ …(4)

Using stoichiometric calculations, the following 2 formulae were derived to calculate the mass of potassium carbonate and potassium hydrogencarbonate in the catalysts derived from fruit peel ash:

Mass of $K_2CO_3 = 0.02764 \, V_1$ g

Mass of $KHCO_3 = 0.02002(V_2 - 2V_1)$ g

2.4 Transesterification of sunflower oil to biodiesel using catalysts derived from fruit peel

3.3g of methanol, 10 g of sunflower oil and varied masses of fruit peel derived catalysts (1.5% to 3.5% by weight of oil) were refluxed at 65°C for 2 hours. The biodiesel was then separated from the glycerol with a separating funnel, washed with deionised water until neutrality, and dried using anhydrous sodium sulfate.

Transesterification was also carried out with 1% KOH which is the conventional catalyst.

The biodiesel synthesized was characterized using ^{1}H NMR and the percentage conversion of oil to biodiesel was determined from the integration ratios of the methyl and alpha protons.

2.5 Evaluating the quality of biodiesel synthesized using fruit peel derived catalyst

2.5.1 Glycerol test (total and free glycerol)

It is important to monitor the total glycerol content in biodiesel as high levels of glycerol lead to severe operational problem such as injector deposits and filter clogging. The determination of total, free and combined glycerol in the biodiesel sample was carried out utilizing a modification of American Oil Chemists' Society Method Ca 14-56 Total, Free and Combined Glycerol (Iodometric-Periodic Acid Method) (AOCS Official Test Method Ca 14-56. 1991) by oxidation of glycerol with periodic acid and subsequent periodate titration.

2.5.1.1 Free Glycerol Test

A sample of 5.00 g of biodiesel was transferred to a 100ml volumetric flask. 9.0ml of dichloromethane was added, followed by 50.0 ml of water. The mixture was shaken and the solution was made up to 100 ml with deionised water. On standing the mixture separated into 2 layers, the aqueous and oil layer. A volume of 25.0 ml of periodic acid and 25.0ml of the aqueous layer were transferred into another conical flask. 10ml of potassium iodide was added and mixture was allowed to stand for 60 seconds. The mixture was topped up to 125 ml with deionised water and the mixture titrated with sodium thiosulfate using starch as indicator. A blank was prepared

with the same reagents, but without the sample. The volume of sodium thiosulfate required was used to calculate the percentage of free glycerol.

The following formula was used to calculate the percentage of glycerol:

$$\text{Glycerol (\%)} = \frac{\frac{[B-S][M][0.0230]}{[W]*0.294}*100\%}{}$$

Where B = ml of thiosulfate to titrate the blank, M = normality of thiosulfate, S = ml of thiosulfate to titrate the sample, W = weight of sample extracted in g

2.5.1.2 Total Glycerol Test

A 5.00 g sample of biodiesel was refluxed with 15.0 ml of 0.7 mol dm^{-3} potassium hydroxide in 95% ethanol for 30 minutes. The mixture was quantitatively transferred to a 100ml volumetric flask and 9ml of dichloromethane followed by 2.5ml of acetic acid were added. The glycerol content was determined as described in the free glycerol test. The percentage of total glycerol was compared with European Biodiesel Standard (EN14214).

2.5.2 Density

Mass of 25.0 ml of biodiesel was determined to 3 decimal place precision and the density calculated using the following formula:

$$Density = \frac{Mass}{Volume}$$ where M = mass in g and V= volume in cm^3

The density of biodiesel was compared with European Biodiesel Standard (EN14214).

2.5.3 Heat of combustion

A sample of 10.00 g biodiesel was weighed into a crucible. A wick was placed into the fuel and the total mass measured. A clean test tube was filled with 10.00 g of deionised water and placed in a calorimeter. A thermometer was inserted and the initial temperature taken. The crucible was positioned at the bottom of the test tube and the set-up insulated. The wick soaked in fuel was lit. The flame was extinguished when the temperature reached 90°C. The difference in mass of biodiesel was recorded. The experiments were repeated till consistent results were obtained. Heat of combustion was calculated with the formula:

$$Q(J/g) = \frac{mc\Delta\theta}{mass\ of\ biodiesel\ used}$$ Where m=10g, θ = temperature change, c= specific heat capacity of water= 4.186Jg^{-1} K^{-1}.

To compensate for heat loss to the surrounding, the heat of combustion of dodecanol was determined using the calorimeter and compared with literature value. The difference between the experimental value and literature value will be the heat loss to the surrounding.

