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Process Optimization of Solvent-Free Transesterification of Palm Kernel Oil for Biodiesel Production

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Abstract

This study investigates the production of biodiesel as a sustainable alternative fuel to enhance global energy security. Biodiesel was synthesized from palm kernel oil through NaOH-catalyzed transesterification in the presence of cellulose as an auxiliary material. Systematic process optimization was conducted to determine the conditions that maximize product yield. The optimum parameters were identified as a reaction temperature of 140 °C, reaction time of 7 h, catalyst loading of 0.4 g NaOH, cellulose loading of 0.5 g, and agitation speed of 800 rpm, under which a maximum biodiesel yield of 92.85% was achieved. Comprehensive physicochemical characterization of the product was performed using Fourier Transform Infrared Spectroscopy (FT-IR), Gas Chromatography-Mass Spectrometry (GC-MS), Thermogravimetric Analysis (TGA), and Nuclear Magnetic Resonance (NMR) spectroscopy. The analytical results confirmed the successful conversion of triglycerides to fatty acid methyl esters (FAME), the principal constituents of biodiesel. Thermal analysis indicated good thermal stability up to approximately 240 °C, while compositional and structural data demonstrated compliance with established international biodiesel specifications, specifically ASTM D6751-07b and EN 14214:2003 standards. Engine performance testing showed that the produced biodiesel could effectively power a conventional diesel engine without operational difficulties. Additionally, the biodiesel exhibited immiscibility with water, indicating favorable storage and handling characteristics. Beyond its primary application as a renewable transportation fuel, the physicochemical properties of the product suggest potential utility as a functional additive in surface coating formulations and decorative materials. Overall, the findings demonstrate that palm kernel oil is a viable feedstock for high-yield biodiesel production under optimized conditions, supporting its role in sustainable energy diversification.

Keywords:

Palm Kernel Oil,
Biodiesel,
Transesterification,
Fatty Acid Methyl
Esters (FAME),
Process Optimization

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1. Introduction

The increasing global energy demand, coupled with concerns about environmental pollution and depletion of fossil fuels, has driven the urgent need for alternative sustainable energy sources (Hou et al., 2023). Biodiesel, derived from vegetable oils and animal fats through transesterification with alcohol, leading to the formation of fatty acid methyl esters (FAME) has emerged as a promising candidate (Farouk et al., 2024). Triglycerides are a sustainable resource for the manufacturing of biodiesel because they are generated from plant and animal fats and oils. This encourages environmental sustainability and lessens reliance on fossil fuels. The renewable biofuel thus offers numerous advantages over conventional diesel fuel, including reduced greenhouse gas emissions and improved biodegradability (Khanna et al., 2011; Wilms et al., 2023).

The sustainable idea of generating biofuels from biomass which are of low economic value is encouraging the use of cellulose and cellulosic materials in biodiesel production. Cellulose cannot undergo transesterification; transesterification involves swapping the alcohol group on a triglyceride molecule with another alcohol (like methanol or ethanol) to produce biodiesel. Cellulose is a tough carbohydrate polymer; its structure requires a different process to break it down into usable fuel precursors. Pretreatment is therefore employed to break down cellulose into simpler sugars or smaller cellulose chains (Abubakar, 2019). Regardless of pretreatment, the reaction with palm kernel oil (a source of fatty acids) which involves forming an ester bond between the fatty acid and the hydroxyl group on cellulose is an esterification process. But when fatty acid (carboxylic acid) reacts with a

hydroxyl group (alcohol functionality) on cellulose to form an ester bond fatty acid cellulose ester (FACE) is produced (Lease et al., 2021; Tarasova et al., 2023).

Biodiesel production traditionally involves using large volumes of organic solvents (usually methanol). Recently, solvent-free transesterification is recognized as a more environmentally friendly approach compared to traditional methods. This approach minimizes waste generation and simplifies the purification process. Palm kernel oil (PKO), a readily available feedstock with favorable fuel properties, is a suitable choice for biodiesel production (Chetty et al., 2024; Makone, 2013).

Solvent-free transesterification process to convert PKO into biodiesel usually involves the use of catalyst, typically an alkali or acid, to facilitate the reaction between triglycerides and alcohol. Traditional methods using acid catalysts, especially acid chlorides can be harsh on cellulose and generate environmentally unfriendly byproducts. The reaction is conducted under various conditions of temperature, time, and catalyst loading. And the yield of biodiesel is measured for each set of conditions to identify the optimal parameters for maximizing production (Kedir et al., 2023). Up to 98% biodiesel yield can be achieved under optimal conditions identifying reaction temperature, catalyst concentration, reaction time, and cellobiose catalyst to oil ratio as crucial parameters (Aboelazayem et al., 2022); (Eke et al., 2023).

However, the entire optimization processes still have certain limitations. One major challenge is scalability; replicating the lab-scale findings to large-scale commercial biodiesel production might present unforeseen

challenges. Improving the processes in tandem with economic and environmental considerations could help identifying the most commercially viable processes.

The current study makes use of readily available palm kernel oil (PKO) sourced locally to investigate the optimization of solvent-free production of biodiesel using NaOH as catalyst and reaction conditions (temperature, time, and catalyst loading). The esterification process is environmentally benign and economically attractive. The produced biodiesel was characterized using established analytical techniques to confirm its properties and adherence to relevant standards.

