ABUAD INTERNATIONAL JOURNAL OF NATURAL AND APPLIED SCIENCES
ISSN: 2955-1021
AIJNAS Volume 3, Issue 2, 2023 pp 42-46
https://doi.org/10.53982/aijnas.2023.0302.06-j

https://journals.abuad.edu.ng/index.php/aijnas

AIJNAS

Inhibiting Acid Formation and Oxidation of Groundnut Oil Biodiesel Using Green Additives

Edema, O.S
Department of Petroleum Engineering, Delta State University, Oleh campus, Nigeria.
Corresponding author: Edema, O.S

Abstract
The engine performance of biodiesel had become a major concern. Improving the acid and oxidation stability of groundnut oil biodiesel (GOME), with various plant waste extracts, was carried out on in this study. Freshly prepared GOME was blended with onion extract (OE) and ginger extract (JE), at the rate of 100:1 parts per million, and stored at a temperature of 30±5^{0}C for 28 days. At the end of the experimental period, the acid content and oxidation value of the biodiesel treated with both natural additives, were lower when compared to the biodiesel with additives. It was observed that untreated GOME acid value increased from 1.37 - 2.23 mgKOH/g, the acid value of the GOME containing OE increased from 1.35 – 1.81 mgKOH/g, and the acid content of the GOME treated with JE increased from 1.34 – 1.94 mgKOH/g. Regarding the oxidation stability, it was observed that the un-amended GOME oxidative stability decreased from 3.14 h to 2.44 h, the GOME amended with OE additive declined from 5.37 to 4.57 h, while the GOME treated with JE additive decreased from 4.99 h to 4.21 h. The findings of this study had revealed that incorporating natural additives into GOME, yield biodiesel with better oxidation stability. It was also noted that the blended GOME met the ASTM approved recommendation for biodiesel; unlike the results recorded for the GOME that was untreated with the natural additives.
Keywords: *Additives, biodiesel, ginger rhizome, onion bulb, storability*

INTRODUCTION

Rapid industrialization and population growth has caused drastic increment in energy demand, which supplies mainly come from fossil fuels which produce lots of greenhouse gases (GH). Fossil fuels are indirectly prime movers of most Nations' economy, and carbonization through emissions from the combustion of fossil fuels is one major contributor (climate change); hence decarbonization of the environment is among the ideals for the achievement of sustainable development goals (Amran *et al*., 2022). Therefore, the quest for energy structure for internal combustion engines with lower carbon footprints has increased research into bioenergy utilizing indigenous biomaterials (Eboibi *et al*., 2022). Although, biofuel combustion produced a significant amount of greenhouse gases, its GH level is remarkably lower than the volume produced through the combustion of petroleum fuel. Ashraful *et al.* (2014) reported that the burning of fossil fuels produces larger volumes of particulate matter, and carbon and sulfur oxides, and carbon and sulfur oxides, when compared to their counterpart biofuels; hence biofuels are considered to be more ecofriendly compared to petroleum fuels.

Biodiesel is one of the most promising types of biofuel. It is produced mainly from organic lipids, such as vegetable oils and animal fat. Biodiesel is considered as one of best alternative choice in this era of climate change problems and the depletion of petroleum reserves (Ghiaci *et al*., 2011). According to Prasad and Singh (2020), biodiesel has bright prospects because it emits lower poisonous particulate matter and gasses during combustion under ambient environmental conductions, when compared to most petroleum derived fuels. Agarwal and Khurana (2013), and Eboibi *et al*. (2022) stated in their different reports that biodiesel has more environmental friendly characteristics due to its higher degree of biodegradability, lower carbon and sulphur oxides profiles, and its recyclability. Just like other organic oils, biodiesel experiences alterations in its acids value, its physicochemical behaviors, and in other related fuel properties. Fuel properties of plant's oil and its derivatives are subjective to the plant's variety, cropping system, maturity stage, storage conditions and post-harvest treatments. Biodiesel acidic content, physiochemical parameters, and fatty acid profile are dependent on their corresponding values in the parent plant or animal oil (Nuhanovic *et al*., 2018; Eboibi *et al*., 2021; Ekruyota and Uguru, 2021; Awad *et al*., 2022).