3. Result and Discussions

3.1 Yield of fruit peel ash

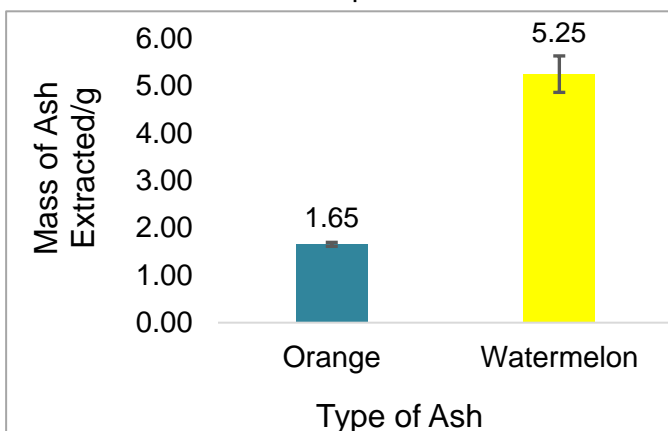Watermelon peel yielded a significantly greater mass of ash than orange peel after calcination and extraction with water as the p- value of one tailed Mann-Whitney test is 0.005.

Figure 1. Yield of fruit peel ash after extraction with water

3.2 Characterisation of catalyst derived from fruit peel ash

3.2.1 By Energy Dispersive Spectroscopy (EDS)
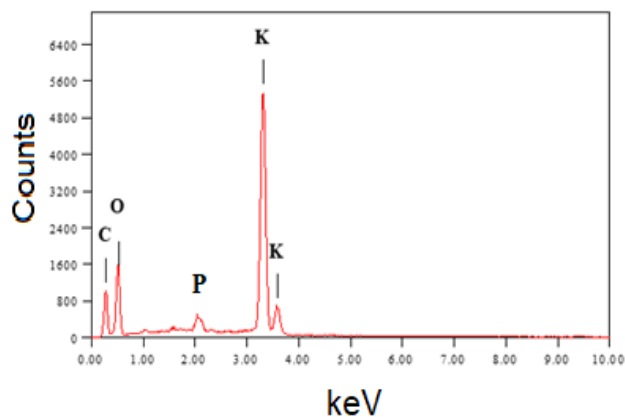
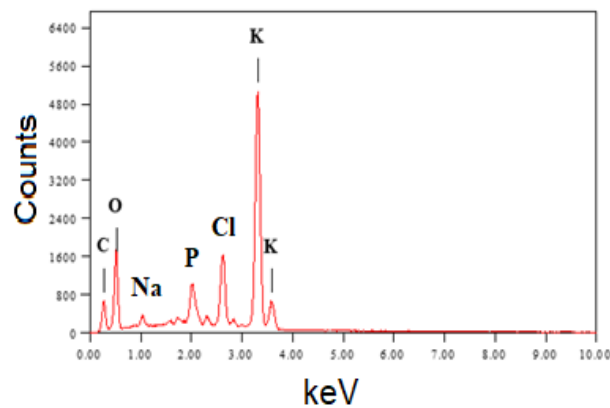**Figure 2:** EDS spectrum of orange peel derived catalyst

Figure 3: EDS spectrum of watermelon peel derived catalyst

The EDS spectra of catalysts derived from orange peels and watermelon peel (Figure 2 & Figure 3) reveal peaks corresponding to potassium, carbon and oxygen. The catalyst derived

from watermelon peel also contains sodium, phosphorus and chlorine. Potassium is the main element present in both catalysts, with the percentage being 41.45% and 41.75% respectively. These values are found to be between the % of K in K_2CO_3 and $KHCO_3$, suggesting that the catalysts contain a mixture of both K_2CO_3 and $KHCO_3$.

