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Production Of Biodiesel From Southern DRC (Bunyakiri) Palm Nut Kernels Oil.

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Abstract:
In order to lead against greenhouse gas (GHG) emissions which consisted of limiting global warming to 1.5◦ C, several long-term targets were set during the UN Climate Change Conference (COP21) including the development of green technologies and the use of low-carbon sources (non-edible vegetable oil) to replace petroleum-based fuels. Biodiesel synthesis from palm kernel oil in the presence of methanol and potash (KOH) as catalysts was investigated as an effective response to gas emissions from fossil sources. The oil was extracted from palm kernels using a volatile Soxhlet solvent ($C_4H_{10}O$*). The oil was extracted from palm kernels using a volatile soxhlet solvent(*$C_4H_{10}O$*).*

The obtained results show yields of 50.24% and 75.2% for the extraction of oil and biodiesel, respectively. The investigated physicochemical properties of the extracted oil indicated a density of 0.907 g.cm^{-3} *and an acid number of 1.84 mg.KOH.g*$^{-1}$*, a saponification number of 247 mg.KOH.g*$^{-1}$*, an iodine number of 18 g I /100g, and a viscosity of 8.475 mm*^{2}*.s*$^{-1}$*. The obtained biodiesel showed densities of 0.875(20°C), 0,864 (40°C) g.cm*$^{-3}$*, a calorific value of 40.18 MJ.K*$^{-1}$*g*$^{-1}$*, average cetane index of 51.4 and an iodine index of 116, 67. These values conformed to the standard limits of ASTM D6751 and EN14214.*

Graphic Abstract

Keywords: *Palm nuts; Valuation; Transesterification; Biodiesel; Biodegradability; Soxhlet.*

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I. Introduction

On December 12, 2015, at the UN Climate Change Conference (COP21) in Paris (Paris Agreement), the heads of state and government set a long-term goal concerning greenhouse gas emissions, which is to limit the increase in global warming to 2◦ C in this century while continuing efforts to limit it to 1.5 ◦ C in the future. In this context, several avenues have been explored, including using agricultural oil as a feedstock to replace petroleum-based fuels, a more environmentally friendly and sustainable form of energy.

Agricultural biofuels are derived from plant or animal organic matter, also known as biomass, and are used in engines (Poitrat *et al.,* 1999). Biofuels, under development for more than 40 years, are considered an alternative to petroleum-based fuels (Tedjini Fatma *et al.,* 2020). They represent a renewable energy source that does not pose any major environmental risks and thus represent a sustainable and viable development path (B. M. Amine, 2022). They contribute to the reduction of greenhouse gas emissions and thus to the improvement of air quality (S. K. Hoekman et al., 2012). In addition, they can replace fossil fuels (Gerhard Knothe, 2010) and ensure a certain economic stability by reducing energy dependency (B. M. Amine, 2022).

Among these alternatives, palm kernel oil has attracted attention as a potential source of safe, cheap, and clean sources for biodiesel production (Korus *et al.,*1995). Two edible oils are extracted from the latter: Palm oil (extracted from the pulp and accounts for 18 to 26% of the weight of the grape) and palm kernel oil (extracted from the almond and accounts for 3 to 6% of the weight of the grape and 50% of the dry weight of the almond (Koti, 2022). Currently, these two oils are mainly used for food production and cooking. The palm is processed into biofuel and the rest of the world's Palm oil production (about 10 to 22%) is used in industry (FAO, 2024).

The term biofuel is a generic term and includes bioethanol, biodiesel, bio-oil, biogas, Fischer-Tropsch liquids, and biohydrogen (Kenthorai *et al.,* 2018). Of these biofuels, only biodiesel can be an alternative to conventional diesel fuel (Moser *et al.,* 2009). The American Society for Testing and Materials (ASTM) standard defines biodiesel as a blend of long-chain monoalkyl esters of fatty acids derived from renewable resources and intended for use in diesel engines. It can be used in diesel engines alone or blended with diesel fuel (Katz, 2012). Biodiesel is a first-generation biofuel.

