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Original Research Article

Improving the Oxidative Stability of Biodiesel Produced from Water Melon Oil using a Local Antioxidant

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ABSTRACT

Due to increasing biodiesel production from vegetable oils, there is need for more research on how biodiesel stability and quality can be improved. Therefore, this study has compared the oxidative stability of biodiesel produced from watermelon seed oil with and without the addition of a natural antioxidant - Mitrcarpus scaber. The work examined the biodiesel stability properties such as kinematic viscosity, peroxide and acid values over time. It was found that for a period of 16 days, the biodiesel sample containing the antioxidant showed more stability as seen in the lower peroxide, acid and kinematic viscosity values compared to the biodiesel sample without antioxidant. This implies that under storage conditions, biodiesel stability as well as quality can be ensured when the biodiesel is combined with natural antioxidants such as Mitracarpus scaber.

1. INTRODUCTION

The world is anxiously in search of alternative energy sources to fossil fuel. This is due to the numerous challenges of depleting reserves, increasing global warming, rise in sea levels and environmental pollution associated with fossil fuel usage (Devarajan 2019). A major cause of these challenges is the emission of greenhouse gas gases from combustion processes using fossils (Liu et al., 2019). Since biodiesel is cleaner and burns with reduced greenhouse gas emission and its' fuel properties are similar to petrodiesel, it has attracted more research attention as a suitable alternative. Despite these advantages, several demerits have also being identified. Several demerits of biodiesel production include high viscosity, NO_x and smoke emissions, as well as reduced oxidation stability (Devarajan 2019).

Oxidation stability is of more interest due to its usefulness. The oxidation potential determines the extent of biodiesel corrosiveness (Hoang et al., 2019). Besides, biodiesel is known to exhibit some corrosive nature

with the onset of oxidative degradation (Zuniga-Diaz et al., 2018). Due to this usefulness, research is actively investigating different approaches of improving the oxidative stability of biodiesel. Studies have shown that addition of curcumin (Santos et al., 2016), application of heat (Ferrari et al., 2005), the fatty acid methyl ester profile (Nogales-Delgado et al., 2019) and storage conditions (Canha et al., 2017) are means of improving the stability of biodiesel. Similarly, different oil processing methods have been shown to optimize the oxidative stability of biodiesel (Lepak et al., 2016).

A recent study conducted by Buosi et al. (2016) demonstrated the efficiency of antioxidants in protecting biodiesel from oxidation effects. The effect of oxidation on biodiesel stability have been investigated for feedstock such as soybean oil (Ferrari et al., 2005), waste cooking and soybean oils (Lepak et al., 2016), rice bran oil (Zuniga-Diaz et al., 2018), safflower oil (Nogales-Delgado et al., 2019), catfish oil (Fu et al., 2018) and Jatropha curcas oil (Nurudeen et al., 2014). Though Dunn (2005) and Nogales-Delgado et al. (2019) found that synthetic antioxidants were more effective than natural antioxidants in improving biodiesel stability, Ferrari et al. (2005) concluded from their research with the Rancimat equipment that the presence of natural antioxidants has a more direct effect on biodiesel stability. However, more research is needed to support this view presented by Ferrari et al. (2005).

To this end, this study will compare the oxidative stability of biodiesel produced from water melon oil with and without the addition of *Mitracarpus scaber*. Though mitracarpus scarber is a medicinal plant with antimicrobial properties (Bisignano et al., 2000), studies have shown that it also possess antioxidant property (Fawole et al., 2013). Besides, this study will take into cognizance the effect of time variation on the biodiesel stability by investigating its' influence on the kinematic viscosity, peroxide and acid values of the water melon oil.

2. MATERIALS AND METHODS

2.1. Sample Collection and Preparation

The watermelon fruits were obtained from the refuse dumps in Temboga market in Benin City, Edo State, Nigeria. The seeds were separated from the fruits and dried for 5 days in the sun at ambient temperature for easy dehulling of seeds. The seeds were dehulled after which they were further dried in an electric oven at 60 ^{o}C for 5 hours so as to reduce the moisture content to an appreciable value in order to ease the extraction process. The prepared dehulled seeds were grounded so as to improve the surface area for extraction.

