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Alkali Homogeneous Catalyzed Methyl Ester Synthesis from *Chrysophyllum albidum* Seed Oil: An Irreversible Consecutive Mechanism Approach

Esonye Chizoo

Abstract

This chapter considers the application of alkaline (NaOH) based catalyzed methanolysis of seed oil from *Chrysophyllum albidum* (African star apple) as a viable route for synthesis of methyl esters (biodiesel). Specific consideration was given to the chemical kinetics and thermodynamics of the irreversible consecutive mechanism of the process on the basis of higher application of methanol/molar ratio (>3:1) as a feasible approach for generating required data for commercial scale-up of the process. The application of power rate law revealed that second order model was the best fitted model on the 328 K, 333 K and 338 K temperature and 0–100 min ranges studied. Rate constants of the glyceride hydrolysis were 0.00710, 0.00870 and 0.00910 wt% min⁻¹ for the triglyceride (TG), 0.02390, 0.03040 and 0.03210 wt% min⁻¹ for the diglycerides (DG) and 0.01600, 0.03710 and 0.04090 wt% min⁻¹ for the monoglycerides (MG) at the above respective temperatures. The activation energies were 2.707, 7.30 and 23.33 kcal/mol respectively. TG hydrolysis to DG was the rate determining step. Rates of reactions were found to increase with increase temperature and mixing rate (200, 400 and 800 rpm). No optimal mixing rate was detected and the highest mixing rate of 800 rpm was the most favorable in the mixing range under investigation. The possible reason for the absence of lag period is formation of methyl esters, which acted as a solvent for the reactants, and consequently, made the reaction mixture a homogeneous single phase. The quality of the produced methyl esters were found to compare with international standards. All the results lead to more diverse and novel applications of the seed oil in biodiesel productions.

Keywords: alkali, methyl ester, synthesis, irreversible consecutive mechanism, *Chrysophyllum albidum*

1. Introduction

Alkali based catalysis in transesterification of seed oils have been reported by several researchers as been preferred to other catalysts due to their ability to promote faster methanolysis process [1]. They are equally more readily and widely

available and as well as cheaper. Hence, the application of alkali based catalysts helps to promote economical biodiesel production process by achieving cheaper cost of raw materials, shorter reaction and production duration and safer handling. It is therefore easier to achieve standard operating procedures (SOP) and good manufacturing processes (GMP) with less hazards while applying homogeneous alkali-catalyzed transesterification process (**Figures 1** and 2). Consequently, it will be easier to achieve speedy translation of pilot researches unto industrial scale by using alkali homogeneous catalysts. The application of such alkali-catalysts like NaOH, KOH has been challenged by their promotion of saponification reaction process, which results in low biodiesel yield, expensive separation requirement, waste generation and high energy consumption [4]. The above challenge can be overcome by sourcing vegetable oil feedstocks with low free fatty acid (FFA) content. Obviously, the application of acid catalysts such as H_2SO_4 , HCl , BF_3 and H_3PO_4 and organic sulfuric acids in biodiesel synthesis from low FFA seed oil feedstocks has a great economic loss effect to the transesterification process since it