Oxidation is a major problem of biofuel produced from plant and animal materials, because it affects both the shelf life and stability of the biofuel. Hazrat *et al.* (2021) reported that oxidation causes degradation of the fuel; thus compromising most of the fuel's properties and the engine's performance. This factor (oxidation susceptibility) has greatly affected the patronage, utilization and commercialization of the various forms of biofuels (Kumar, 2017). Factors that affect biofuel oxidative stability include production technique, storage condition, plant's maturity stage, plant variety and farming system. Though, oxidation of biofuels is quite higher than conventional fuels, these deficiencies can be corrected through amendment of the biofuels with special organic or inorganic extracts (Dunn, 2008). Numerous studies have been carried out on improving the stability of biofuel through the use of additives, mainly synthesized or natural products (Liang *et al.,* 2006; Tang *et al*., 2008; Moniru, 2017; Hazrat *et al*., 2021). Devi *et al*. (2017) in their investigation into fuel properties optimization, reported that natural extracts have more environmental friendliness, when compared to synthesized fuel properties enhancers; hence, the utilization of petroleum-based extracts should be avoided during stabilization of biodiesel.

Agricultural materials are the major parent materials for natural extracts production, irrespective of the method used for the biofuel production. Findings have revealed that agricultural products have complex internal structures; hence, their bioengineering properties (which affect the fuel quality) varies widely among the plants and animals (Uguru *et al*., 2019; Ekruyota *et al.,* 2021; Uguru *et al*., 2023). Eboibi and Uguru (2017) stated that the stability of biomaterial's engineering properties is dependent on the storage condition, farming practice and handling operations. Researches results have revealed that plants and animals' engineering behaviors are greatly influenced by both intrinsic and extrinsic factors; and these factors can be managed significantly, through appropriate pre-harvest or post-harvest treatments (Uyeri and Uguru, 2018; Sanmartin *et al*., 2018; Obukoeroro and Uguru, 2021, Edema *et al*., 2022; Uguru *et al*., 2023). From related literature review, few reports have demonstrated the utilization of farm waste products to produce natural extracts, which can be used to improve biodiesel shelf-life. The purpose of this study is to evaluate the impact of extracts produced from onion (*Allium cepa*) bulb and ginger (*Zingiber officinale* Roscoe) rhizome waste on the fuel properties and shelf-life of biodiesel produced from groundnut oil.

MATERIALS AND METHODS

Plant material cultivation

The groundnut used for the biodiesel production was planted at the research centre of Delta State University of Science and Technology, Ozoro, Nigeria. Organic cropping system was adopted for the groundnut kernels production. The soil was sandy loam textural type and rich in humus. Ozoro experiences dual climatic seasons annually – wet (rainy) and dry season; with the rainy season lasting longer than the dry season (Uguru *et al*., 2022). During the groundnut cropping period, the mean environmental temperature was about 28±4^{0}C, and annual rainfall was approximately 1200 mm. The groundnut planted and harvested for a period of 4 month, i.e., January, 2022 to April, 2022.

Onion bulbs and ginger rhizome

Onion bulbs and ginger rhizomes wastes (dry outer skin) were obtained from a local market. Both onion and ginger are spices, commonly consumed by human beings due to their appreciable nutritional and medicinal values

Groundnut oil production

The harvested groundnut pods were sundried, shell and the kernels separated from the shells. These kernels were milled and the oil was separated by adopting the solvent technique, while the excess solvent was removed through evaporation, as explained by Eboibi *et al.* (2022).

Plant extract preparation

The onion bulbs and ginger rhizomes wastes were oven dried (temperature ~ 50^{0}C), ground with a grinder and sieved with a 0.850 mm sieve. 10 g of the particulate was mixed with 1 L of ethanol, and allowed to stand for 24 h at room temperature. Thereafter, the supernatant was then centrifuged at a speed of 3000 rpm for 25 min, sieved with grade 1 filter paper, before it was evaporated to remove the ethanol as explained by Devi *et al*. (2017).