Bunyakiri is a region (as shown in Figure 1) known for the cultivation of cassava, bananas, and palm nuts. One of the main concerns of the people of Bunyakiri is to strengthen economic activities such as palm oil production. For the producing countries, it represents a huge source of income for the local economy, both for export to non-producing countries and for local industry (Rival, 2020). The production of palm oil, a widely used product in Bunyakiri, generates various wastes, including the shells of the palm kernels (Koti, 2022). This waste is disposed of in landfills or incinerators (Fandougouma Omar, 2023), which leads to environmental problems: Pollution of the air, soil and subsoil, groundwater, and sources of certain infectious diseases. Palm kernel shells are non-recyclable waste, accounting for 7 to 8 % of the weight of palm bunches, and are produced in large quantities in the cultivation areas, causing space problems and polluting the environment if disposed of untreated (Okpala, 1990; Basiron, 2007).

The utilization of organic by-products from the food industry has attracted the interest of researchers for two reasons: environmental protection and economic utilization of organic residues (Krisnangkura, 1986). To date, very few studies have focused on the utilization of palm kernel oil for biofuel. Palm kernel oil could provide a good yield in biodiesel extraction compared to rapeseed.

In the present study, palm kernel kernels were used to produce biodiesel. Palm kernel kernels are non-recycled waste and contain a significant amount of fat, approximately 50% of oil by weight.

This work will contribute to efficient waste management which is part of the sustainable development framework. Promote the production and use of biodiesel instead of mineral-derived diesel which can lead to greenhouse gas emission reduction and green technology progress.

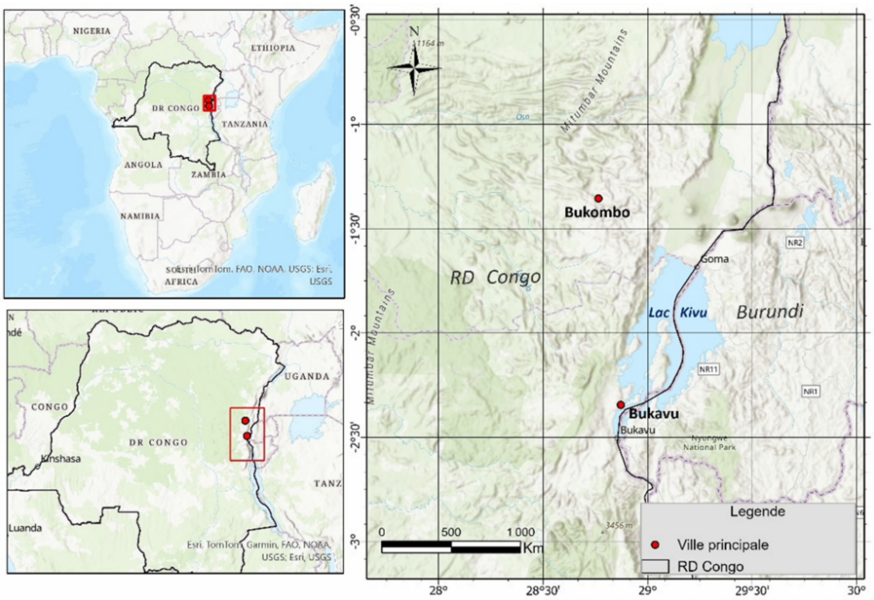


Figure.1. *Bunyakiri, is a territorial entity located in the far north of the province of South Kivu and 77 km from the city of Bukavu in the Democratic Republic of Congo (DRC). It is located at 28° 45' 54" and 28° 52' 18" east longitude and 1°-2° 20' 42" south latitude.*

II. Materials And Methods

Raw materials and chemicals

Figure 2 shows the palm nuts collected from the Bunyakiri market and the crushed palm kernels (particle size (2-5mm)). The chemical reagents and solvents of laboratory and analytical grade, including a volatile Soxhlet solvent ($C_4H_{10}O$), methanol, and potash (KOH) were used in this work.