2. Materials and Methods

2.1. Materials

The palm kernel oil was purchased commercially at the Oja Tuntun market in Ilorin, Nigeria, which is located at latitude $8^{\circ} 29' 18''$ N and longitude $4^{\circ} 32' 06.3''$ E.

Cellulose was isolated from sugarcane bagasse. Analytical grade acetic acid, carbon tetrachloride, ethanol, hydrochloric acid, hydrogen peroxide, iodine monochloride, phenolphthalein 1% solution in ethanol, potassium hydroxide, sodium hydroxide, sodium thiosulphate solution, starch, urea, and deuterated chloroform (CDCl_3) were purchased from Sigma Aldrich.

2.2. Methods

2.2.1. Spectroscopic and Instrumental Characterization techniques

Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric analysis (TGA)

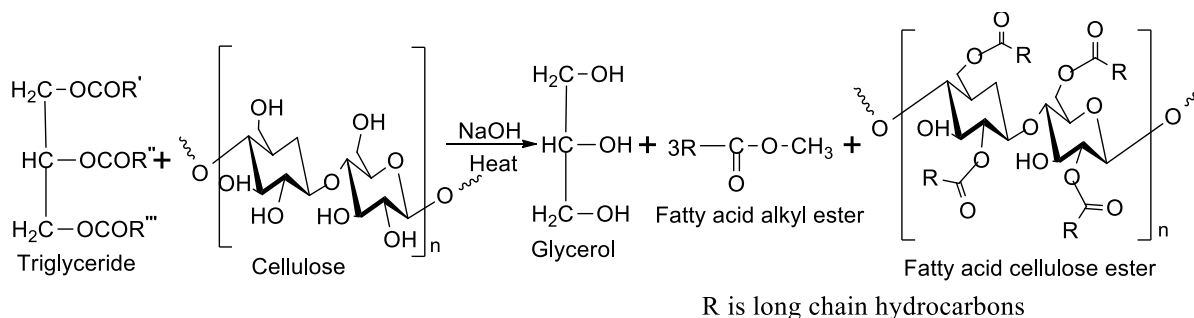
of the samples was carried out at the Center for Synthesis and Catalysis, University of Johannesburg, South Africa using Shimadzu IR Affinity-1S and Perkin-Elmer STA 600 respectively. An average of 50 scans were performed in the region $4000 - 400 \text{ cm}^{-1}$ for FTIR and TGA carried out between 25°C to 900°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ in airflow. GC-MS of biodiesel was carried out using the GCMS - QP2010SE SHIMADZU, JAPAN while the $^1\text{H-NMR}$ analysis was recorded in deuterated chloroform on Bruker Avance 500 MHz NMR spectrophotometer.

2.2.2. Pre-treatment process of palm kernel oil (PKO)

PKO was heated to 80°C , then a 2% solution of 30% citric acid ($\text{C}_6\text{H}_8\text{O}_7$) by volume of oil was added, and the oil mixture was constantly agitated at 80°C for 20 minutes before being allowed to cool to room temperature. The mixture was centrifuged for 20 minutes after 1 hour to separate the dewaxed oil.

2.2.3. Esterification Reaction of Cellulose with Palm Kernel Oil (PKO) in a Non-solvent Medium

Pretreated PKO (100 ml) was transferred into a 250 ml round bottom flask and then mixed with 2 g of cellulose and 0.4 g of NaOH. The mixture was heated at 120°C for 4 hours under stirring at 800 rpm. The mixture obtained was transferred into a separating funnel. The mixture was separated into two layers, that is the upper and lower layers for biodiesel and glycerol respectively. The biodiesel was purified by gently washing it with warm water to remove any residual catalysts or soaps, drying it, and storing it in a clean sample bottle.



Scheme 1: Reaction scheme for the transesterification reaction between triglyceride (PKO) and cellulose

2.2.4. Optimization Studies for the Production of Biodiesel

The procedure summarized in scheme 1 was repeated at different reaction times, temperatures, amount of NaOH, cellulose load, and agitation speed to obtain the optimum yield of biodiesel production.

2.2.5. Physical Method of Characterization of Biodiesel and PKO

The saponification value, free fatty acid, iodine value, acid value, Specific Gravity, density, viscosity, pH value, Cloud point, pour point, and Flashpoint of the biofuel were determined using standard methods (Kmar and Kant, 2013)

2.2.6. Engine performance Test of Biodiesel produced

The test procedure was adopted from literature (Bello and Agge, 2012), with some modifications. The engine test was conducted using a single-cylinder, water-cooled, and air-cooled diesel engine. Model: ZS11 15 25HP/2200RPM. Biodiesel (1 liter) was poured into the tank of the engine to power the diesel engine.

3. Results and Discussion

3.1. Optimization of biodiesel production

The effect of temperature, reaction time, amount of catalyst, stirring and amount of cellulose on the yield of biodiesel was investigated by changing a particular variable while keeping the others constant in turn. The result is presented in Table 1.