Biodiesel production

The groundnut kernel biodiesel was produced through the transesterification technique. A mixture of 1% (by weight) of catalyst (sodium hydroxide) and methanol to groundnut oil (molar ratio of 6:1) were poured into a flask and heated for about 3 h at a temperature of 60^{o}C. During the heating period, the mixture was centrifuged at a low speed of 300 revolutions per minute. The product was transferred into a separating funnel and left to stand for 24 h, before the biodiesel (methyl ester) was separated from the glycerine.

This raw biodiesel was washed by using distilled water, dried in a water bath at 80°C for 1 h, and later with anhydrous sodium tetraoxosulphate (VI) oxide (Devi *et al*., 2016; Eboibi *et al*., 2022).

Blending of the biodiesel and laboratory analysis

The OE and JE were incorporated into the freshly prepared GOME (groundnut oil methyl ester), at a rate of 100 parts of GOME to 1 part of OE or JE. Then the blended and unblended GOME was poured into glass bottles, coded and stored inside a cabinet under ambient room temperature. Acid value and oxidation stability tests were carried out on all the samples at an interval of seven days, starting from the production date till the 28th day after production.

Oxidation stability determination

The induction period procedure was used to evaluate the oxidation stability of the prepared biodiesel samples in accordance with the guidelines approved by ASTM D-6751, at a temperature of 110^{0}C.

Acid value determination

The titration method was used to determine the acid value of the biodiesel, using phenolphthalein as the endpoint (neutrality) indicator, and potassium peroxide (KOH) as the standard. The titration procedure was done in accordance with ASTM D974 approved guidelines (Eboibi *et al*., 2022).

Data analysis

Raw results obtained from the laboratory tests were analyzed by using charts, with the aid of Microsoft Excel for Windows, to establish the influence of the blending materials on the GOME.

RESULTS AND DISCUSSION

Impact of the plant's extract on the acid value

The results of the effects of the two plants' extract on the acid value of the GOME are presented in Figure 1. Figure 1 revealed that the extracts, regardless of their source significantly inhibited acid formation during storage. During storage at a temperature of 30±5^{0}C, the following increments in acid values in the biodiesel were noted: untreated GOME from 1.37 - 2.23 mgKOH/g (representing 69.34% increment), GOME treated with OE from 1.35 – 1.81 mgKOH/g (34.07% increment), and GOME amended with JE from 1.34 – 1.94 mgKOH/g (44.77% increment). Despite the general increment in the biodiesel acid value during storage, the increment was higher in the unblended GOME when compared with the biodiesel treated with OE and JE. Similar retardation of acid production in biodiesel during storage, associated with organic extracts therapies were reported by Devi *et al.* (2017), and Tang *et al.* (2008). Nuhanovic *et al.* (2018) reported that plants materials contain significant amount of antioxidants and other oxygen scavengers, which help to lower acid formation in biofuels during storage.

It was noted from the tested results that OE had a higher resistance to acid production when compared to the results, obtained from the JE treated GOME. A situation that is attributed variations in phytochemicals and antioxidants compositions of the green extracts, caused by maturation stage, crop variety and treatments applied to the different crops in the field (Edafeadhe and Uguru, 2020). According to the study of Beautin Nirsha *et al.* (2023), agricultural materials biochemical properties are influenced by processing and handling techniques; although, field operations and environmental factors, tend to alter the cellular chemical reactions and physiological properties.

Furthermore, Bianchin *et al.* (2017) stated that spices contain high proportion of antioxidants and other relevant phytochemical compounds; thus they have potentials for optimizing biodiesel fuel properties, and stabilizing these properties during storage and high operational temperatures. The tocopherol and ascorbic acid contents in onion extracts are promising oxidation scavengers in biodiesel, hence improving its stability and utilization (Sousa *et al*., 2014). Biodiesel acid value is a vital parameter used to evaluate its performance, as a high acid value is an indication of high oxidation and deterioration of the biodiesel.

