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A comparative study of the effect of field practices on the fuel properties of groundnut kernels biodiesel

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Abstract
The impact of pre-harvest treatments (field practices) on the fuel (biodiesel) properties produced from groundnut kernels was evaluated in this work. Ahigh-quality oil-yielding groundnut hybrid (SAMNUT 11) was grown under five different soil treatment regimes. The regimes were organic and conventional, though the treatment concentrations were systematically varied. Biodiesels produced from matured kernels (for the different treatment plans) were tested following the American Society for Testing Materials (ASTM) International and European Biodiesel (EN) procedures. Results obtained revealed that the biodiesel density ranged between 856 kg/m^3 and 869 kg/m^3, the acid value ranged between 0.695% and 1.118%, the iodine value ranged from 27.54 mg/L to 34.63 mg/L, the phosphorus concentration varied from 8.21 mg/L to 10.25 mg/L,the ester content ranged between 91.87% and 98.34%, and the alkali metals varied from 2.143 mg/L to 3.428 mg/L. All biodiesel produced fromthe pre-harvest treated kernels met the EN-ISO 12185 and EN 14213 standards for densities and ester contents, respectively.It was observed that the T2 and T3 acid values were 0.871% and 0.695%, respectively, while the T4 and T5 acid values were 1.033% and 1.118%, respectively, and all failed to meet both ASTM and EN standards, though the organically produced kernel's biodiesels had better prospects. Furthermore, it was observed that the iodine values of the biodiesels, obtained from the five treatment plans, were within the EN 14214 approved standards for biodiesel. The findings portrayed that the organic manure had a more positive impact on the groundnut kernels, compared to groundnut grown with fertilizers. As observed from the results, the biodiesel produced from the organic kernels hada better fuel quality than that acquired from the convectional kernels.
Keywords: *Biodiesel, fertilizer, fuel properties, organic manure, pre-harvest treatment*

INTRODUCTION

Compression ignition (CI) Internal combustion (IC) engines are widely used in various sectors – transportation, industrial, agricultural and the power sector. It had been observed that the emissions produced through the combustion of fossil (conventional) fuel-powered IC, have a lot of negative consequences on the environment (Ghanbari *et al.*, 2021). Apart from the emissions given off during the combustion of fossil fuels, the numerous procedures involved during their extraction, production and marketing are major causes of environmental pollution. Akpokodje *et al.* (2019) stated that millions of barrels of crude oil are accidentally or intentionally spilled into the environment, during the process of crude oil exploration, transportation and refining. This is a major problem in several oil producing nations, as it has caused severe environmental degradation. According to Fayaz *et al.* (2021), gasses and particulate matter emitted by fossil diesel-powered tankers, ocean liners, and other petroleum transportation utilities are carcinogenic to humans.

Biofuel production will help alleviate the serious hitches associated with the exploration, production and marketing of several conventional fuels in several countries; thereby making these countries less susceptible to the severe impacts of fossil fuel production and supply (Huang *et al.*, 2013). Konur (2021) stated that biofuel is a sustainable alternative to fossil fuels due to its renewability and low greenhouse gas (GHG) emissions. The United States Environmental Protection Agency (USEPA) after intensive research stated that, several forms of biofuels currently in use for engine operations, have the potential to yield lower GHG emissions, when compared to conventional fuels, that is, within the next 30 years using special pollution models (USEPA, 2010; Huang *et al.*, 2013). The adverse effects of global climate arebecoming more severe; largely due to the increment in CO_2 emissions into the surrounding air throughburning of conventional fossil fuels.