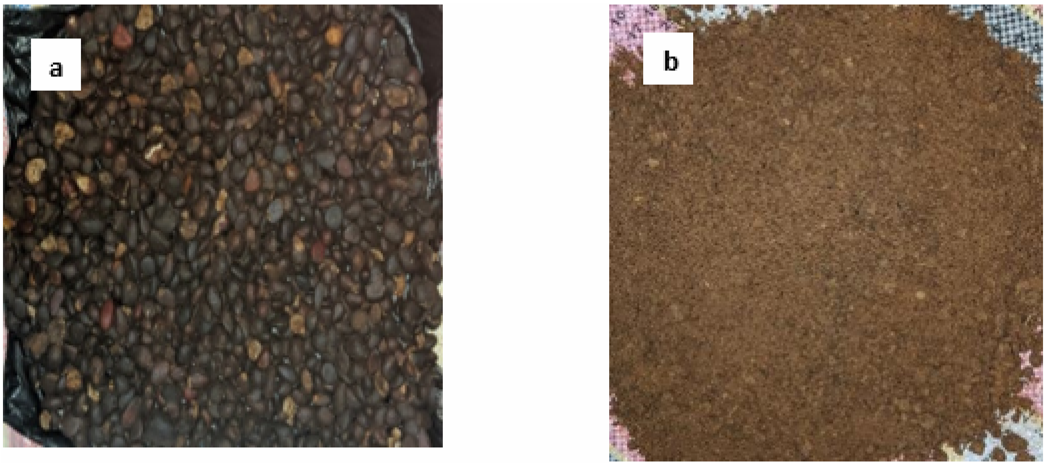


Figure 2. *Palm nuts and* Crushed palm kernels

Oil extraction from POME

Oil extraction from Palm kernel

After drying, grinding, and sieving the palm nut kernels (Figure 3a), the powder obtained is dried in an oven at 105 °C for one hour and then cooled in a desiccator for 30 min. Then, approximately 30 g of the powder is introduced into a cartridge and placed with the test sample inside the Soxhlet apparatus, in the presence of petroleum ether as solvent. Finally, the removal of the solvent was carried out by distillation. The residue is dried in an oven at 70-80 °C, then cooled in a desiccator for 30 min. The final product is obtained after evaporation of traces of solvents using a steam rota (Figure 3b).

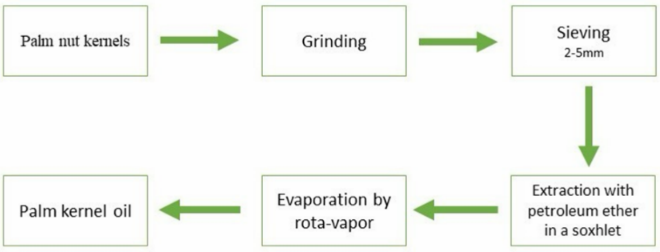


Figure 3a. Scheme of oil extraction from palm nut kernels

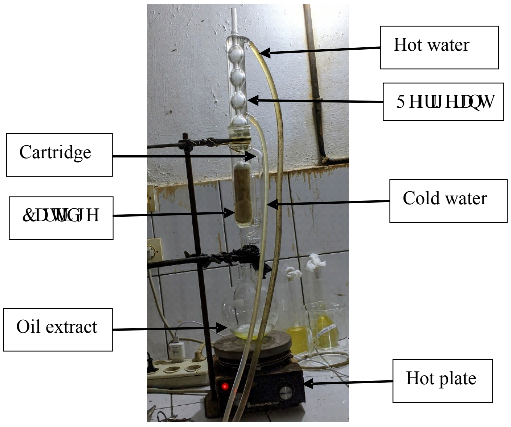


Figure 3b. Experimental oil extraction setup

Production of biodiésel by transesterification

Reaction

55 mL of palm kernel oil was introduced into the reactor immersed in a water bath and heated to 60 °C. Then, the catalyst is dissolved in alcohol until completely dissolved to obtain an alkoxide mixture. This mixture is poured into the hot palm kernel oil flask. Then, the mixture is stirred using the magnetic bar previously introduced into the flask (600 rpm); while heating up to the set temperature which is between 65°C to 80°C. Finally, the temperature is maintained for 90 minutes.