3.2.2 Composition of K_2CO_3 and $KHCO_3$
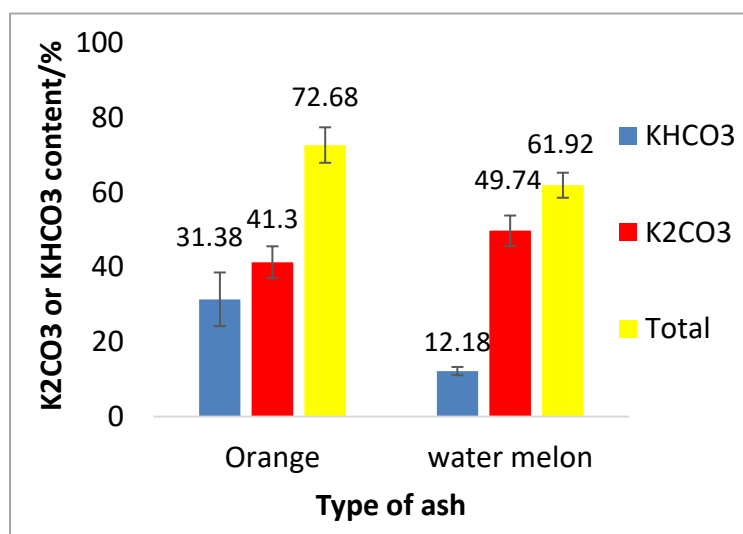
Figure 4: Composition of orange peel ash and watermelon rind ash

Using double indicator titration, the percentages of potassium carbonate and potassium hydrogencarbonate in the orange peel and watermelon peel derived catalysts were determined (Figure 4). Interestingly, watermelon peel derived catalyst contains more potassium carbonate while orange peel derived catalyst contains significantly more potassium hydrogencarbonate (p-value = 0.02). Orange peel derived catalyst contains a greater total percentage of potassium carbonate and potassium hydrogen carbonate.

3.2 Transesterification of sunflower oil into biodiesel using fruit peel derived catalysts

Figure 5(a). Structure of oil

Figure 5(b). Structure of biodiesel
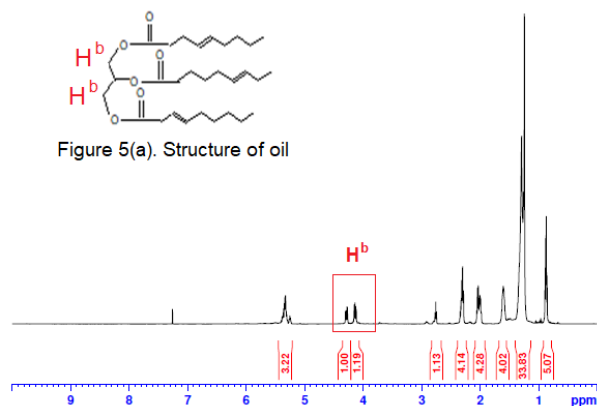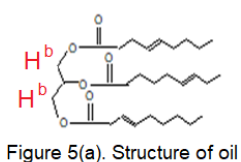
Figure 6a. ^{1}H NMR spectrum of sunflower oil
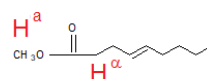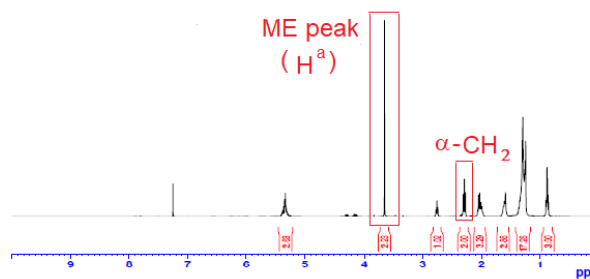
Figure 6b. ^{1}H NMR spectrum of biodiesel synthesized using orange peel ash as catalyst

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Methanol, sunflower oil and fruit peel derived catalysts (1.5% to 3.5% of mass of oil) were refluxed for 2 hours. Biodiesel obtained was characterized using ^{1}H NMR. Figures 6a shows that the doublet at 4.12 to 4.31 ppm corresponding to the glycerol protons (H^b) in oil has disappeared and instead a sharp peak at around 3.6 ppm corresponding to the methyl group (H^a) in biodiesel has appeared (Figure 6b). This shows that acid transesterification has been successful.

The following formula (Knothe, 2001) was used to calculate the percentage conversion of waste oil to biodiesel:

$$\left[\frac{2A_{ME}}{3A_{\alpha\text{-CH}_2}} \right] \times 100$$

A = integration value from NMR spectrum
ME : peak corresponding to methyl protons
α-CH$_2$: peak corresponding to alpha protons

Table 1 shows the percentage conversion of oil to biodiesel by different percentages and types of catalyst.