Table 1: Effect of temperature, reaction time, catalyst on the yield of biodiesel

Time (h)	Percentage Yield (%)	Temp (°C)	Percentage Yield (%)	Cellulose(g)	Percentage Yield (%)	Stirring Rate(rpm)	Percentage Yield (%)	NaOH (g)	Percentage Yield (%)
4	85.60 ± 0.5	110	77.85 ± 0.60	0.5	92.85 ± 0.20	500	84.75 ± 0.25	0.1	63.75 ± 0.55
5	88.65 ± 0.35	120	83.10 ± 0.70	1.0	87.83 ± 0.13	600	86.65 ± 0.35	0.2	72.35 ± 0.05
6	89.40 ± 0.1	130	88.05 ± 0.40	1.5	83.21 ± 0.22	700	88.75 ± 0.45	0.3	85.25 ± 0.15
7	92.85 ± 0.15	140	92.85 ± 0.40	2.0	76.85 ± 0.40	800	92.85 ± 0.15	0.4	92.85 ± 0.15
8	88.45 ± 0.25	150	87.75 ± 0.25	2.5	72.02 ± 0.29	900	89.55 ± 0.55	0.5	90.05 ± 0.35
						1000	88.65 ± 0.55	0.6	87.25 ± 0.45
								0.7	83.55 ± 0.15
								0.8	74.55 ± 0.45

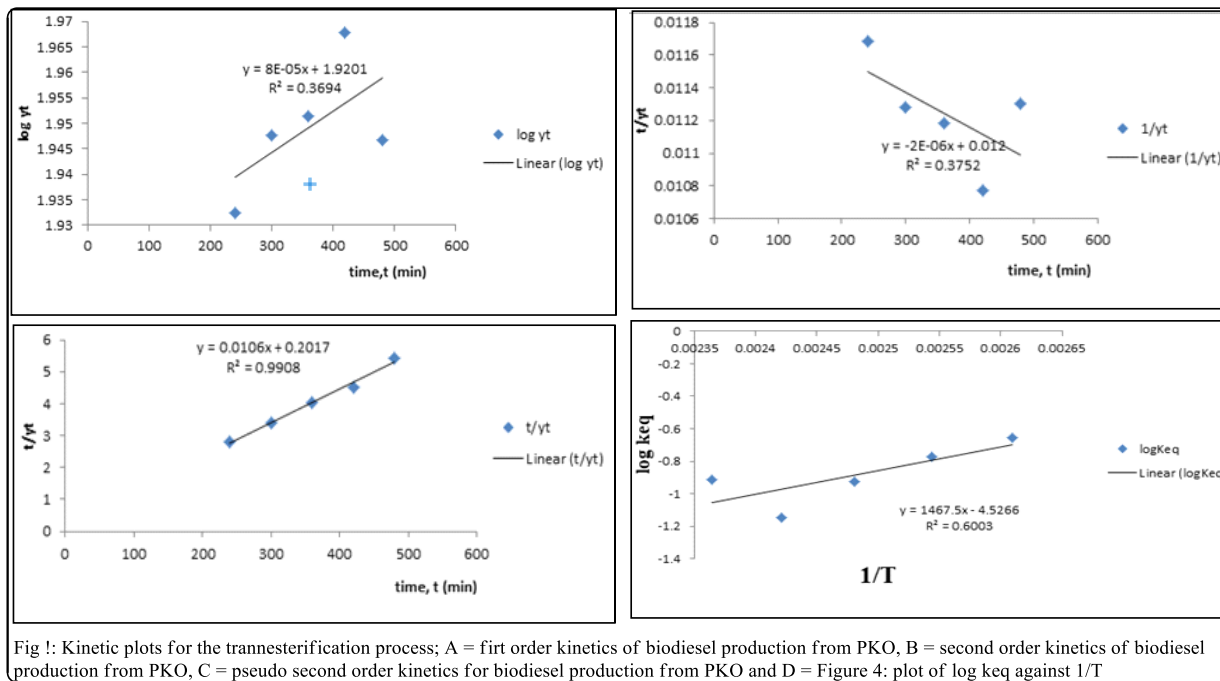
When all other parameters were held constant, the impact of reaction time was studied at intervals of 1 hour from 4 to 8 hours, and the results showed that a 92.85% conversion yield was achieved at 7 hours of reaction. Consequently, the alkaline-catalyzed transesterification of palm kernel oil with cellulose to biodiesel was completed in 7 hours. Because it affects both the rate of reaction and the yield of methyl ester, temperature is an important transesterification parameter. Palm kernel oil was more successfully converted to biodiesel up to an equilibrium temperature of 140 °C when other variables were held constant and reaction temperatures were raised from 110 °C. The best conversion yield was 92.85% at 140 °C. This is because triglycerides saponify more quickly at higher temperatures (Alum, 2024).

Examination of the impact of catalyst on the transesterification processes at different NaOH concentrations (0.1 g to 0.8 g) found that the highest conversion yield of 92.85% was obtained at 0.4 g of NaOH, 7 hours, 140 °C, and 0.5 g of cellulose. The ester yield increased from 63.75 to 72.35 to 85.25% when the NaOH concentration was raised from 0.1 to 0.4 g, and an optimal product yield of 92.85% was attained at 0.4 g. Beyond this point, increasing the alkali concentration led to a decrease in yield. Consequently, a persistent elevation of the sodium hydroxide load over the ideal concentration has an adverse effect on the production of biodiesel. A prior study found that employing a catalyst at a high concentration increased reaction rates and the production of soap.