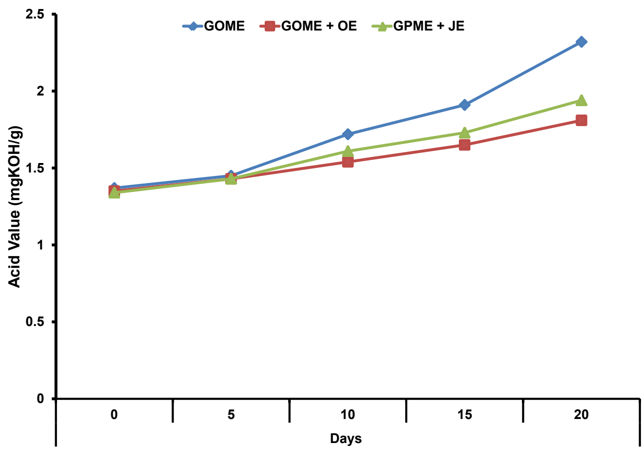

Figure 1: The effect of storage duration on acid formation

Oxidative stability

The results of the oxidative stability of the three biodiesel categories are presented in Figure 2. As seen in Figure 2, the additives had substantial effects on the GOME oxidative stability. The GOME treated with OE and JE, were more stable than the non-antioxidant amended biodiesel. At production day, the GOME had oxidative stability of 3.14 h, while GOME + OE and GOME + JE had oxidative stabilities of 5.37 h and 4.99 h respectively; while at storage day 28, the untreated GOME, GOME + OE and GOME + JE oxidative stabilities were, 2.44 h. 4.57 h and 4.21 h, respectively. This revealed that the GOME containing the natural additives had a better oxidation stability, compared to the GOME without natural additives. Similar results were obtained by Davi *et al.* (2017), where ginger extract hindered the oxidation of biodiesel produced from non-edible oil. Also, Liang *et al.* (2006), investigated the impact of organic and inorganic additives on the stability of palm oil diesel, and reported that the organic antioxidant considerably impeded the oxidation of the palm diesel.

Despite the depreciation in the biodiesel stability, the values recorded for the green extracts treated biodiesel never exceeded the European biodiesel standard approved value of 4.0 h. It was also further revealed that extracts produced from non-edible (waste) agricultural products can be used to enhance the performance of biodiesel. Davi *et al.* (2017) reported that additives produced from spices have the ability of inhibiting oxidation of biodiesel. Liang *et al.* (2006) further stated that additives that contain antioxidants have the ability of retarding the oxidative degradation of biodiesel; hence, they should be incorporated into crude biodiesels to increase their shelf-life. This study's findings had shown that extracts from onion and ginger wastes materials which are readily available in many countries including Nigeria, can be used to stabilize biodiesel engine fuel performance during storage, thus improving the commercialization and patronage of biodiesel in these nations.

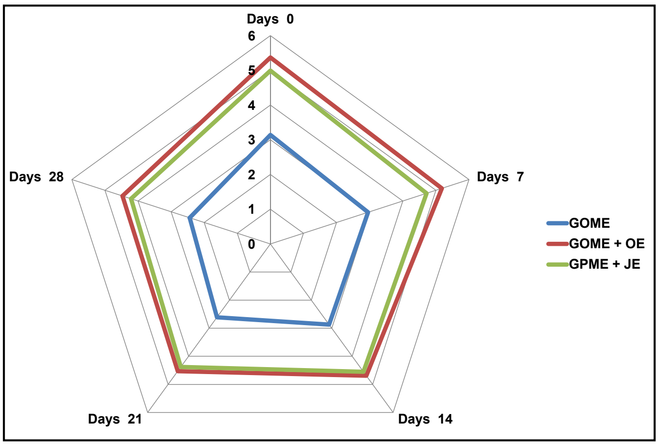

Figure 2: The effect of additives on GOME oxidation level

CONCLUSION

This study was conducted to evaluate the possibility of using extracts produced from plants waste materials, in improving the shelf-life of biodiesel. Extracts produced from onion bulbs and ginger rhizome wastes (dry skins) were used to blend groundnut oil biodiesel (GOME) at the rate of 1000 parts per million (ppm). The findings revealed that both onion bulbs and ginger rhizomes extracts have substantial influence on the GOME stability. It was noted that the increment in the GOME acidity (acid value) was higher in the untreated GOME, when compared to the GOME amended with either onions bulb or ginger rhizomes extracts. Additionally, the findings of this study depicted that organic extracts had better prospects of oxidation inhibition. Interestingly, these results had revealed that waste agricultural materials can be used to produce extracts that can be utilized to enhance the performance and stability of biodiesel for use in internal combustion engines.