Table 1. Percentage conversion of oil to biodiesel by different catalysts

Type of Catalyst	Biodiesel Conversion/%
1.5% Orange	95.3
2.5% Orange	96.3
3.5% Orange	97.0
1.5% Watermelon	92.3
2.5% Watermelon	93.7
3% Watermelon	95.5
3.25% Watermelon	96.2
3.5% Watermelon	17.2
1% KOH	97.0

Interestingly, the percentage conversion for oil to biodiesel using 3.5% watermelon peel derived catalyst is much lower than the rest. This is because the watermelon peel derived catalyst contains more potassium carbonate which is more alkaline than potassium hydrogencarbonate, hence forming soap with the triglyceride present in oil. The process of soap formation was postulated to have occurred via the following reactions, as illustrated by the following equations:

$$2CH_3OH + K_2CO_3 \longrightarrow 2CH_3OK + H_2O + CO_2$$
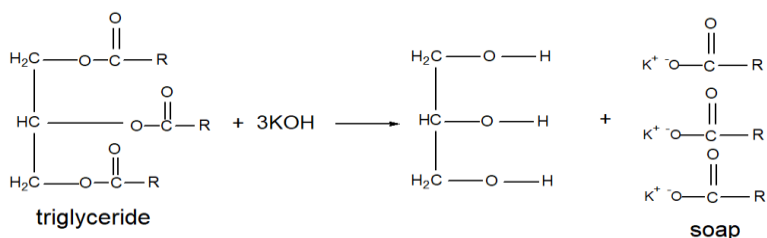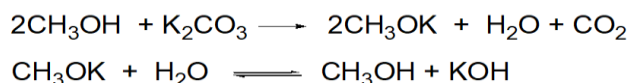
$$CH_3OK + H_2O \rightleftharpoons CH_3OH + KOH$$

Table 2. compares the percentage conversion of oil to biodiesel by the best performing catalyst for both fruit peels (3.25% watermelon peel and 3.5% orange peel) with other studies. The percentages conversion of the biodiesel derived from orange peel and water melon peel are comparable to 3% Date Seeds catalyst and 1% KOH catalyst but slightly worse than the 2.75% banana peel catalyst.

Table 2. Percentage conversion of oil to biodiesel by different catalysts

| Type of Catalyst	Oil to Biodiesel Conversion/%	Reference
3.25% Watermelon Peel	96.2	This study
3.5% Orange Peel	97.0	
1% KOH	97.0	
3% Date Seeds	96.7	Khelafi, Kalloum, Boulal, Mansir, Bakache and Taufiq-Yap (2018)
2.75% Banana Peel	98.5	Etim, Anietie, Betiku, Olaniyi, Ajala, and Ojumu (2018)

3.3   Evaluating the quality of biodiesel

3.3.1 Density
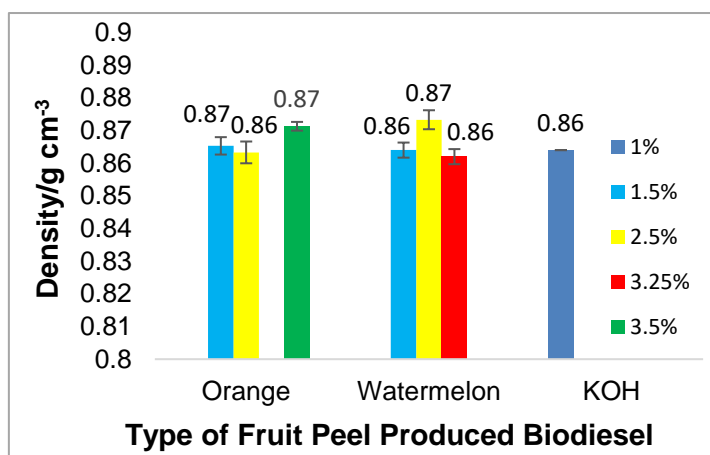
Figure 7. Density of biodiesel produced using orange peel, watermelon peel and KOH catalysts

According to the European Standard for biodiesel (EN 14215), the density of biodiesel should be between 0.86 to 0.90 g/cm³. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel (Ryan, Dodge, & Callahan, 1984). The densities of the biodiesel produced by orange and watermelon peel derived catalyst were comparable with that produced by potassium hydroxide) and are within European Standards.