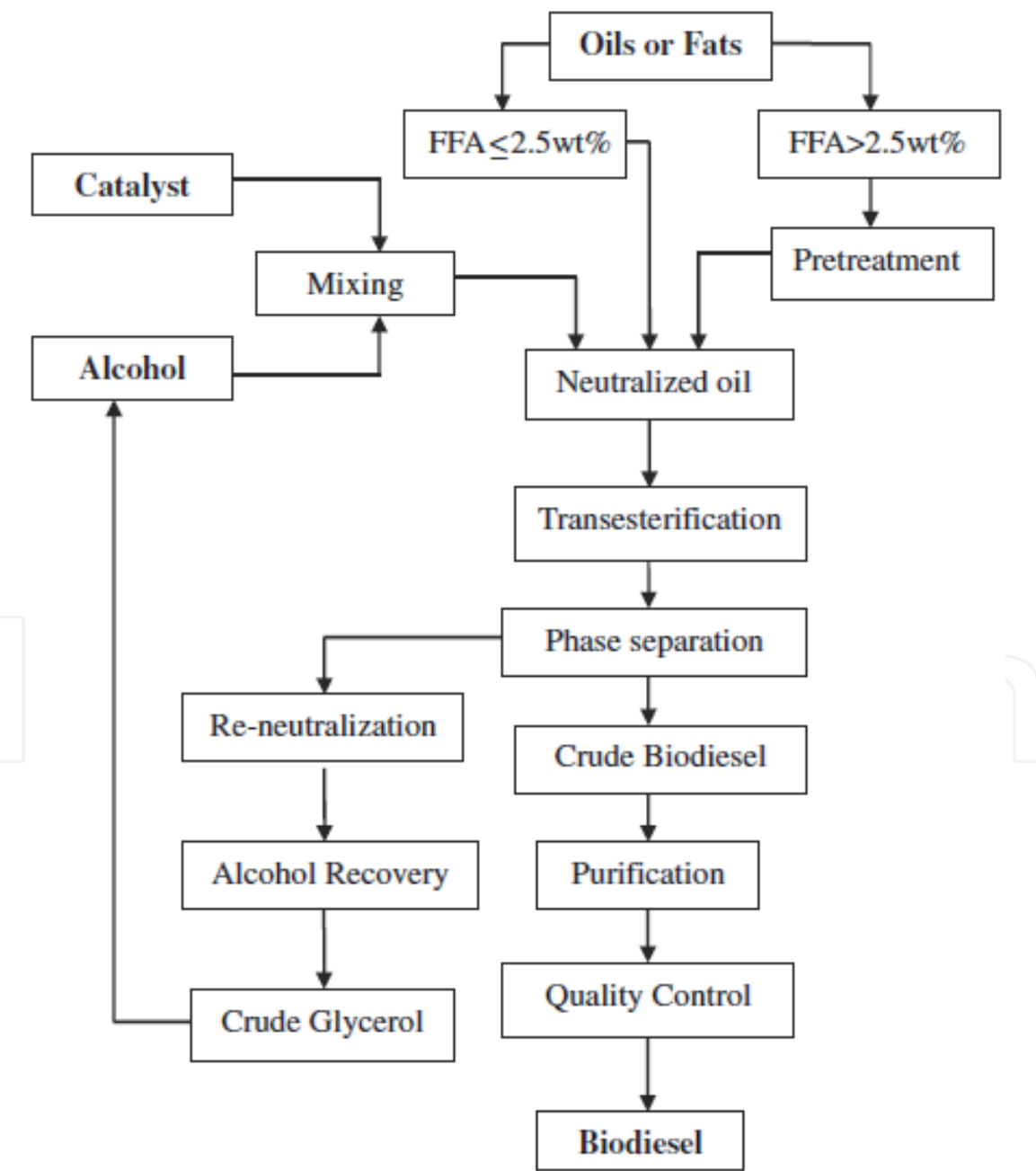


Figure 1.
Simplified process flow chart of alkali-catalyzed biodiesel production [2].