Process is strengthened during the biodiesel synthesis process by the oil and catalyst mixture's agitation speed [xx]. Mixing intensities of 500 rpm, 600 rpm, 700 rpm, 800 rpm, 900 rpm, and 1000 rpm were explored at the ideal circumstances established in this work. The best conversion rate was obtained at 800 rpm of stirring. This was 92.85%. The reverse reaction was preferred as the stirring rate increased, as seen by the reported drop in biodiesel output observed beyond the ideal stirring rate. An analysis of how the amount of cellulose used affected the output of biodiesel throughout the transesterification process showed that 0.5 g of cellulose produced the highest conversion yield of 92.85%. Decreased ester formation resulted from adding more cellulose beyond 0.5 g. When the cellulose content exceeded 0.5 g, the process of biodiesel separation became more complex. As a result, for every amount of cellulose under study, the separation process was allowed to run for 24 hours. With the explanation that part of the glycerol might have stayed in the biodiesel phase, the presence of more than 0.5 g of cellulose slowed the separation and decreased the relative yield of esters.

3.2. Kinetics of the transesterification of cellulose and palm kernel oil

The experimental data plot of the logarithm of the percentage of biodiesel yield ($\log y_t$) against time (t) (Fig 1 (A)), could not fit into the first-order kinetics model since a positive slope was obtained with a very low correlation coefficient ($R^2 = 0.369$).



Similarly, due to the negative slope of the graph, the experimental data did not fit into the second-order reaction kinetics model, and it also has a very low R^2 value of 0.375, as shown in (Fig 1 (B)). The experimental data plot fit better into the pseudo-second-order kinetics model for the production of biodiesel by transesterification of cellulose with palm kernel oil in the presence of NaOH as a catalyst, yielding a straight-line graph from the plot of t/yt versus time t (mins). A good correlation coefficient ($R^2=0.990$) was obtained (Fig 1 (C)). The pseudo-second-order rate constant, k_2 , was determined to be $4.9 \times 10^{-4} \text{ \% /ml. min}^{-1}$

3.3. Thermodynamic parameters for the transesterification of cellulose and palm kernel oil

The thermodynamic parameters; enthalpy change H , entropy change S , and Gibb's free energy change G were derived for the transesterification process for the biodiesel synthesis is presented in Table 2.

Table 2: Enthalpy, Entropy, and Gibb's free energy for the production of biodiesel

Temp. (K)	Keq	Log Keq	ΔH (kJmol ⁻¹)	ΔS (Jk ⁻¹)	ΔG (kJmol ⁻¹)
413	0.0715	-1.1456	-32.90	7.02×10^{-2}	3.9
423	0.1225	-0.9118	-32.90	7.021×10^{-2}	3.2

Using the Vant Hoff equation, the equilibrium constant k for the process was found to be 413 and 423 K. When $\log keq$ was plotted against $1/T$, Fig. 1(C) showed a straight-line graph with an appropriate R^2 value of 0.6003 and a positive slope. According to Table 2, the thermodynamic studies show that the process's enthalpy change (H) is $-32.90 \text{ kJ.mol}^{-1}\text{K}^{-1}$ and that it was exothermic at 413 and 423 K. The system becomes more disordered at the same temperature due to the entropy change (S). The G (Gibb's free energy) values of 140 and 150 °C, respectively, indicated that the reaction was non-spontaneous.

3.4. Physicochemical characterization of biodiesel produced

Table 3 displays the biodiesel's characteristics along with the industry standards. One of the most important factors in determining the energy content of biodiesel is density. As to ASTM D6751-07b and EN-14214 guidelines, the ideal density range for biodiesel is between 0.830 and 0.900 kg cm⁻³.

This property affects the effectiveness of fuel atomization, making it especially important in airless combustion systems. The PKO and the biodiesel it produced had densities of 958 and 889 kg/cm⁻³ at 15 °C, respectively, according to the results, indicating that they were suitable for use in engines.

Table 3: Physicochemical properties of Biodiesel

Parameters	Units	PKO	Biodiesel	U.S. ASTM D6751-07b	EU-EN14214: 2003
Density; at 15 °C	kg/m ³	958	889	830-900	860-900
Specific gravity		0.93	0.874	-	-
Viscosity; at 40 °C	mm ² /s		3.6	1.9-6.0	3.50-5.00
Cloud point	°C	15	-5	-	-
Pour point	°C	20	-10	15 max	-
Smoke point	°C	-	70		
Flash point	°C	252	128	93 min.	120 min.
Fire point	°C	280	180		
Ester content	% mass	?	?		
Acid value	Mg KOH/g	1.12	0.46	0.50 max.	0.50 max.
Iodine value	g/100g	0.6	0.50	-	0.50 max.
Saponification value	Mg KOH/g	200.85	215.49	-	-
Oxidative stability	Mins	-	5		
Cetane number	Mins		50.219		
Refractive index			108		
pH		-	7.25	-	-
Solubility			Insoluble in H ₂ O		
TBN	mgKOH/g		7.7138		
Colour	-	Brown	Dark brown	-	-
Odour	-	Burnt smell	Burnt smell	-	-

The degree of atomization of biodiesel inside combustion chamber is determined by its kinematic viscosity. At 40 °C, the biodiesel's kinematic viscosity was measured and found to be 3.6 mm²s⁻¹. This falls within the specified range of 1.9-6.0 mm²/s as stated in ASTM