Despite its numerous benefits, biodiesel has some drawbacks, including poor fuel properties, increased pressure on available landmass and aquatic resources, environmental pollution, and food insecurity (Karthikeyan *et al.*, 2014; Fayaz *et al.*, 2021).Biodiesel has a high viscosity, which impedes engine fuel injector operations, causing wear and tear on fuel pump elements and resulting in large fuel droplet formation containing metallic and plastic particles (Gundoshmian *et al.*, 2021).According to Mosnier *et al.* (2013), biofuel production necessitates convectional farming practices, which include the use of agricultural chemicals to increase crop productivity and meet demand. Most agricultural chemicals release nitrous oxide (apotent greenhouse gases) into the environment, which contribute immensely to climate change effects (Melillo *et al.* 2009; Mosnier *et al.*, 2013).These limitations associated with the production and utilization of bio-energy are adequatelymitigated through advanced crop production methods and improved biofuel production techniques (Eboibi *et al.*, 2022).

Several authors have reported that blending biodiesel with appropriatenanoparticles can help improve the fundamental fuel properties of the biodiesel (Oni and Oluwatosin, 2020; Jahanbakhshi *et al.*, 2021). Nanoparticles are some of the common materials used to enhancethe performance, and the chemical and thermal properties of biodiesel, due to their appreciable engineering properties (Babu and Raja, 2015). Ndukwe and Adeyemo (2021) reported that blending watermelon seed biodiesel with copper tetraoxosulphate (vi) oxide ($CuSO_4$) helped to reduce the iodine and acid values of the biodiesel produced; hence, enhancing the performance of IC engine. According to Sathiyamoorthi *et al.* (2016), cerium oxide(CeO_2) helps to enhance neem seed biodiesel's brake specific fuel consumption, brake thermal efficiency, in-cylinder pressure and the heat release rate of engines. Although much work has been done on how post-harvest treatmentscause several alterations, in the fuel qualities of biodiesel acquiredfrom food stuffs;there is no recorded literature on the effect of pre-harvest treatment on the fuel properties ofbiodiesel produced from food stuffs. Therefore, thevital point of this novel work is to examine the effect of pre-harvest treatment (field practices) on the biofuel quality of groundnut (Arachishypogaea) kernel oil biodiesel.

MATERIALS AND METHODS

Research area description

The cultivation of groundnut used for the production of the biodiesel was carried out between December 2021 and April 2022, at the research centre of Delta State University of Science and Technology, Ozoro, Nigeria. The center has a geographical location of Latitude 5°33'44.41''N and Longitude 6°14'57.13''E, with a bimodal annual rainfall distribution pattern (Uguru *et al.*, 2020). According to data obtained from the university's metrological station, Ozoro's daily temperature varied between 25°C and 35°C. The soil type was mainly of the alluvial class with a high infiltration rate and moderate organic matter content (Eboibi *et al.*, 2018; Uguru *et al.*, 2021a).

Crop cultivation

SAMNUT 11, a groundnut hybrid known for its high quality oil production (Uguru *et al.*, 2020), was chosen for this research. The land was manually tilled, and the groundnut kernels were planted at the rate of 3 kernels per hole, at a spacing of 0.3 m x 0.3 m. The field was divided into five plots, and the plots were subjected to soil treatments, as shown in Table 1.

Table 1: Treatment design

Plot	Treatment
1	Control
2	Organic manure at the rate of 1000 kg/ha
3	Organic manure at the rate of 2000 kg/ha
4	NPK 20:10:10 fertilizer at the rate of 150 kg/ha
5	NPK 20:10:10 fertilizer at the rate of 300 kg/ha

Groundnut sample collection and preparation

The groundnut was harvested at peak maturity - the kernel showing its camouflage colour and becoming plumped (Uyeri and Uguru, 2018; Uguru *et al.*, 2021b). The groundnut plants (including the pods) were dried on a platform, under the sun for ten days, before the threshing and shelling operations (Uguru and Nyorere, 2019). After shelling, the kernels were separated from the shells, cleaned and inspected manually to discard damaged kernels. This was required to raise the processing machine's efficiency, and also to improve the GKO's yield and quality. The sorted groundnut kernels were taken to the laboratory for groundnut oil production.