2.2. Extraction of watermelon Seed Oil

The Soxhlet extraction procedure was adopted for the extraction of the watermelon seed oil and this process was carried out at the National Centre for Energy and Environment, University of Benin. The seeds were blended and weighed and then poured into a tray and the Soxhlet extraction chamber bag was filled with the seeds. The bag was then placed in the extraction chamber with hexane (the solvent used) and the set up was heated using a heating mantle. The apparatus was set up and the heating mantle turned on to begin extraction. Three runs were used per extraction chamber bag filled so as to ensure proper extraction of oil. The residue was discarded each time the required number of runs was completed with the bag refilled with fresh biomass (Ajay et al., 2016).

2.3. Characterisation of Watermelon Seed Oil

The extracted oil was characterised to determine its physico-chemical properties. The properties that were determined include oil yield, peroxide value, acid value, Free fatty acid (FFA) value, viscosity, density, saponification value, iodine value and specific gravity according to the methods of A.O.A.C (1990).

2.4. Biodiesel Production

The oil was poured into a glass reactor and then heated to 50 ^{o}C. Also, 185 g of methanol was measured into a beaker and 0.5 g NaOH pellets which served as a catalyst was added and it was gently heated in order to dissolve all the sodium hydroxide pellets. The mass of methanol was calculated on a molar ratio basis. The

catalyst was allowed to dissolve in the methanol before contact with the oil. The methanol/catalyst mixture was then poured into the reactor and it was immediately sealed to prevent vaporization of the alcohol. The glass reactor was placed on a magnetic stirrer to begin the reaction. Biodiesel production was carried out at a oil-methanol ratio (1:6), concentration of catalyst (1.5 wt%), temperature (60 ^{o}C), stirring speed (1600 rpm) and methanol volume (430 ml). Biodiesel samples were withdrawn at different intervals of time and they were allowed to separate from glycerol in separating funnels. The yield was measured and recorded. All the biodiesel samples produced were washed with distilled water followed by drying in an evaporator, leaving the clear amber yellow oil which was then characterized (Mazrreku et al., 2016).

2.5. Oxidative Stability

The potential use of locally sourced *Mitracarpus scaber* in enhancing oxidative stability of the biodiesel produced was investigated. Firstly, the leaf of the plant was grinded into powdery form using an electric grinding machine. The grinded leaf was then mixed with 70% ethanol. The mixture was allowed to stay for two days, thereafter; the solution was filtered using a filter paper. The filtration was carried out thrice in order to ensure a better filtration process. Two samples of biodiesel were prepared namely sample A and sample B (Control) with a volume of 100 ml each. Air was bubbled into the biodiesel samples in order to enhance the oxidation process. The filtrate (antioxidant) was mixed with sample A only and the mixture was allowed to stay for two days. The samples were analyzed for their kinematic viscosity, peroxide value and acid value at an interval of four days each as a measure of their oxidation stability.

3. RESULTS AND DISCUSSION

3.1. Characterization of Watermelon Seed Oil

The watermelon oil extracted was characterized to determine the suitability of the watermelon seed oil for biodiesel production. The results of the characterization are presented in Table 1. From the Table, the yield reported was 49.8%. This yield is close to what was obtained for watermelon (Adebanjo and Kehinde, 2013), Jathropha curcas (Jean et al, 2014) and melon seeds (Achu et al, 2005). The results obtained in the current investigation presented in Table 1 show that the properties of watermelon oil closely resembles that of other feedstock used in biodiesel production. In this study, the watermelon oil has been closely examined for its viscosity, peroxide and acid values because the quality of any biodiesel is determined by these properties. The peroxide value 7.6 meq/kg reported in Table 1 is moderate and suitable for biodiesel production. This is because the peroxide value of oil is an indication of its extent of exposure to the atmosphere (Nurudeen et al., 2014).

Table 1: Characterization of the watermelon seed oil

Parameter	Value
Specific gravity	0.92
Acid value (g/KOH)	15.82
Peroxide value (meqperoxide/kg)	7.60
Viscosity (mm^2/sec) (EN ISO 3104+AC)	28
Saponification value (mg/KOH)	189.80

This peroxide value is close to the 7.9 meq/kg reported by Mirjana and Milovanovic (2005). Since peroxide value determines the extent of rancidity (i.e. deterioration) of an oil or fat, the peroxide value obtained in this study implies that the oil is of good quality. Similarly, the acid value indicates the effect of atmospheric oxygen on exposed oil. A high value implies that the oil/fat has become stale due to storage under inappropriate conditions (Nurudeen et al., 2014). Though the acid value obtained for the watermelon oil in this study (15.82 mgKOH/g) was relatively high, research has shown that this value is acceptable though it can be further reduced with addition of antioxidants (Buosi et al., 2016). Saponification serves as a measure the degree of unsaturation in a sample of oil. Thus, the higher the saponification value, the more suitable the oil is used for the production of soap rather than for biodiesel production. Due to its effect on the operation of the fuel injection equipment, viscosity is an important bio-fuel property (Islam and Beg, 2004). A

kinematic viscosity higher than the stipulated limit (35 mm^2/sec max.) may affect the quality of the biodiesel to be produced from the Watermelon oil. Thus, the kinematic viscosity 2.8 mm^2/sec obtained in this study indicates that the oil is suitable for biodiesel production.