D6751-07b and EN-14214 standards. The fuel spray pattern and engine starting ease are influenced by kinematic viscosity; the higher the viscosity, the larger the fuel droplet sizes, which leads to an improper air-fuel mixture and more particulate matter emissions (Nurun

et al, 2015). Moreover, a fuel's peak heat release rate, degree of fuel impingement, and air-fuel mixing rate all decrease when its viscosity falls below the recommended level (Hellier et al., 2015). This study's parameter's outcome guarantees correct combustion inside the engine chamber while preventing the production of hazardous byproducts. Similar to this, biodiesel with a higher specific gravity delivers a slightly larger amount of fuel to the engine, increasing power output (Ayhan, 2007). The biofuel produced has an average specific gravity of 0.874, which is within ASTM guidelines. The study biodiesel's pour point—the temperature at which wax begins to dissolve in the fuel—meets ASTM requirements. PKO has a higher pour point (20 °C) than biodiesel (-10 °C). A greater biodiesel pour point is due to increased saturated fatty acid contents. The pour point of palm kernel oil drops during transesterification.

On the other hand, the flash point; the lowest temperature at a barometric pressure of 101.3 kPa at which the liquid sample provides sufficient vapour for the air-vapour mixture above the surface to flash momentarily when exposed to the standard source of ignition, is a measure of the flammability of fuels. It is an important safety criterion in the transportation and storage of biodiesel. PKO has a flashpoint of 252 °C and the value of the study biodiesel was 128 °C. PKO's flash point increased after the transesterification reaction, indicating that its volatile properties had improved. The flashpoint is a vital indicator for fuel production since it defines the lowest temperature at which the material's vapours ignite. As a result, this score represents the safety of biodiesel throughout transportation, storage, and handling. Related to this is the fire point, the temperature at which the vapour produced by

fuel will continue to burn for at least 5 seconds after being ignited by an open flame. The fire points of PKO and its biodiesel are 280 °C and 180 °C, respectively. This signifies that they have high fire points, and the fire point of the biodiesel is higher than that of PKO, which is due to a drop in viscosity and enhancement of volatile behavior by making the biodiesel more volatile than PKO after the transesterification reaction. The cloud point determined for the biodiesel was discovered to be -5 °C, which is lower than that of PKO (15 °C). The lowest commonly used indicator of a fuel's low-temperature operability is the cloud point. The tiniest crystal fragments are visible when the fuel cools. Larger crystals fuse together to form a cluster that finally gets big enough to stop the fluid from flowing at temperatures lower than the cloud point. Crystals might land at the bottom of a storage tank or clog filters.

PKO and its biodiesels had iodine values of 0.6 and 0.50 g I₂/100 g, indicating the presence of a minimal number of C=C bonds in the oil due to a significant level of saturation. Low Iodine values show that they are all non-drying oils. It also means that the biodiesel is mainly made up of saturated molecules and have high cetane value and is a more efficient fuel than fuel. The restricting of fatty acid unsaturation is critical because heating highly unsaturated fatty acids causes the polymerization of glycerides, which can lead to deposit formation (Mittlebach & Remschmidt, 2024).

During transesterification, the iodine value, and thus saturation, rises. Because the flexure point for good fuel is 100, the biodiesel would be ideal for usage as an alternative fuel for diesel engines in terms of carbon deposit production. The biodiesel produced in this study has a relatively low acid number of 0.46 mg KOH g⁻¹. The maximum value prescribed by

ASTM D 6751 is $0.5 \text{ mg KOH g}^{-1}$ hence the value of acid in the biofuel is within tolerable unit. However, the studied PKO and its biodiesel have saponification values of 200.85 and $215.49 \text{ mg KOH g}^{-1}$, respectively. This suggests the existence of a high concentration of fatty acids, which may result in the production of soap. High soap content affects the separation of biodiesel and glycerol fractions. Its presence in biodiesel might cause unstable combustion and thicken the exhaust smoke.

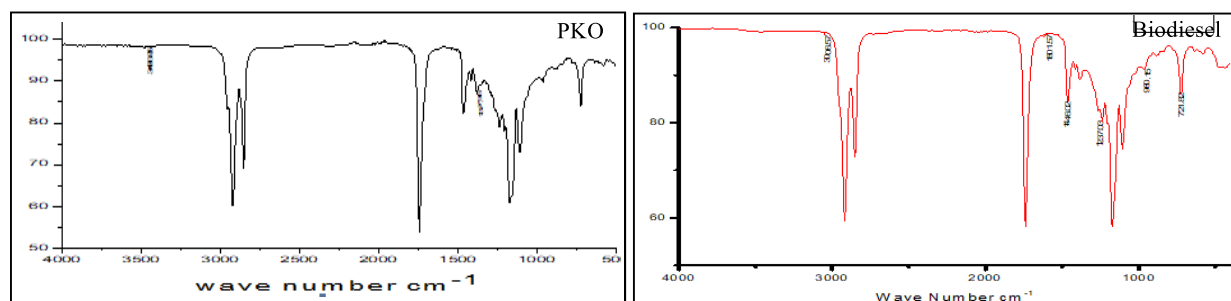


Fig 3: FTIR spectra of PKO and Biodiesel

It is evident from the prominent peak at 1741.69 cm^{-1} that the methyl ester's $\text{C}=\text{O}$ group is responsible for the presence of carbonyl functional groups in biodiesel. This implies that methyl esters are produced from triglycerides in PKO (Oyerinde and Bello, 2016; Saifuddin and Refai, 2014). The main spectrum region needed to distinguish palm kernel oil from its biodiesel chemically was the fingerprint region. Similar to previous work (Soares et al. 2018), the peak at 1446.02 cm^{-1} corresponds to the asymmetric stretching mode of $-\text{CH}_3$, which is present in the biodiesel spectrum but absent in the PKO spectrum. In line with a prior study by Sabrina and colleagues, the peak at 1377.96 cm^{-1} attributed to the glycerol group $\text{O}-\text{CH}_2$ (mono-, di-, and triglycerides) in the palm kernel oil spectrum was absent in the biodiesel spectrum.