Decantation and washing

After stirring for one hour, the mixture is poured into a separatory funnel. Then leave to rest for 24 hours for separation to take place. After a day of rest, the mixture presents two separate products, namely: glycerol and biodiesel (B. M. Amine, 2022). The biodiesel floats and forms the top layer and the glycerin will be collected from the bottom of the bulb.

Washing removes traces of alcohol and catalyst by adding a quantity of distilled water to the separating funnel. Finally, we recover the biodiesel (Figures 4 and 5).

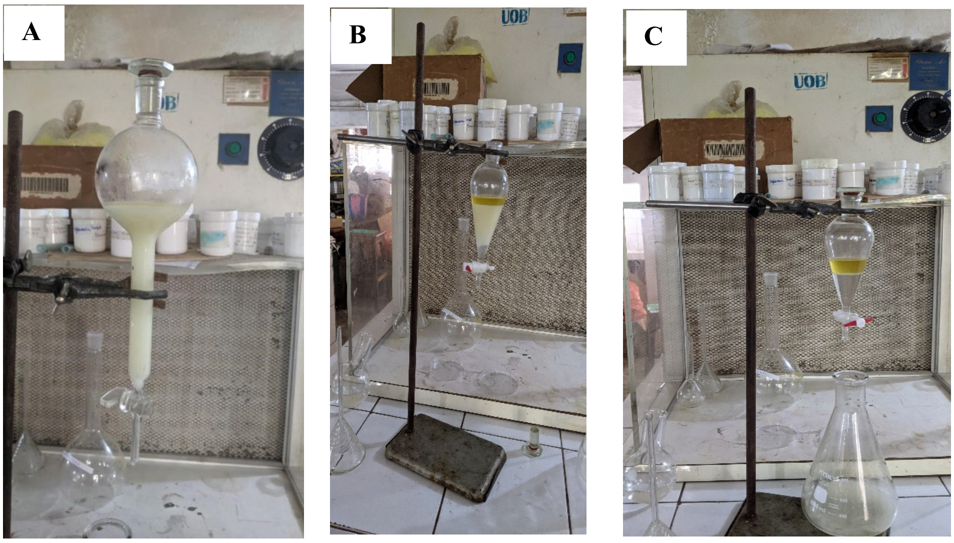


Figure 4. Montage des opérations de lavage du biodiesel. A : premier lavage ; B : deuxième lavage et C : troisième lavage

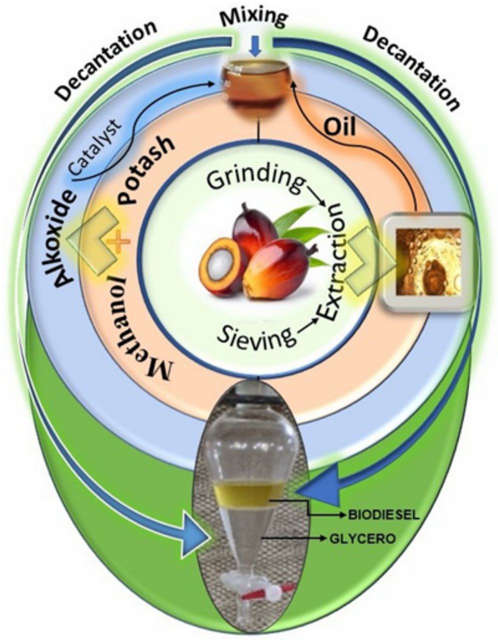


Figure 5. Biodiesel synthesis process steps

Distillation of biodiesel

Distillation involves heating the sample slowly to the boiling temperature of water. This ensures that the water and methanol are evaporated (T°eb of methanol = 65 °C). After distillation, the percentage of lipids is expressed in the weight of dry matter.