REFERENCES

Agarwal, A.K., & Khurana, D. (2013). Long-term storage oxidation stability of Karanja biodiesel with the use of antioxidants. *Fuel Processing Technology*, *106*, 447–452.

Amran, N.N., Bello, U. and Syafiq, Ruslan, M.S.H. (2022). The role of antioxidants in improving biodiesel's oxidative stability, poor cold flow properties, and the effects of the duo on engine performance: A review. *Heliyon* 8: e09846 - e09860

Ashraful, A.M., Masjuki, H.H., Kalam, M.A., Fattah, I.M.R., Imtenan, S., Shahir, S.A. & Mobarak, H.M. (2014). Production and comparison of fuel properties, engine performance and emission characteristics of biodiesel from various Non-edible vegetable oils: A review. *Energy Conservation Management*, *80*, 202–228.

Awad, N.A., Mohamed E., Emad, H.E., Ahmed, S.M. I., Yasser, S.G.A., Mohamed, S.G., Reda, M.Y.Z., Rokayya, S., Ebtihal, K., Uguru, H., & Khaled, S. (2022). Evaluation of the effect of elite jojoba strains on the chemical properties of its seed oil. *Molecules*, *27*, 3904 - 3913

Beautin Nirsha, R., Anish, C.I., Danielsam, N., Sanith, S., Gobalakrishnan, S., Jaya Rajan, M., Mahmoud, H., Amal. A.A., Sami, R., Rada, M., Zewail, Y., Uguru, H., Aljuraide, N.I., & Murthy C. (2022). Characterization and Dye Removal application Using Initiated Carbon Originated from rubber seed shell Biomass. *Journal of Biobased Materials and Bioenergy*. 17, 152–158

Devi, A., Barman, R. & Deka, D. (2016). Designer biodiesel: an optimization of fuel quality by blending multiple oils, proceedings of the first international conference on recent advances in bioenergy research. *Springer Proceedings in Energy*, 131–48.

Devi, A., Das, V.K., & Deka, D. (2017). Ginger extract as a nature based robust additive and its influence on the oxidation stability of biodiesel synthesized from non-edible oil. *Fuel*, *187*, 306–314.

Dunn, R.O. (2008). Antioxidants for improving the storage stability of biodiesel. *Biofuels, Bioproducts Biorefining, 2*(4), 304 – 318

Eboibi, O., & Uguru, H.E. (2017). Storage conditions effect on physical, mechanical and textural properties of intact cucumber (cv *Nandini*) fruit. *International Journal of Engineering and Technical Research. 7*, 48 – 56.

Eboibi, O., Akpokodje, O.I., Nyorere, O., Oghenerukevwe, P., & Uguru, H. (2021). Effect of pre-harvest applications of organic manure and calcium chloride on the storability of tomato fruits. *Annals of Agricultural Sciences, 66*, 142–151

Eboibi, O., Edafiadhe, E.D., & Uguru H. (2022). Comparative analysis of the fuel properties of biodiesel produced from different groundnut varieties. *International Journal of Advanced Academic Research*, *8*(9), 10-23

Edafeadhe, G.O.I., & Uguru, H. (2020). Effect of pre-harvest treatment on the tensile and biochemical properties of okra (*Abelmoschus Esculentus* L) Fibre. *Direct Research Journal of Chemistry and Material Science*. *7*(1), 7-11

Edema, O.S., Ekperi, R.E., Akpokodje, O.I. & Agbabi, P.E.O. (2022). A comparative study of the effect of field practices on the fuel properties of groundnut kernels biodiesel. *International Journal of Natural and Applied Sciences*, *2*(3), 132–138

Bianchin, M., Pereira, D., Reis, A.S., Almeida, J.F., Silva, L.D., Moura, C., & Carpes, S.T. (2017). Rosemary essential oil and lyophilized extract as natural antioxidant source to prevent lipid oxidation in pork sausage. *Advance Journal of Food Science and Technology, 13*(5), 210-217.