3.5. FT-IR Spectra Analysis of PKO and Biodiesel

The FT-IR spectra of biodiesel and palm kernel oil are displayed in Figure 3. Very slight differences were observed between the two spectra since the end result of the transesterification process, biodiesel, is chemically similar to its precursor, palm kernel oil.

The absorption band of the biodiesel sample at 1382.59 cm^{-1} was attributed to $\text{C}-\text{H}$ or CH_2 -bends. This demonstrates that the samples include $\text{C}-\text{H}$, or methyl or CH_3 . The characteristic absorption band at 1204.20 cm^{-1} was assigned to the $\text{C}-\text{O}$ stretching and bending vibration mode of methyl esters. The peak in biodiesel spectrum at 1237.02 cm^{-1} , is indicative of the stretching vibration mode of $\text{O}-\text{CH}_3$. The $\text{C}-\text{O}-\text{C}$ stretching vibration mode of aliphatic ethers was attributed to the peak at 1166.38 cm^{-1} (Ilesanmi et al., 2019). On the other hand, the different peaks found between 1030.98 and 1240.08 cm^{-1} suggest both $\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibration modes. They may also depict $\text{O}-\text{CH}_3$ bending vibration mode in the spectrum (Isah et al., 2015). The particular peak at 721.82 cm^{-1} , which the $-\text{CH}_2$ groups overlapped, had the rocking vibrational mode of *cis*-disubstituted olefins and then out-of-plane vibration. In biodiesel, this group represents the methylene functional group $-(\text{CH}_2)_n-$, indicating the presence of long-chain aliphatic structure in biodiesel.

3.6. GC-MS analysis of biodiesel

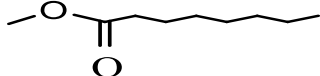
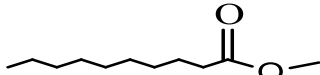

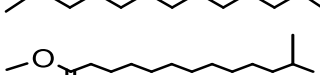
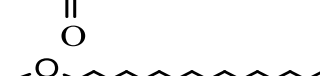
The GC-MS analysis reveals fifteen (15) distinct chemicals in the biodiesel sample (Table 4) and Table 5 lists the fatty acid components of methyl esters found in the biodiesel sample.

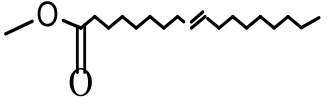
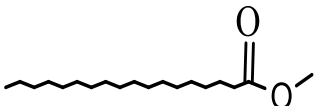
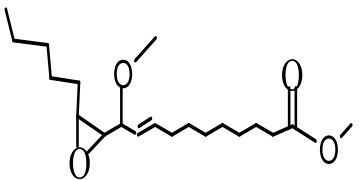
Table 4: Composition of biodiesel produced

Compounds Name	Peak #	Retention Time	Area %
Octanoic acid methyl ester	1	5.573	1.7
2- Decanone	2	6.399	0.83
2-Undecanone	3	7.767	2.13
Dedecanoic acid methyl ester	4	8.207	2.19
2-Tridecanone	5	10.858	0.81
Dodecanoic acid, methyl ester	6	11.281	47.73
2-Dodecanone	7	13.915	0.51
Tridecanoic acid 12- methyl- methyl ester	8	14.262	17.96
Z-2-Octadecen-ol acetate	9	16.404	0.47
Hexadecanoic acid, methyl esters	10	17.029	8.80
9-Octadecanoic acid, methyl ester (E)	11	19.230	10.31
methyl stearate	12	19.560	2.16
methyl (11R, 12R, 13S)-12, 13-epoxy-17-(1,5-Dimethyl)-10,13-dimethyl-2	13	20.775	0.50
1,3,2-Dioxaborolane 2-ethyl-4-(3-oxinary	14	25.081	2.82
	15	25.370	0.28

The percentage of methyl esters present in the biodiesel has been determined to be 91.43% (Table 4). With 47.73%, Methyl dodecanoate $C_{18}H_{26}O_2$ as the most prevalent monosaturated methyl ester in the biodiesel profile. Because high degree of unsaturation in fatty acid methyl esters limits its suitability as fuel due to high polymerization tendency, which is caused by peroxidation [43], therefore the study biodiesel is stable and a very good fuel.