Extracted oil physicochemical characterization

Yield

The yield is calculated by the following relationship:

R = (   ) ×100 **Eqn. 1**

R (%) = yield of oil extracted, m = mass(g) of oil extracted, m0 = mass (g) of sample.

Density

The principle is based on measuring the mass, at room temperature, of a volume of fatty substance contained in the pycnometer previously calibrated at the same temperature. The density is given by the following formula (Hussein *et al.,* 2010):

D = **Eqn. 2**

D = density, P1 = weight (g) of the empty pycnometer, P2 = weight(g) of the pycnometer filled with distilled water, and P3 = weight (g) of the pycnometer filled with oil.

Acid number

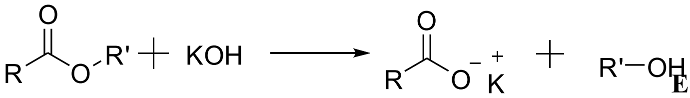
The determination of the acidity of the extracted oil is done on the dried and weighed oil. Dissolve a test portion in ethanol, brought to close to boiling point, and previously neutralized with an ethanol solution of potassium hydroxide at (0.1N) in the presence of phenolphthalein. The acid number is given by the following relationship (Ridha *et al.,* 2016):

I_A **Eqn. 3**

V = volume (ml) of potash used, N = normality of the solution, P = mass (g) of the test portion, IA = acid number.

Saponification index

If we treat an ester with sufficiently concentrated and hot potash, we regenerate following a total reaction of alcohol and the potassium salt of the acid then we form an ester Eqn. 4.



Eqn. 4

The saponification index is given by the formula established below:

I_S **Eqn. 5**

V0 = volume (ml) of HCl used for the blank test, V = volume (ml) of HCl used for the sample to be analyzed, P = test portion (g), N = normality of the hydrochloric acid HCl 0.5N, IS = saponification index.

Iodine index (AFNOR T60 203)

The diode index is the number of grams of iodine fixed per 100 grams of oil. This index provides information on the degree of overall establishment of fatty chains analyzed. The HÜBL method is chosen to determine the iodine value. When the oil is unsaturated, the iodine index is high (Alloune et al., 2012). For palm kernel oil the value is between 12 and 19 according to the NF EN ISO 396 standard.

Viscosité

There are several methods of measuring the viscosity of a liquid. The so-called potassium permanganate method was chosen (Jean-Pierre Faroux *et al.,* 1999, Bernard Castaing, 2003).

$\eta =$ **Eqn. 6**

Vg = volume of the drop (m^3), $\varphi KMnO4$ = density of the potassium permanganate solution ($kg.m^{-3}$), η = viscosity of the fluid (poisuille (Pl)), r = radius of the drop in meters (m), v = speed of the drop ($m.s^{-1}$, φe = density of the sample ($kg.m^{-3}$), g = terrestrial gravity constant ($9.81\ m.s^{-2}$).

Characterization of biodiesel

Yield of alkyl esters from transesterification

The conversion rate is defined as the mass of the biodiesel produced, divided by the mass of the oil initially used. The mass yield of the product obtained is calculated by the relationship below (Eqn.7). The quantity of alkyl esters will be optimal after rigorously carrying out the synthesis steps (transesterification reaction) (Olakunle Isamotu *et al.,* 2020).

R (%) = ( ) X 100

Eqn. 7

Calorific value

An empirical equation was used to evaluate the heat of combustion in kcal/kg, based on the saponification (Is) and iodine (Ii) indices (Haïdara *et al.,* 1996).