3.3.2 Heat of combustion
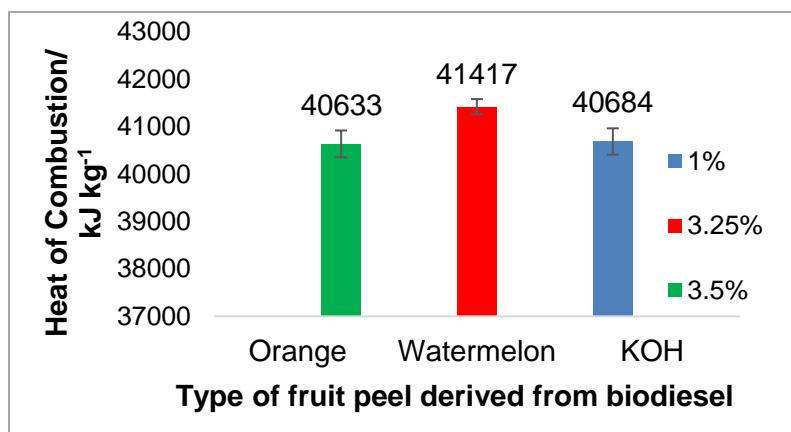
Figure 8. Heat of combustion of biodiesel produced using orange peel, watermelon peel and KOH catalysts

Heat of combustion is the amount of energy liberated when a unit quantity of fuel is combusted. The heat of combustion of biodiesel produced by the best catalyst from each fruit peel (3.5% orange peel and 3.25% watermelon) is not significantly different from that produced by KOH (p-values of Kruskal Wallis Test = 0.11).

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3.3.3 Total glycerol content

European standard for total glycerol is below 0.25%. Figure 9 reveals that biodiesel synthesized using 1.5 to 3.5% orange fruit peel derived catalyst and 3.25% watermelon fruit peel derived catalyst met the specification of European Standard while biodiesel synthesized using 1.5% and 2.5% watermelon fruit peel derived catalyst exceeded the standard. This is due to watermelon peel derived catalyst being less effective, resulting in incomplete transesterification and leading to larger amounts of bound glycerol (reaction intermediates) being formed. The result is in good agreement with the lower percentage conversion of oil to biodiesel by 1.5% and 2.5% watermelon peel derived catalysts.
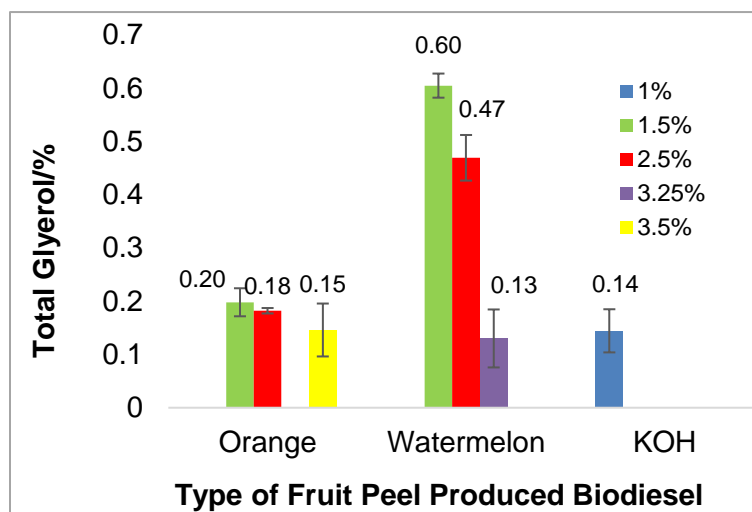
Figure 9. Total glycerol content of biodiesel produced using orange peel, watermelon peel and KOH

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4. Conclusion and Future Work

The catalysts derived from the orange and watermelon fruit peels contained mainly potassium carbonate and potassium hydrogencarbonate. Catalyst derived from watermelon fruit peel contains more potassium carbonate while that derived from orange peel contains more potassium hydrogencarbonate. Catalysts derived from orange peel results in greater percentage conversion of oil to biodiesel than that derived from watermelon peel. The orange fruit peel-derived catalyst at 3.5% is also a comparable catalyst to potassium hydroxide catalyst in terms of oil to biodiesel conversion, total glycerol content and density. Furthermore, the quality of biodiesel obtained by the orange fruit peel-derived catalyst at 3.5% met the European Standards and is therefore suitable for commercial use. As orange fruit peels are a common food waste, the use of it to provide catalysts for the production of biodiesel reduces waste and at the same time produces a green fuel.

The scope of this study could be expanded by investigating the use of orange peel derived catalysts to catalyse the transesterification of recycled oil instead of fresh oil, as well as further evaluating other properties of biodiesel such as flashpoint, acid value and iodine number. The percentage of watermelon peel derived catalyst used during transesterification could be further optimized to increase the percentage conversion of oil to biodiesel.

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