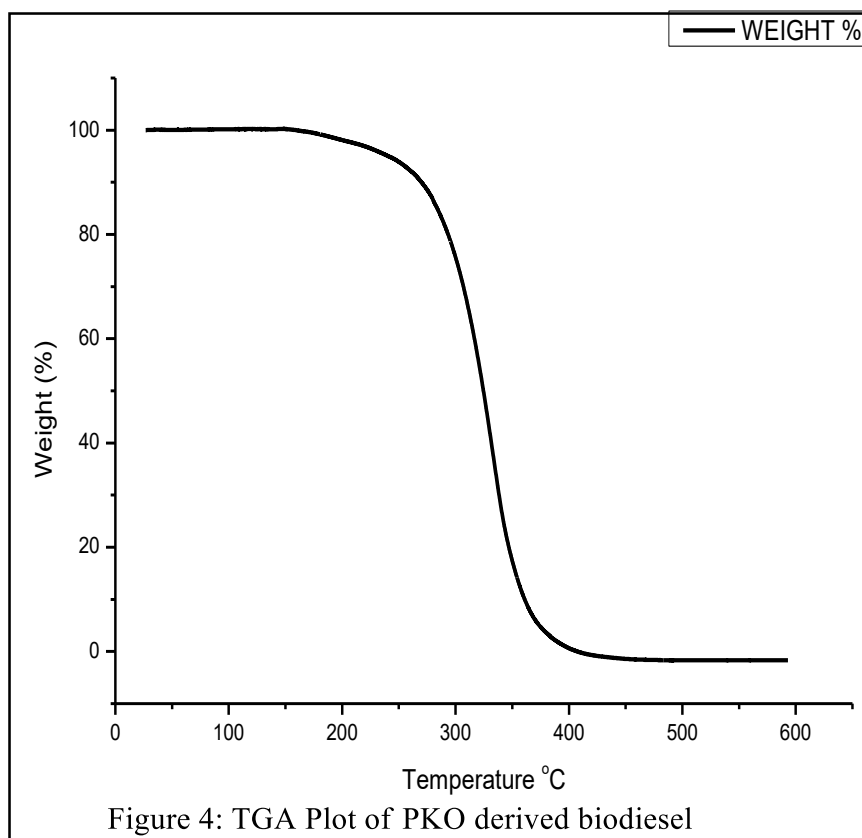
Table 5: Fatty Acids Methyl Esters present in biodiesel produced

Name	Formula	Mol wt	R. Time	Area %	Molecular structure
Methyl Octanoate	$C_9H_{18}O_2$	158	5.537	1.78	
Methyl Decanoate	$C_{11}H_{22}O_2$	186	8.207	2.91	
Methyl Dodecanoate	$C_{13}H_{26}O_2$	214	11.281	47.73	
Methyl 12-methyltri decanoate	$C_{15}H_{30}O_2$	242	14262	17.96	
Palmitic acid, methyl ester	$C_{17}H_{34}O_2$	270	17.029	8.80	

Methyl tras-9-octadecanoate	$C_{19}H_{36}O_2$	296	19.230	10.31	
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	298	19.560	2.16	
Methyl (11R, 12R, 13S)-12,13-epoxy-11-methoxy-9-Octadecenoate	$C_{20}H_{36}O_4$	340	20.775	0.50	

3.7. Thermogravimetric analysis (TGA)

The biodiesel produced is thermally stable up to 240 °C, according to TGA tests (Figure 4). The breakdown temperature range of the biodiesel is 240–350 °C when heating at a rate of 10 °C/min. The thermogravimetric profile of the biodiesel shows that mass loss starts at 240 °C. The GC-MS finding suggests that a substantial amount of saturated fatty acids may be associated with the stability. It is probable that at higher temperatures, unsaturated products will lead to reactions in which they combine to generate cyclic dimers, monomers, and polymers (Zahoor et al., 2014).



3.8. NMR Analysis

Figure 5 is the ^1H and ^{13}C NMR spectra of biodiesel produced. The ^1H -NMR spectrum of the biodiesel sample contains at least 10 signals of significant intensity. These signals are caused by protons from the major components of biodiesel. Peaks of ^1H -NMR spectrum in the sample spectra at δ 5.19 - 5.35 ppm signifying unsaturated fatty acids are those of olefinic hydrogen and also contain those of glycerol proton. The hydrogen attached to methylene glycerol carbons shows a peak at δ 3.99 - 4.29 ppm, the bis-allylic carbons proton at δ 2.63 - 2.77 ppm, the chemical shift value at δ 2.15 - 2.31 due to -carbonyl methylene proton, and at δ 1.47-1.62 ppm resonance is due to -carbonyl methylene proton. The allylic protons ($-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$)

were detected at δ 1.88 - 2.02 ppm, the saturated $(\text{CH}_2)_n$ groups at δ 1.14 - 1.26 ppm, and the methyl protons at δ 0.75 - 0.88 ppm (Zahoor et al., 2014).

The single peak at δ 3.7 ppm and multiplet peaks around δ 2.3 ppm, due to methoxy protons, confirms the synthesis of fatty acid methyl ester. The triplet at δ 0.8 ppm is caused by terminal methyl protons while the peak at δ 1.2 ppm is caused by carbon chain methylene protons and a singlet at δ 1.6 ppm by carbonyl methylene protons. While the chemical shift value at δ 2.19 is due to -carbonyl methylene proton, the signal at δ 5.3 ppm is due to olefinic hydrogen. These peak assignments are consistent with similar characterization (Tariq et al., 2011).