$Pc = 11380 - Ii - 9.15 \times Is$ **Eqn. 8**

Pc = higher calorific value (kcal/kg) (with 1 kcal/kg = 4.18 kJ/kg), Ii = iodine number, Is = saponification number.

Cetane number

The quickest way to determine the cetane number is to apply the Klopfenstein equation. This equation can be obtained from the iodine and saponification indices of methyl esters determined experimentally (Haïdara *et al.,* 1996).

Icetane = 58.1 + 2.8 **Eqn. 9**

Icetane = 46.3 + **Eqn. 10**

n = number of carbons, N = number of double bonds, x = saponification number, y = iodine number.

III. Results And Discussions

Yield

After extraction and elimination of traces of solvent, the yield obtained is 50.24%. This value remains quantitatively higher than that found by (Dahama Siham *et al.,* 2021) which is 44.21% obtained from Peanum harmala seeds. This shows that palm nut kernels contain a high level of fat.

Palm kernel oil physicochemical characterization

Table 1 groups together the values of the physicochemical characteristics of the oil obtained from palm nut kernel powder.

Table 1. Physico-chemical characteristics of palm kernel oil

Paramètres	*Unités*	*Average contents*	*Standards*
Density	-	0,907	ISO (0,899-0,914)
Acid number	mg de KOH/g	1,84	-
Saponification index	mg de KOH/g	247	-
Iodine index	mg d'I_2/100g	18	NF EN ISO 396 (12-19)
Viscosity at 40°C	mm^2/s	8,475	ISO3104 (2,3-9,8)

The density value determined is in the order of 0.907. This value corresponds to that of vegetable oils, which is generally between (0.906 and 0.919) at 20 °C (Berrada et al., 1972, Rahmani *et al.,* 2005). The acid value is 1.84 mg KOH/g. This low acid value gives the palm kernel oil good stability (B. C. FATMA Zohra, 2017). From this analysis, the saponification index is very high (247 mg KOH/g). This shows that the carbon chain of the fatty acids is short. The viscosity of 8.475 mm^2 /s is considered high compared to biodiesel. This could be due to the presence of large molecules in the oil, which move slowly due to the internal attractive forces between the aliphatic chains of the glyceride molecule. The experimental value of the iodine value is 18 mg I_2/100g. According to the NF EN ISO 396 standard, this value is between 12 and 19 mg I_2/100g.

Mechanism of the transesterification reaction

The transesterification reaction is chemically balanced as shown in Figure.6. The first two reactions are rapid because the primary ester functions are transesterified first. The last reaction is slower. In basic catalysis, the mechanism is as follows:

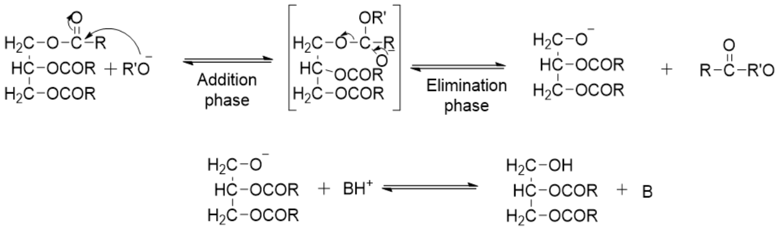


Figure 6. Mechanism of the base-catalyzed methanol transesterification reaction of vegetable oil.

According to the author Benbouzid.M.A., this reaction initially consists of a nucleophilic attack of the alkoxide anion on the carbonyl (of the triglyceride) to form an intermediate carbanion (addition phase) and a nucleophilic departure during the folding of the oxygen doublet (elimination phase). The alkoxide is regenerated as soon as an alkoxide function of the glycerol occurs (B. M. Amine, 2022). With NaOH, KOH, K_2CO_3, or other similar catalysts, the alkoxide formed is often identified as the catalytic species. The third reaction (mono yields ester) seems to be the crucial step of the reaction, as monoglycerides are more stable intermediates than diglycerides (Berna Hamad, 2009).