Extraction of groundnut kernel oil (GKO)

Soxhlet extraction technique was adopted for the groundnut oil production. The groundnut kernels were crushed using a wooden mortar and pestle, to increase the surface contact area of the groundnut kernel during the reaction process (Redfern *et al.*, 2014). Then the groundnut oil was extracted from the crushed groundnut kernels with nhexane, using a Soxhlet extractor apparatus (Ndukwe and Adeyemo, 2021).

Production of groundnut kernel oil methyl ester

The following conditions and materials were used for the GKO biodiesel production: agitation speed ~ 400 of rpm, reaction temperature ~ 850^{C} , duration ~60 minutes, catalyst ~ Sodium hydroxide, catalyst concentration ~ 0.5%, methanol to oil ratio ~ 20%

and standing duration under gravity ~ 24 h. The raw biodiesel produced was then dried inside a water bath at a temperature of 75°C for 1 h, before it was purified as described by Panneerselvam *et al.* (2017).

Ester content determination

The GKO biodiesel ester value was determined in accordance with EN 14103 approved procedures

Acid value determination

The GKO biodiesel acid value was determined in accordance with EN 14104 approved procedures through titration and the acid number of the biodiesel calculated using Equation 1 (Handojo *et al.*, 2020).

$$\text{Acid value} = \frac{\text{titre (ml)}}{\text{weight of sample used}} \times 5.61 \qquad 1$$

Iodine value determination

The GKO biodiesel iodine value was determined in accordance with the EN 14111 approved procedures, using the titration method

Phosphorus value determination

The Phosphorus value of the GKO biodiesel was determined in accordance with ASTM D-6751 (2020) standard, using the optical emission spectroscopy with inductively coupled plasma.

Density determination

The determination of the GKO biodiesel density was done by using the procedures provided by ASTM D5002 (2022); Equation 2 was used to calculate the density of the biodiesel.

$$\text{Density} = \frac{\text{Weight of sample (g)}}{\text{Volume of sample (mL)}} \qquad 2$$

Alkali metals determination

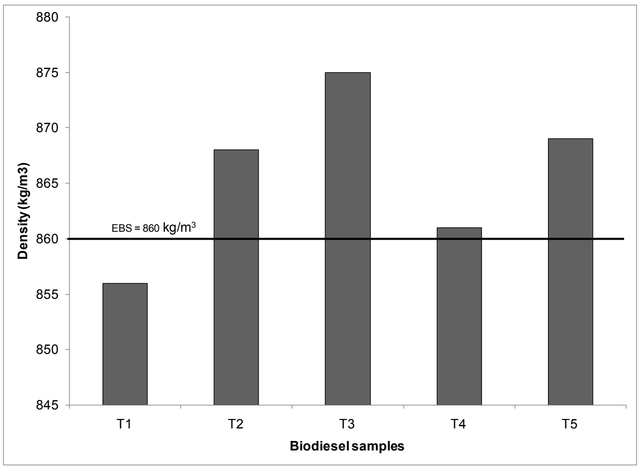
The alkali metals (potassium and sodium) concentrations in the biodiesel were measured by using the Varian AA240 Atomic Absorption Spectrophometer, in accordance with the American Public Health Association (APHA) 1995 procedures.

RESULTS AND DISCUSSION

Density

The result of the biodiesel densities from all the pre-harvest treated kernels is presented in Figure 1. The findings depicted that field practices (pre-harvest treatment) had considerable impact on the biodiesel density. This is because all the kernels were totally subjected to different forms of pre-harvest treatments and they produced biodiesel with densities meeting the minimum allowable international standard. Densities of organically produced kernels (T_2 and T_3) were 868 kg/m^3 and 875 kg/m^3 respectively; while the densities of conventionally produced kernels (T_4 and T_5) were 861 kg/m^3 and 869 kg/m^3 respectively. Also it was observed that the density of the control kernel's biodiesel was 856 kg/m^3 which failed to meet the 860 kg/m^3 approved by ASTM and BS for CI engines.

