Optimisation of Bio-Diesel made from Non-Edible Avocado Seed Oil (ASO) Using Homogenous $\text{H}_2\text{SO}_4$/KOH Catalyst

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ABSTRACT

Bio-diesel has proven to be a better alternative to fossil diesel due to its eco-friendly, ease of production, high cetane rating and sustainability (renewable) which are the major drawback of fossil fuel. In this study, a non-edible avocado seed oil was used to formulate biodiesel. The avocado seed oil was extracted using cold press mill. The seed oil was then subjected to esterification to reduce the acidic value to $<1\text{mgKOH/g}$ using sulphuric acid catalyst ($\text{H}_2\text{SO}_4$). Subsequently, the optimisation of the transesterification process was carried out by investigating the effect of different blend of molarity of oil to methanol (1: 6, 1.5:6, 2: 5, and 2.5:4.5) concentration of KOH catalyst % weight (0.5, 1, 1.5 and 2), reaction time in minutes (55, 65, 75, and 85) and reaction temperature (55,60,65 and 70) $^\circ\text{C}$ on the yield of ASO biodiesel (%). The study revealed that highest ASO biodiesel yield (%) was observed with KOH 1% weight concentration; 75 min reaction time, 65$^\circ\text{C}$ and 1: 6 molarity of oil to methanol. The physico-chemical parameters of ASO biodiesel assessed were in conformity with ASTM standard and with literature. The assessment revealed that ASO biodiesel has some improved properties over fossil diesel. Therefore, it can be used solely or as a blend in diesel engine.

Keywords: ASTM, esterification, optimisation, transesterification, biofuel, sustainability

Introduction

The Fossil fuel which has been a major drive to global economy has suffered setback due to its environmental concern and poor sustainability as it is not renewable. This has necessitated research into alternative bio-based feedstock to produce bio-fuel. Bio-fuel according to Abdul-Wahab and Takase; Onimisi et al. [1, 2], refers to an alternative fuel, made from renewable resources such as vegetable oils, animas such as animal fats and once used cooking oils. Van Gerpen et al., [3] further explained that biodiesel is a liquid obtained chemically from chemical reactions between either vegetable oils or animal fats and an alcohol. Apart from being
environmental benign, bio-diesel which is one of the important components of bio-fuel, has numerous advantages over fossil- diesel, such as high sustainability [4]; biodegradable [5], non-toxic emission [6], high cetane rating (which translate to smooth engine operation with least noise) [7], lower health risk [8], ease of production [9]. Higher flash point (minimum of 100°C) [10, 11], stable product (ease of transportation) than fossil-diesel and can be blend readily with fossil-diesel [12].

Several routes for the formulation of bio-diesel have been identified by several studies. For instance, [13] affirmed that high cetane rating bio-diesel can be produced via pyrolysis (anaerobic thermal degradation). However, ash contents, and carbon residues that accompanied the end products are the major setback of the process [4]. Demirbas [14] is of the opinion that pyrolysis process is better with the production of bio-gasoline than bio-diesel. Sigh and Sigh [15] revealed that Micro emulsion method has been used to synthesise bio-diesel from soybean oil, however, [16] reported that biodiesel formulated from micro-emulsion process undergo partial combustion thereby leading to deposit of carbon in the engine [16]. Yusuff et al. [5] acknowledged the feasibility of producing biodiesel via supercritical process. However, transesterification process enjoyed wide acceptability and utilisation due to its simplicity of process, low cost, improved desire property and quality bio-diesel product [17, 18, 19].

Transesterification process (otherwise known as alcoholysis) involves displacement of alcohol from ester by another alcohol. This is furthered explained by [1, 17] that production of bio-diesel via transesterification involve the use of alcohols, usually the first C₁ and C₂ chain alcohol (methanol and ethanol), in a chemical reaction with vegetable oil or animal fats in presence of alkaline catalyst to form long chain of fatty acid of methyl ester. Methanol is easily accessible and affordable, Romano and Sorrichetti [11] reported that bio-diesel formulated with methanol is reported to have desired and improved physico-chemical parameters such as high reactivity and high yield. While ethanol is eco-friendly, and can be synthesised from sugarcane molasses, however, bio-diesel formulated using ethanol is easily forms emulsions which lead to difficult in separating end products (especially with used oils) [20]. However, several studies recommended pre-treatment of oil or fat before subjected it to bio-diesel process. This pre-treatment process (esterification) involves the use of concentrated hydrochloric acid (HCl) or Sulphuric acid (H₂SO₄) to reduce the free fatty acid (FFA) to <1mgKOH/g [21], as high FFA in oil aids
saponification [11] and reduce the quantity yield of biodiesel [22]. According to [23], two-step method is more suitable for improving the desired quality and quantity of biodiesel.