3.2 Oxidation Stability Test

The oxidation stability of the produced biodiesel has examined with reference to its peroxide value, acid value and kinematic viscosity. A comparison of the oxidative stability was conducted with/without the addition of an antioxidant (*Mitracarpus scaber*) to determine the effectiveness of the natural antioxidant in stabilizing the oxidation property of the produced biodiesel. A measure of these properties (peroxide value, acid value and kinematic viscosity) will be examined over time because research has shown that the oxidative stability of biodiesel is determined by the storage condition of period of sunlight exposure and temperature.

The result of the peroxide value as a measure of the oxidative stability of the biodiesel is shown in Figure 1. From Figure 1, sample A (Biodiesel + *Mitracarpus scaber*) and sample B (biodiesel only) displayed an increase in the peroxide value throughout the duration of the experiment with sample B having a higher increment in peroxide value in comparison with sample A. The analysis showed that sample A had an initial peroxide value of 1.8 meq/kg and a final peroxide value of 2.6 meq/kg which represents a 44.4% increase in peroxide value. Similarly, sample B had an initial peroxide value of 1.8 meq/kg and a final peroxide value of 3.4 meq/kg which represents 88.9% increase in peroxide value. The reason for the continuous increase in peroxide value that was displayed by both sample A and sample B was due to the fact that when biodiesel oxidizes, its peroxide value increases with time and if an antioxidant is not present, there will be a continuous increment which can significantly affect the fuel property of biodiesel which in turn will lead to inefficiency in the use of the biodiesel in engines (Ayoola et al., 2016). The analysis showed that the antioxidant (*Mitracarpus scaber*) has a potential of enhancing the oxidative stability of the biodiesel because it was able to suppress the continual increase in the peroxide value during the period of oxidation by attacking the radicals responsible for the increment in the peroxide value and making them less reactive, interfering with the chemical reactions that form the radicals, and chemically remove the pro-oxidants like trace metals. Previous report by Kiralan et al. (2018) using Cold pressed plum kernel oil showed 78.6% increase in peroxide value during 12 days of investigation. This finding is in agreement with the oxidation stability study of this report which recorded an increment (88.9%) in peroxide value during 16 days of investigation. In addition, the report by Obadiah et al. (2013) using Jatropha oil recorded an increment in peroxide value of 58.3%.

Analysis of the acid value in order to determine how stable the biodiesel is when subjected to oxidation is depicted in Figure 2. From Figure 2, sample A (biodiesel + *Mitracarpus scaber*) and sample B (biodiesel only) displayed an increase in the acid value throughout the duration of the experiment with sample B having a higher increment in acid value in comparison with sample A. The analysis showed that sample A had an initial acid value of 3.37 mg KOH/g and a final acid value of 7.85 mg KOH/g which represents an increment of 132% of the initial amount. Sample B having an initial acid value of 3.37 mg KOH/g had a final acid value of 15.15 mg KOH/g which is approximately five times (349.56% increment) the initial amount of peroxide value. The notable increase in the acid value arose because when biodiesel oxidizes, the Acid Number increases as the fatty acid breaks down into shorter chain acids. Previous report by Obadiah et al. (2013), recorded an initial acid value of 0.5 mg KOH/g with a final acid value of 6 mg KOH/g which is equivalent to an increment of 900% without any addition of antioxidant.

The kinematic viscosity of the biodiesel was monitored for 16 days as a check for the oxidative stability of the biodiesel and the result is displayed in Figure 3. From Figure 3, sample A (Biodiesel + *Mitracarpus scaber*) and sample B (biodiesel only) displayed an increase in the kinematic viscosity throughout the duration of the experiment with sample B having a higher increment in peroxide value in comparison with sample A. The analysis showed that sample A had an initial kinematic viscosity of 6.54 cST and a final kinematic viscosity of 8.31 cST which represents 27.1% increase in Kinematic viscosity. Similarly, sample

B had an initial kinematic viscosity of 6.54 cST and a final kinematic viscosity of 11.25 cST which represents 72.02% increase in kinematic viscosity.