Experimentally, it had been verified that density affects the combustion and performance of biofuel just like other conventional fuels, as extremely high or low density fuel is dangerous to the engine. Phankosol *et al.* (2014) stated that fuel density directly affects the operation and performance of all CI engine fuel pumps and injectors. Similarly, Tüccar *et al.* (2018) in their investigation into the fuel properties of green fuels reported that, biofuel with very high density tends to hinder the fuel flow within the engine, thus causing wears of the engine parts. Therefore, the biodiesel produced from the kernels grown with fertilizer is considered as having a better density than the biodiesel produced from kernels grown with manure.



EBS = European biodiesel standard

Figure 1: Biodiesel density

Ester content

Results of the ester content of the biodiesel produced from the various pre-harvest treated groundnut kernels are presented in Figure 2. Figure 2 revealed that field practices have significant impact on the quality of biodiesel produced, as theester content of the biodiesel followed this pre-harvest treatment order; T1< T4 < T2 < T3 <T5. It was also observed that regardless of the nature of treatment applied to the crops in the field, allthe kernels produced (by the groundnut plants) yielded biodiesel with ester contents that were higher than the minimum value of 96.5% recommended by EN 14213. Also the findings depicted that the biodiesel gotten from kernels grown with manure (T_2 and T_3) recorded higher ester content of 97.21% and 98.34% respectively, when compared with the biodiesel gotten from kernels grown with fertilizer (T_4 and T_5).

This finding portrayed that soil treatment helps to enhance the oil and ester content of groundnut kernels, which ordinarily is of a lower ester quality. According to Thoai *et al.* (2017), ester is a vital parameter that is used to determine the quality of oil-seeds' biodiesel; and the higher the ester content, the better the biodiesel's suitability for CI engines. According to Munoz *et al.*, (2012), biodiesel with poor (low) ester content is an indication of poor trans-esterification reaction process, which can lead to serious carbonization problemsin CI engines.

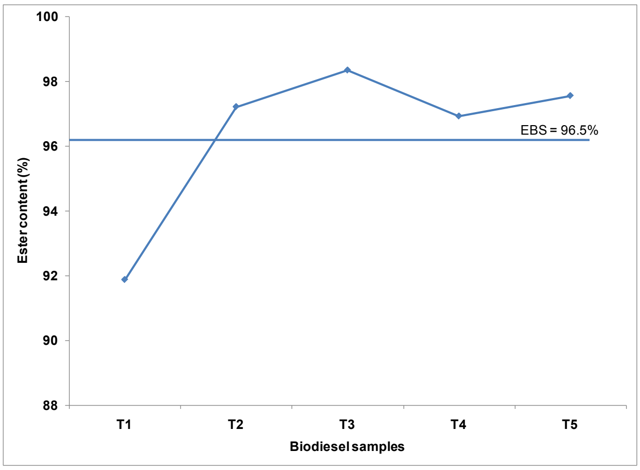


Figure 2: Ester content

Alkali metals

Figure 3 shows the results of the alkali metals concentration of the biodiesel. The control had the lowest alkali metals concentration (2.143 mg/kg) among the five biodiesel samples investigated in this research work. Regarding field practices, the kernels grown with manure tend to produce biodiesels with lower potassium and sodium concentrations (2.843 mg/kg and 3.121 mg/kg respectively), when compared to the biodiesels produced from kernels grown with fertilizer. The high alkali metals concentrations (2.908 mg/kg and 3.428 mg/kg) recorded in the T_4 and T_5 biodiesel can be linked to the higher percentage of potassium in the fertilizer used for the groundnut cultivation. Metals are major contaminants in biodiesels which affects its oxidation stability (Jain and Sharma, 2014). Furthermore, Munoz *et al.*, (2012) reported that sodium and potassium can result in the production of in soluble soaps within the fuel system.