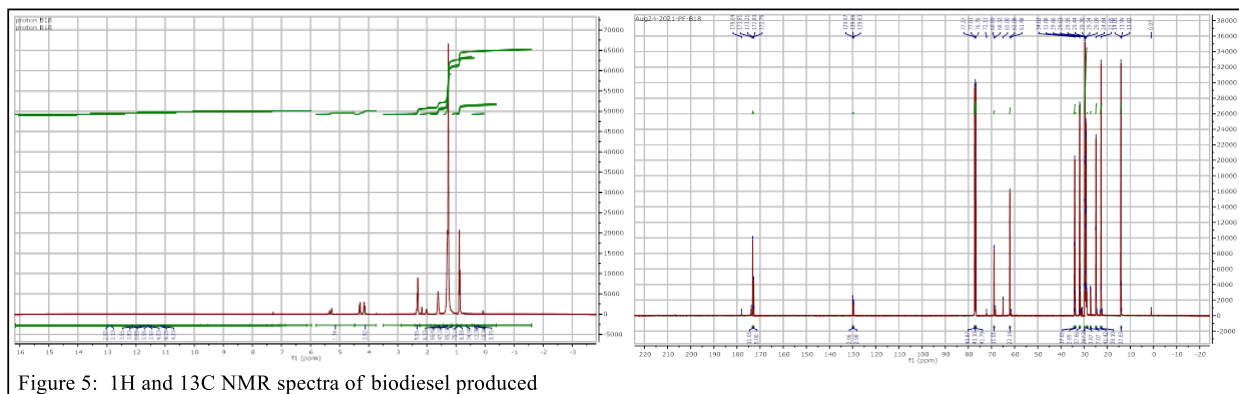


Figure 5: ^1H and ^{13}C NMR spectra of biodiesel produced

The ^{13}C NMR spectrum show the typical ester carbonyl ($-\text{COO}-$) and ($-\text{OCH}_3$) peaks at 172 and 61 ppm, respectively. The presence of peaks around 128 and 129 ppm in the spectra of PKO biodiesel revealed the presence of unsaturated fatty acid. The appearance of a peak between 22-34 ppm is linked to the $-\text{CH}_2-\text{CH}_2$ group of fatty acid methyl ester, and the signal at \sim 14 ppm is due to the formation of the CH_3 group of methyl ester.

3.9. Engine performance Test of Biodiesel produced

The biodiesel produced by the transesterification of cellulose and PKO in a non-solvent medium (B100) powered the single-cylinder water-cool and air-cooled diesel engine, Model ZS11 15 25HP2200, without blending.

4.0. Conclusion

Biodiesel was produced via the transesterification of cellulose and palm kernel oil using NaOH as the catalyst. The optimum equilibrium condition for the production of biodiesel was achieved at a reaction temperature of 140 °C, 7 hrs reaction time, 0.4 g NaOH, 0.5 g cellulose, and 800 rpm with 92.85 % conversion yield. The plot of experimental data fitted better into the pseudo-second-order kinetics model for the production of the biodiesel yielding a straight-line graph from the plot of t/yt versus time t (mins) with a high correlation coefficient, ($R^2=0.990$).

The pseudo-second-order rate constant, k_2 value was found to be 4.9×10^{-4} % /ml. min⁻¹. The thermodynamics studies at 140 and 150 °C show that the enthalpy changes (ΔH) of the reaction were found to be -32.90 kJmol⁻¹k⁻¹, which revealed that it was an exothermic process. The entropy change (ΔS) at the same temperature increases the degree of randomness or disorderliness. The reaction was found to be non-spontaneous at 140 and 150 °C with ΔG (Gibb's free energy) values of 3.9 and 3.2 kJmol⁻¹.

Physico-chemical analysis revealed that the biodiesel produced complies with the ASTM D6751-07b and European standard EN-14214:2003 concerning the physicochemical properties and methyl esters, which guarantees the proper functioning of the engine. FT-IR spectra of the biodiesel show the presence of the peaks at 1446 cm⁻¹, 1237, 960, and 721 which are typical for methyl ester. The disappearance of the absorption peak at 1377 cm⁻¹ which was assigned to O-CH₂ in either mono, di, or triglycerides indicates the complete conversion of glycerol to biodiesel.

GC-MS analysis shows the composition profile of methyl ester in PKO biodiesel with the highest percentage of Methyl Dodecanoate 47.73 %, Methyl 12-methyltridecanoate 17.96 %, Methyl trans-9-octadecenoate 10.31 %, and Palmitic acid methyl ester 8.80 %. The GC-MS analysis shows about 15 different compounds present in biodiesel. The Thermogravimetric profile of the biodiesel shows that the biodiesel is thermally stable up to a temperature of 240°C, above that temperature it started producing a loss in mass. Therefore, the thermal stability of biodiesel was attributed to the concentration of saturated fatty acid present in the biodiesel sample.

¹H NMR analysis also supported the FT-IR and GC-MS analysis with the presence of signals which confirmed the formation of fatty acid methyl ester by the appearance of singlet peak at 3.7 ppm and multiplet peaks around ~2.3 ppm which is attributed to methoxy protons. ¹³C NMR spectrum revealed the characteristic peak of ester carbonyl (-COO-) and (-OCH₃) at 172 ppm and 61 ppm respectively. The presence of unsaturated fatty acid in ¹³C NMR spectra of biodiesel was confirmed by the presence of peaks around 128 and 129 ppm. The peak around 22-34 ppm is related to the -CH₂-CH₂ group of FAME and the signal at ~ 14 ppm arises due to the CH₃ group of methyl ester formed. The physicochemical and instrumental analyses revealed that the biodiesel produced via the transesterification of cellulose and PKO complies with the conventional standard which guarantees the proper functioning of the engine and the PKO biodiesel produced fires diesel engine.

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