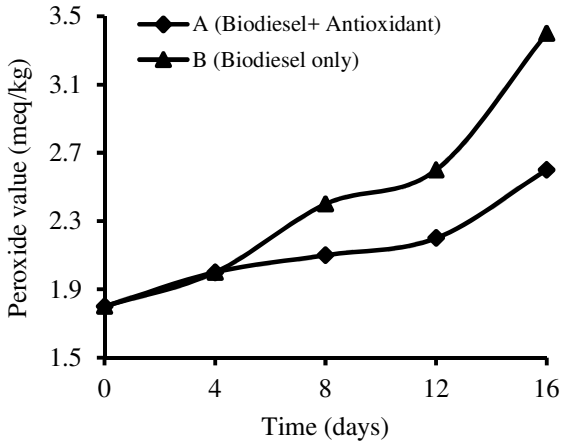

Figure 1: Variation of peroxide value with time

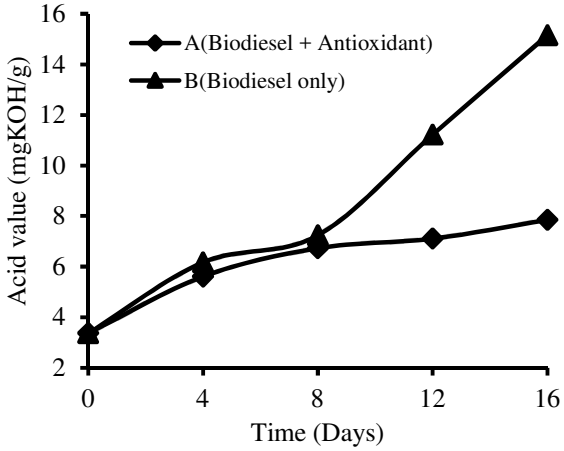

Figure 2: Variation of acid value with time

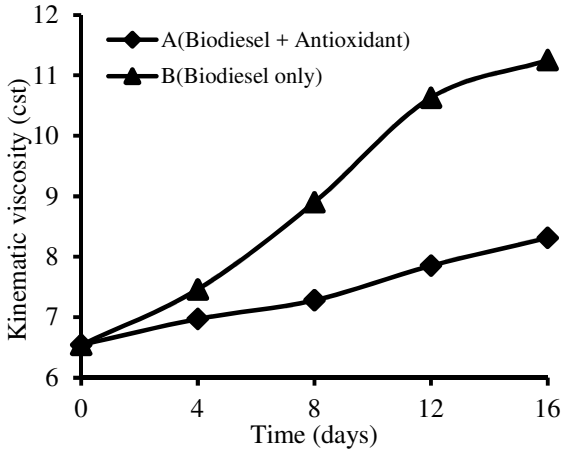

Figure 3: Variation of kinematic viscosity with time

When biodiesel degrades, the kinematic viscosity increases as the fatty acids polymerize and clump together and this is the reason why there was a continual increment in the Kinematic viscosity throughout the duration of the investigation. From the result, it is evident that the antioxidant offers a potential of stabilizing the Biodiesel during the period of investigation since the increment in kinematic viscosity displayed was far lower than Sample B which does not contain any antioxidant and no wonder it displayed such a higher increment in kinematic viscosity. Previous study by Obadiah et al. (2013) during storage of *Pongamia* biodiesel and *Jatropha* biodiesel recorded an initial kinematic viscosity of 4.8 cSt and 4.4 cSt respectively. When the biodiesel was left without an addition of antioxidant, the kinematic viscosity rose to 14.76 cSt and 14.7 cSt respectively and this corroborate our study of a higher increase in kinematic viscosity of biodiesel fuel when it oxidizes.

4. CONCLUSION

A comparative study on improving the oxidative stability of biodiesel produced from watermelon oil with and without the use of a natural antioxidant (*Mitracarpus scaber*) has been reported in this study. Since biodiesel quality depends on the properties of viscosity, peroxide and acid values, this study has shown that the addition of *Mitracarpus scaber* to the biodiesel improves its' stability by reducing the effect of these properties when exposed to the atmosphere. For 16 days, increases of 44.4%, 132% and 27.1% were observed for biodiesel combined with natural antioxidant, unlike the corresponding increases of 88.9%, 349.56% and 72.02% when the natural antioxidant was absent.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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