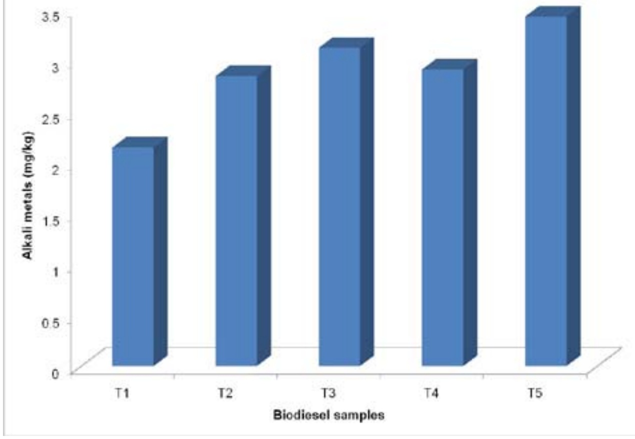


Figure 3: Alkali metals

Acid value

Figure 4 shows the acid values of the biodiesels produced from the different pre-harvest treated groundnut kernels. It was observed that the biodiesel acid value ranged between 0.695% and 1.118%. The findings depicted that the organically produced groundnut kernels (T_2 and T_3), produced biodiesels with lower acid values, compared to the acid numbers of the conventionally produced groundnut kernels (T_4 and T_5). T_2 and T_3 acid values were 0.871% and 0.695% respectively, while T_4 and T_5 acid contents were 1.033% and 1.118% respectively. The findings depicted that none of the biodiesels produced from the different treatment plans, were able to meet both ASTM and EN standards for biodiesel, though the organic produced kernels' biodiesel had betterprospects. Findings disclosed that biodiesels produced from groundnut kernels cultivated with fertilizer generally contained higher acid value than the control biodiesel. This signified that the fertilizers facilitatedacid formation within the groundnut kernels. High acid content facilitates the degradation of biodiesel which can further result to poor combustion efficiency of the biodiesel, apart from causing corrosion to the engine's linings (Munoz *et al.*, 2012).

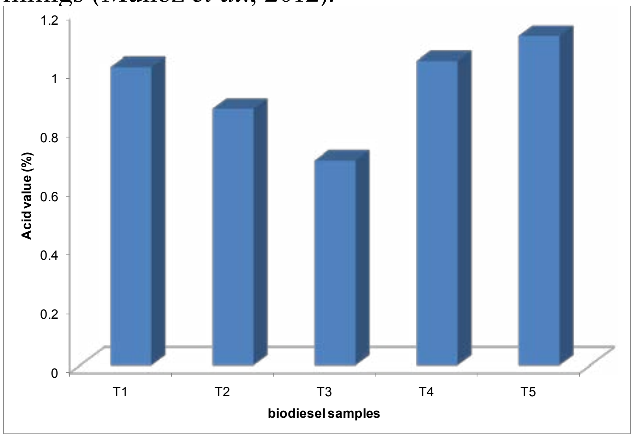


Figure 4: Acid value

Iodine value

The result of the iodine value (IV) of the biodiesel is presented in Figure 5. The iodine value varied from 27.54 mg/L to 34.63 mg/L; with the organically produced groundnut kernels (T_2 and T_3) producing biodiesel with the lowest iodine contents, and the conventionally produced groundnut kernels (T_4 and T_5) producing biodiesel with the highest iodine values. Observations made depicted that the iodine value of T_1 biodiesel was considerably higher than the iodine concentrations of the T_2 and T_3 biodiesels.

Regardless of the field treatment applied to the groundnut plants, the iodine values of the biodiesel produced from the five treatments were within the EN 14214 approved standard. Iodine determines the oxidation stability and degradation of biodiesel, portraying the level of unsaturation of the biodiesel (Munoz *et al*., 2012). High Iodine value has serious consequences on IC engines, due to the oxidation instability of the biodiesel, resulting in engine failure in most cases. According to Vescovi *et al.* (2016), biodiesels having smaller iodine value contain high proportions of unsaturated fatty acids; hence, having higher levels of oxidation stability.