Gidigbi et al [24] revealed that avocados available in different species, but Hass specie is the most common specie in many places. Hass Avocado seed, though represents 12% of the total mass, is usually considered a waste in the production of pulp and oil. Avocado seed oil contains mainly triglycerides and free fatty acid. Therefore, the choice of using non-edible avocado seed oil is partly to reduce waste, and gain economic advantages. Avocado seed oil contain higher percentage of mono-unsaturated fatty acid which made it more suitable for the production of biodiesel, as the department of energy in United States of America [25] affirmed that a perfect biodiesel should contain only mono-unsaturated fatty acids.

**Materials and Methods**

**Materials:**

H₂SO₄, HCl, NaOH, KOH. All reagents were of analytical grade. Avocado seed oil, desiccators, hot plate, Oven, separating funnel, heating mantle, water bath, crucible, thermometer, magnetic stirrer, two neck reaction flask, centrifuge.

Two steps approach was used in the production of biodiesel.

**Methods:**

**Extraction of Avocado seed oil**

Extraction of the avocado seed oil was carried out using the procedure described by Gidigbi et al. [26]

**Pre-treatment of Avocado seed oil (Acid-catalysed- esterification)**

The avocado seed oil was subjected to esterification process according to the method described by [1, 18] with few modification on the amount of avocado seed oil and methanol. The avocado seed oil was firstly heated at 60°C for 20 mins to remove residue moisture. Then, 60ml of methanol was introduced into a 500ml conical flask containing 200ml of preheated avocado seed oil and 0.3ml of concentrated H₂SO₄ was subsequently introduced. The mixture was placed on
a hot plate with magnetic stirrer for 60 minutes at 50°C. The mixture was separated by separating funnel with glycerine at lower layer, and esterified oil at upper later.

Transesterification of the esterified oil

Transesterification process was done in several batches. The transesterification procedure for each batch of esterified avocado seed oil was carried out according to procedure described by Azeez et al [12] and Puasang et al [7, 27]. 50ml of esterified avocado seed oil was measured into 500ml Pyrex conical flask placed on a hot plate with magnetic stirrer. Several batches of transesterification process were carried out using these following reaction conditions; molarity of oil to methanol (1: 6, 1.5:6, 2: 5, and 2.5:4.5), concentration of KOH catalyst % weight (0.5, 1, 1.5 and 2), reaction time in minutes (55, 65, 75, and 85) and reaction temperature (55, 60, 65 and 70) °C. The mixture was separated using separating funnel in which heavier glycerol at lower layer and subsequently tapped off, leaving bio-diesel at upper later inside separating funnel. The bio-diesel was rinsed with warm distilled water to remove unreacted catalyst and methanol. The bio-diesel was subsequently heated to 100°C to evaporate the residue of water present in the bio-diesel and transferred into desiccator to remove remaining water moisture present in the biodiesel.

The percentage yield

Characterisation of the benign biodiesel

The physico-chemical properties of the biodiesel were determined by ASTM and AOAC, (2000).

Percentage (%) Yield

The percentage yield of the biodiesel was done according to the procedure described by produced biodiesel was characterized by [7]

The percentage biodiesel yield was calculated as follows:

\[
\text{Biodiesel yield (\%) } = \frac{\text{Weight of biodiesel}}{\text{Weight of Avocado seed oil}} \times 100
\]

Determination of Flash point, Pour point and Density.
The flash point and pour point of the biodiesel was determined by the method described by American Society for Testing and Materials ASTM [28] D-93, and D-97. While the Ash content of the biodiesel was determined by the procedure according to AOAC [29].

Determination of Saponification, viscosity and acid value

The Saponification and kinematics viscosity was determined by the ASTM [28] D-2500 and D445-06 procedure for analysing fuel while acid value was determined by AOAC [29] procedure.

Determination of Fire point, specific gravity, and iodine value

Determination of Fire point, specific gravity and iodine value was determined by the method described by ASTM [28].

Result and Discussion

Optimisation of Transesterification of Esterified Avocado Seed Oil (EASO)

The influence of different ratio of oil to methanol on the biodiesel yield (%)

The transesterification was carried out with several blend at constant reaction time (65 mins), reaction temperature (60°C) and amount of catalyst (KOH 1% wt). The highest percentage yield (%) of biodiesel was observed in 1: 6 esterified avocado seed oil to methanol, while least percentage yield (%) was recorded in 2.5: 4.5 ratio of Esterified avocado seed oil to methanol. This result is in consonance with Wahab and Takase [1], who reported 93% yield for 6:1 ratio of methanol to neems oil, and Sannia et al [30] reported same value for palm kernel oil. The decrease in percentage (%) yield of biodiesel as the value of EASO altered may be due to the deficiency of alcohol to neutralise triglycerides as [31] reported that transesterification process is a reversible reaction hence huge amount of alcohol is needed to favour forward reaction.
Influence of different reaction time on the percentage yield (%) of Biodiesel