Physico-chemical characterization of biodiesel

Table 2 shows the values of physical and chemical characteristics of biodiesel produced from palm kernel oil.

Table 2. Physico-chemical characteristics of the biodiesel produced

Paramètres	Unités	Teneurs moyennes	Normes
Densité	-	0,875 à 20° C et 0,864°C à 40°C	ASTMD6751 et EN14214 (0,860 et 0,900)
Calorific value	MJ/Kg	40,18	-
Acid number	mg de KOH/g	1,32	-
Saponification index	mg de KOH/g	190,74	-
Cetane number	-	51,4	ASTMD6751 (USA), DIN V51606(Allemagne) et EN 14214(Europe) : respectively : 47,49 et 51
Iodine index	mg d'I_2/100g	116,67	Less than 120 according to standard EN 14241
Viscosity	mm^2 /S	4,46	ASTM D445 (1,9-6,0) et EN14214 (3,5-5,0)

After transesterification, the density obtained (0.875 at 20°C and 0.864°C at 40°C) is lower than that of the starting palm kernel oil, which is 0.907. This indicates that the transesterification reaction has reduced the length of the triglycerides' molecular chains. The density obtained is within the range of the European standard EN 14214 [0.860-0.900]. In fact, density is an important parameter for the injection of diesel fuel into the system.

The highest calorific value (GCV) of the synthesized methyl esters was 40.18 MJ/kg (Table 2). This value is higher than that of mastic oil, which is 39 MJ/kg. This represents a considerable advantage in view of the desired energy output. On the other hand, it is lower than the GC of conventional diesel, whose value is 43 MJ/kg according to the ASTM D240 standard, which is probably due to the excess oxygen in biodiesel.

Table 2 shows that the value of acid value (1.32) decreased after the transesterification reaction of palm kernel oil. This can be explained by the reaction of the strong base with free fatty acids, which decreases the free fatty acid content. The transesterification reaction removed the acidity from the oil.

The cetane index determined is 51.4 (Table 2). This index is higher than that of petroleum diesel, which is between 45 and 50 according to the standard (ASTMD976). The higher the cetane number, the shorter the ignition delay. It also extends the combustion time. The cetane number is one of the most important indicators of the quality of biodiesel.

The iodine number is 116.67 (Table 2) and complies with the EN 14214 standard, as it is below 120 mg I_2/100 g. This proves the presence of double bonds in biodiesel, which can promote oxidation reactions.

The biodiesel produced from palm kernel oil has a viscosity of 4.46 mm^2/s (Table 2), which is within the range of ASTMD 445 (1.9 to 6.0 mm^2/s). s) and EN 14214 (3.5 to 5.0 mm^2/s) standards (Selaimia *et al.,* 2018).

IV. Conclusion

This work involved the production of biodiesel from palm kernel oil, which is obtained from palm nut kernels. The method used made it possible to achieve a good yield (75.2 %) of biodiesel. The results of the analysis of the physicochemical properties of the biodiesel produced gave the values of saponification index (190.74), acidity index (1.32), density (0.875 at 20° C and 0.864 at 40° C), calorific value (40.18), viscosity (4.46) and cetane index (51.4). These physicochemical properties were compared with those of petroleum diesel and with several international standards, namely: ASTMD6751, EN14214, ASTMD6751 (USA), DIN V51606 (Germany), EN 14214 (Europe), EN 14241, ASTM D445 and EN14214 ISO.

Finally, this study shows that biodiesel is easy to use as it is biodegradable and does not contain sulfur or aromatic compounds. Furthermore, the carbon dioxide (exhaust carbon) emitted by biodiesel does not have the same impact on the environment and does not harm the ozone layer.

Author Contributions

All authors contributed to the success of this present research. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

The data presented in this study are available on request from the authors.

Conflicts of Interest

The authors declare no conflict of interest.

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