Ekruyota, O.G. & Uguru, H. (2021). Characterizing the mechanical properties of eggplant (Melina F1) fruits, for the design and production of agricultural robots. *Direct Research Journal of Engineering and Information Technology. 8*, 21-29

Ekruyota, O.G., Akpenyi-Aboh, O.N., & Uguru, H. (2021). Evaluation of the mechanical properties of tomato (Cv. Roma) fruits as related to the design of harvesting and packaging autonomous system. *Direct Research Journal of Agriculture and Food Science*, 9, 174-180

Hazrat, M.A. Rasul, M.G., & Khan, M.M.K. (2021). Techniques to improve the stability of biodiesel: a review, *Environmental Chemistry Letter. 19*(3), 2209–2236.

Kumar, N. (2017). Oxidative stability of biodiesel: Causes, effects and prevention. *Fuel*, *190*, 328–350.

Liang, Y.C., May, C.Y., Foon, C.S., Ngan, M., Hock, C.C., & Basiron, Y. (2006). The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. *Fuel*, *85*(5), 867–870.

Monirul, I.M. (2017). Influence of poly(methyl acrylate) additive on cold flow properties of coconut biodiesel blends and exhaust gas emissions, Renew. *Energy* 101:702–712.

Nuhanovic, M., Topalovic, A., Culum, D. and Ibragic, S. (2018). The effectiveness of natural and synthetic antioxidant additives on the oxidation stability of biodiesel synthesized from fresh and waste sunflower oil. *Orbital: The Electronic Journal of Chemistry, 10*(7), 535–542.

Obukoeroro, J. & Uguru, H.E. (2021). Evaluation of the mechanical and electrical properties of carbon black/carbonized snail shell powder hybridized conductive epoxy composite. *International Journal of Innovative Scientific & Engineering Technologies Research*, *9*(1), 39-49

Prasad, S.S., & Singh, A. (2020). Economic feasibility of biodiesel production from pongamia oil on the island of *vanua levu*, *SN Applied Sci*ence, *2*(6), 1–9.

Sanmartin, C., Venturi, F., Sgherri, C., Nari, A., Macaluso, M., Flamini, G., Quartacci, M.F., Taglieri, I., Andrich, G. & Zinnai, A. (2018). The effects of packaging and storage temperature on the shelf-life of extra virgin olive oil. *Heliyon, 4*(11), 888–918.

Sousa, L. S.; Moura, C. V. R.; Oliveira, J. E.; Moura, E. M. (2014). Use of natural antioxidants in soybean biodiesel. *Fuel*, *134*, 420-428

Tang, H., Wang, A., Salley, S.O.and Simon Ng, K.Y. (2008). The effect of natural and synthetic antioxidants on the oxidative stability of biodiesel. *Journal of the American Oil Chemists' Society. 85*,373–382

Uguru, H., Akpokodje, O.I., & Irtwange, S.V. (2019). Mechanical behaviour of common bean (cv. Butter) seeds as affected by maturation. *Journal of Engineering Research and Reports, 8*(2), 1-12.

Uguru, H., Akpokodje, O.I., & Agbi, G.G. (2021). Assessment of spatial variability of heavy metals (Pb and Al) in alluvial soil around Delta State University of Science and Technology, Ozoro, Southern Nigeria. *Turkish Journal of Agricultural Engineering Research (TURKAGER), 2*(2). 450-459.

Uguru, H., Akpokodje, O.I., Hemdan, D.I., Sami, R., Helal, M., Aljahani, A.H., Ashour, A.A., & Algehainy, N.A. (2023). Effectiveness of plant oil in stabilizing the antioxidants, phenolic compounds and antimicrobial effects of groundnut (*Arachis hypogaea* L) oil. *Materials Express*, *13*,704–716

Uyeri, C., & and Uguru, H. (2018). Compressive resistance of groundnut kernels as influenced by kernel size. *Journal of Engineering Research and Reports*, *3*(4), 1-7.