The transesterification process was carried out with several reaction time of 55, 65, 75 and 85 minutes under constant reaction temperature (65\(^{\circ}\)C), catalyst (KOH 1% wt) and molar ratio (ASO oil 1: 6 Methanol). The gradual increase in bio-diesel yield (%) increases from 55 mins till 75 mins but steadily decreases till 85 mins. Time of reaction provides opportunity for the reaction to complete which enhanced forward reaction, further reaction time may lead to hydrolysis thereby favouring backward reaction and decline in biodiesel yield. This is slightly different to Abdul-Wahab and Takase [1] who reported that highest yield (92.5%) was reported at 60 mins. The variation maybe due to difference in content of fatty acid.

Figure 1: The influence of different ratio of oil to methanol on the biodiesel yield (%)

Figure 2: Influence of different reaction time on the percentage yield (%) of Biodiesel
Influence of varied reaction temperature on the percentage yield (%) of Biodiesel

The transesterification process was carried out with different reaction temperature (55, 60, 65, 70°C) under same condition of reaction time (60 mins) and same concentration of catalyst (KOH 1% wt). The steady increase in the yield (%) was recorded as the temperature increases from 55°C to 65°C, but gradually declined as the reaction temperature increases to 70°C. This may be due to the fact that increase in temperature increase the chemical reaction, thereby leading to higher yield (%) of biodiesel. The gradual yield declination recorded as temperature continue to increase maybe as a result of hydrolysis of methyl ester thereby favouring backward reaction (reactant) against forward reaction (product) [32]. This approach was also notice in the biodiesel formulated using groundnut oil [33]. Although, highest yield (%) was observed at 65°C which was 92.4%, but Verma and Sharma [13] were of the opinion that reaction temperature of 60°C was penned for the highest yield (93%) of most biodiesel.

![Graph](image)

**Figure 3:** Influence of varied reaction temperature on the percentage yield (%) of Biodiesel

Influence of varied catalyst on the percentage yield (%) of Biodiesel

The transesterification process was carried out using varied catalyst concentration while other operation condition such as temperature of reaction (65°C), reaction time (60 mins) and molar ratio of oil to methanol is 1:6 remain constant. A steady increase was observed as the concentration of catalyst increase from 0.5 to 1% weight of Potassium Hydroxide (KOH). Steady
decreases were noted as the catalyst loading increases. This behaviour may be attributed to increase in catalyst usage, [34] affirmed that excessive usage of catalyst tend to form emulsions leading to high viscous product and complicate the recovery of biodiesel. This similar trend was also reported for peanut [35] and waste frying oil [36]. While Kyari and Yunus [37] reported that 1.25 wt% of catalyst concentration yielded 95.8% of the biodiesel.

![Figure 4: Influence of varies catalyst on the percentage yield (%) of Biodiesel](image)

The physico-chemical parameters of the synthesized bio-diesel and compare with fossil diesel and ASTM standard

Table 1 revealed the result of the assessment of physico-chemical properties of the formulated biodiesel and compared with ASTM standard for both Biodiesel and fossil diesel. Specific gravity measures ratio of the biodiesel density to the water. The Specific gravity at 15°C of the ASO biodiesel was at 0.8802. This is still in line with the acceptable range for both ASTM biodiesel (0.88) and fossil diesel (0.85). Also, [38] reported the specific gravity of 0.8700 for biodiesel made from palm kernel oil. Having lower specific gravity (less than 1) suggestive of faster burning fuel which may lead to complete combustion in an engine [39]. Acid value is one of the major properties of biodiesel. It affirms the stability of the biodiesel over a course of time [33]. Acid value of the biodiesel was reported to be 0.46 mKOH/g which is still within the range accepted for biodiesel (ASTM D-664). Onimisi et al [2] reported 0.66 mKOH/g and 0.44 mKOH/g for biodiesels made from White palm kernel oil and black palm kernel oil respectively.
Flash point measures the degree of flammability (catch fire easily) of the biodiesel. ASO biodiesel catch fire easily at 128 °C, which still within the acceptable range for ASTM biodiesel and well above ASTM range for fossil diesel. This demonstrated that ASO biodiesel has an excellent stability with fire, compare to diesel produced from fossil fuel. Therefore, it is safe for both storage and transportation. The iodine value measures the degree of unsaturation in the fatty acids. It also indicates the quality of biodiesel by evaluating the oxidative stability of biodiesel [40]. The iodine value for ASO biodiesel was recorded to be 16.39 g/100. This is still within the acceptable range for European Biofuel standard. This is suggestive that ASO biodiesel is more stable to air, and will not be easily oxidised to peroxide and acid [41].