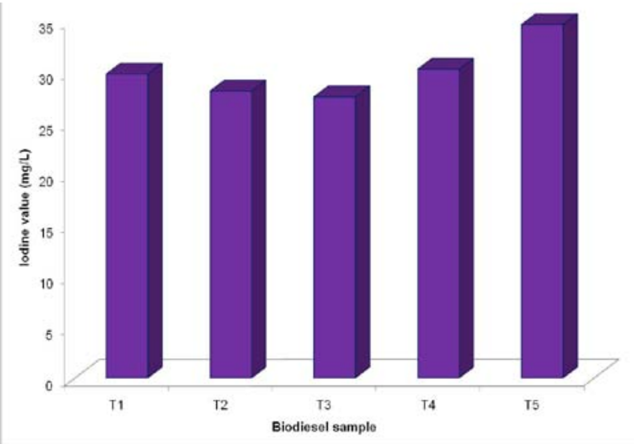


Figure 5: Iodine value

Phosphorus value

The result of the phosphorus concentration of the biodiesel is presented in Figure 6. Figure 6 revealed that field practice had substantial influence on the phosphorus concentration of biodiesels. The phosphorus concentration varied from 8.21 mg/L to 10.25 mg/L. Observations made from the results show that T_4 and T_5 biodiesel recorded the highest phosphorus values (T_4 ~9.78 mg/L and T_5 ~ 10.25 mg/L) among the five treatment plans, while the T_1 had the biodiesel with the lowest phosphorus value (T_1~ 8.21 mg/L). Additionally, it was noticed from the biodiesels produced from manure (T_2 and T_3), and that with lower fertilizer quantity (T_4), had phosphorus concentrations which fell within the standard (10 mg/L) approved by EN 14214. High phosphorus concentration in biofuel can hinder the operation of the emission's control catalytic converters of an engine (Munoz *et al*., 2012).

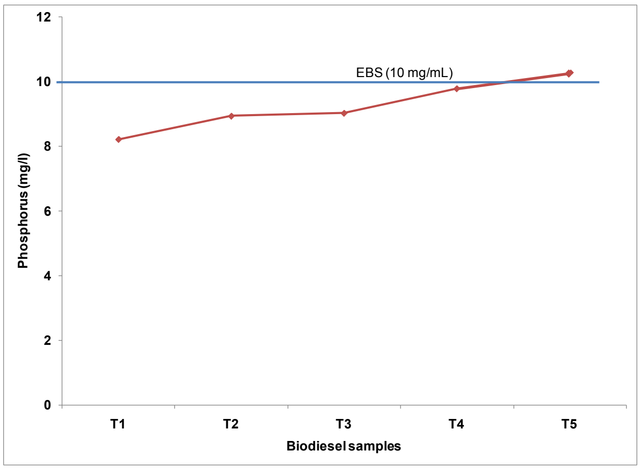


Figure 6: Phosphorus concentration

These findings affirmed earlier reports of Uguru and Obah (2020) and Eboibi *et al.* (2021), which stated that field practices significantly affects the phytochemical properties of agricultural materials. As revealed by the study's findings, cultivating groundnut with larger proportion of NPK 15:15:15 fertilizer, will be detrimental to the quality of biodiesel produced from the kernels. Apart from better biodiesel yield, organic farming will help to cut down GHG, because gasses emitted during the production and utilization of fertilizers contribute partially to the menace of climate change.

CONCLUSION

Biodiesel quality is significantly affected by numerous intrinsic factors. This work investigated the power of field practices (pre-harvest treatment) on the biodiesel quality, produced from groundnut kernels. Findings obtained from this work depicted that soil amendments considerably influenced the quality of biodiesel produced from groundnut kernels. It was observed that biodiesel produced from groundnut kernels grown with manure tends to have better biofuel properties, compared to biodiesel produced from groundnut kernels grown with fertilizer. The ester content, iodine value alkali metal concentrations, acid value and phosphorus concentration of the biodiesel made from the organic kernels was better, when compared with the records obtained from the convectional kernels. This affirmed that organically grown crops can produce biodiesel of higher quality, when compared to conventionally grown crops.

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