Kinematic viscosity is one of the most significant parameters of biodiesel as it reveals the flowability tendency of the biodiesel. Rate of flow of fuel usually has significant impact on fuel injection in the vehicle equipment and spray atomization particularly at low temperatures [42]. The Kinematic viscosity of the ASO biodiesel was reported to be 6.91mm²S⁻¹ at 40°C which is higher than fossil diesel (1.3 - 4.1), and slightly higher than ASTM biodiesel range. Therefore, ASO biodiesel will function optimally when it is blend with fossil diesel inorder to reduce the viscosity, and preserve the vehicle injection system. Maulidiyah et al. [18] also reported that biodiesel made from crude palm oil has 2.24 mm²S⁻¹ at 40°C.

The ash content revealed the quantity of inorganic contaminants present in the fuel sample. This contaminant can be emitted from fuel usage. The ash content of ASO biofuel was estimated to be 0.01 mgKOH/g. This is in consonance with ASTM regulation of 0.01 max ash content [28]. This is show that contaminant in ASO biodiesel has been reduced to bearest minimum, which means ASO biodiesel will not cause air pollution. The saponification value is a vital factor that determine whether an oil is suitable for soap making. Ofoefule et al., and Audu et al. [41, 43] explained that saponification value is usually used to assess the level of impurities in a biodiesel, and to also determine the molecular weight of fatty acids methyl ester. The saponification value for ASO biodiesel reported to be 211.87 mgKOH/g is within the ASTM standard for biofuel. The lower value of saponification signifies high molecular weight of methyl ester, thereby improving the quality and stability of biodiesel oil.

The fire point of a biodiesel indicates a temperature at which biodiesel can sustain combustion. This is temperature at which vapour from fuel can catch fire and stays for at least five seconds.
The fire point for ASO biofuel was recorded as 141°C. The pour point measures the lowest temperature in which a frozen oil can flow. This parameter assesses the stability of fuel oil in the cold weather [42]. The pour point for ASO biodiesel is -1°C. Awolu and Layokun [44] reported -2°C for biodiesel made from neems. The difference may be due to different in seed varieties and locality [45]. The low pour point revealed that the ASO biodiesel will perform optimally in cold region.

**Table 1:** The comparison between the physico-chemical properties of biodiesel oil and ASTM acceptable range for fossil diesel and Biodiesel

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ASO Biodiesel</th>
<th>ASTM Biodeisel acceptable range [28]</th>
<th>ASTM Fossil diesel acceptable range [28]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity at 15°C.</td>
<td>0.8802</td>
<td>0.88</td>
<td>0.85</td>
</tr>
<tr>
<td>Acid value (mKOH/g)</td>
<td>0.46</td>
<td>0.5 (ASTM D-664)</td>
<td>-</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>128</td>
<td>100 – 170</td>
<td>60-80</td>
</tr>
<tr>
<td>(ASTM D93)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodine value (g/100)</td>
<td>16.39</td>
<td>120 max (EN 14214)</td>
<td>-</td>
</tr>
<tr>
<td>Kinematic viscosity (mm²S⁻¹) at 40°C</td>
<td>6.91</td>
<td>4.0-6.0</td>
<td>1.3 - 4.1</td>
</tr>
<tr>
<td>Ash content (mgKOH/g) (%)</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Saponification value (mgKOH/g)</td>
<td>211.87</td>
<td>95 – 370</td>
<td>-</td>
</tr>
<tr>
<td>Fire point (°C)</td>
<td>141</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-1</td>
<td>-5 to -10 (ASTM D97)</td>
<td>-35 to -15</td>
</tr>
</tbody>
</table>

**ASO means Avocado Seed Oil**
Conclusion

The ASO biodiesel was successfully synthesised from non-edible avocado seed oil with enhanced properties over fossil diesel. The optimisation of the transesterification process assessed the influence of oil to alcohol (methanol); concentration of KOH catalyst (weight), reaction time (minutes) and reaction temperature (°C) on the yield of biodiesel (%). The study revealed that highest biodiesel yield (%) was observed with KOH 1% weight concentration; 75 min reaction time, 65°C and 1:6 molarity of oil to methanol reaction conditions.

Further assessment and comparison of physico-chemical parameters conducted on the ASO biodiesel revealed that major properties are in compliance with ASTM standard for fossil diesel. It also affirmed that ASO diesel has the high flash point which make it safer to handle, stored and safe to transport from one location to another. The moderate kinematics viscosity observed in ASO biodiesel proved that there is high tendency of miscibility/blend of ASO biodiesel with fossil diesel. Also, the low ash content present in ASO biodiesel asserted that ASO biodiesel will not cause air pollution (eco-friendly), which is one of the disadvantage of fossil diesel. Therefore, ASO biodiesel has some improved characteristics over fossil diesel.

References


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**HOW TO CITE THIS ARTICLE**