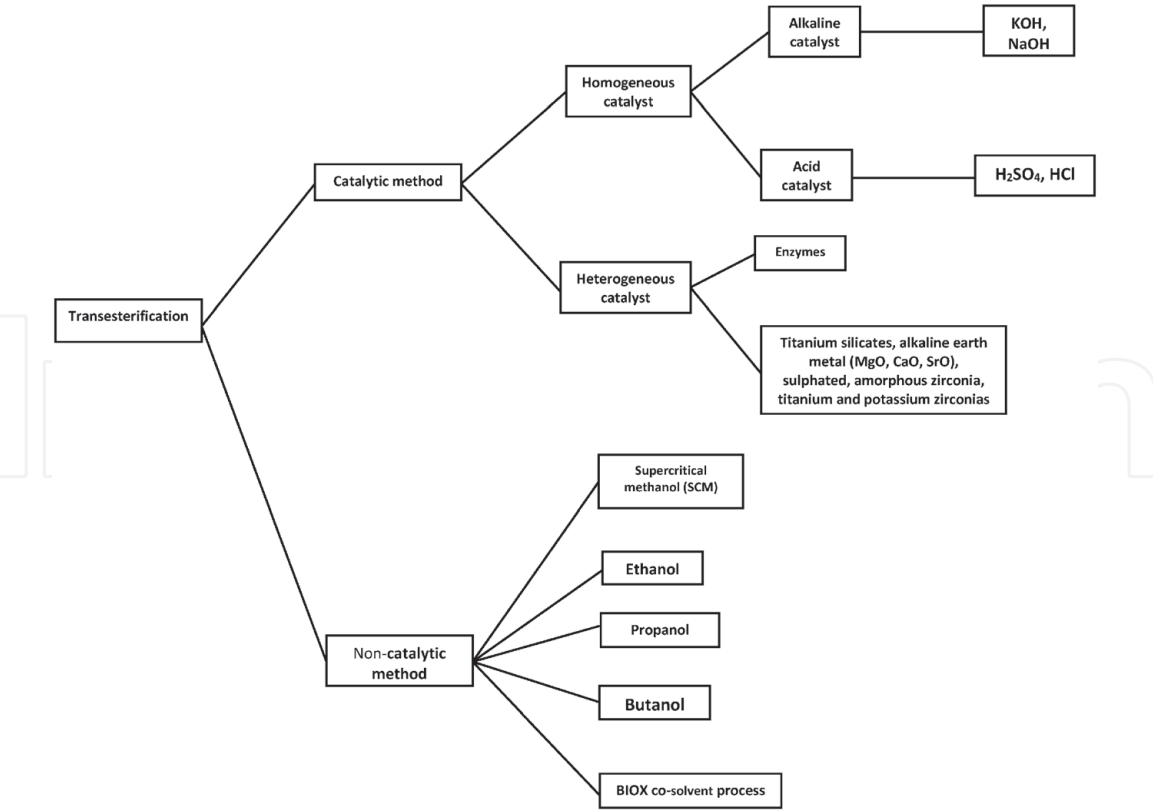


Figure 2.
Classification of transesterification processes [3].

has been reported that acid catalyzed process is about 4000 times slower than base-catalyzed process [1].

Among all the alkali catalysts, sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOCH₃) and potassium methoxide (KOCH₃) are most widely used and it has been reported that the acid numbers for ultimate product applying sodium hydroxide are far higher than those involving sodium methoxide [5]. Sodium hydroxide is commonly used for commercial biodiesel production owing to its low cost and high reaction rate. The effect of sodium hydroxide concentration as a catalyst on reaction duration at 50 and 60 °C and methanol/oil molar ratio of 6:1 on safflower oil methanolysis showed that in both cases, reaction time decreased proportional with increase in catalyst concentration from 1% to 2% while above 2% saponification reaction was more favored [6]. Also, it has been reported that triglyceride conversion increased when the catalyst (NaOH) concentration was raised from 1% to 3% during canola oil transesterification experiment [7] while studies on the effect of catalyst type and concentration on the rapeseed oil ester yields has shown that the sodium hydroxide gave higher biodiesel yield than sodium methoxide [8]. It implies that 1% KOH was the optimal catalyst concentration when the FFA is between 0.25% and 1.5% in accordance with the previous reports [9]. The same trends were observed for varying the concentration of NaOH from 0% to 1.5%, which was also recommended in [10]. However, contrary reports have been presented on methanolysis of sunflower while ascribing yield loss to the fact that hydroxide catalysts could promote triglyceride saponification and more biodiesel dissolution in glycerol [11]. Moreover, the reactions using NaOH catalyst were fastest of all. Though alkaline catalysts have many advantages as mentioned earlier, their application is highly challenged by the presence of free fatty acid and moisture in vegetable oil and animal fat feedstocks. The application such feedstocks in transesterification process promotes soap formation due to presence of high free

fatty acid and this results in partial consumption of the catalyst, thereby reducing the methyl ester yield. Basically, in alkali conditions, the acceptable total FFA and water contents are 0.5% and 0.1–0.3%, respectively [12]. Acid catalysts such as, phosphoric, hydrochloric, organic sulphonic and sulfuric acids are commonly preferred for biodiesel production when the FFA is high [12].

The major challenge in biodiesel application as a renewable and alternative fuel to petrodiesel is the lack of sustainability of its generation [13, 14]. The successful scale-up of laboratory results in transesterification requires information obtained through kinetics studies. Hence, chemical kinetics data are required to arrest the above problem. Chemical kinetics deals with the dynamics of chemical reactions: the rate (velocity) of the process and the way by which the reaction takes place. The rate law is the keystone for the chemical reaction mechanism which helps in describing the relationship between the reaction rate and the concentration of the chemical reactants [15]. The mechanism of the transesterification reaction involving an alkaline homogeneous catalyst has been reported to follow series of sequential steps (Eqs. (1)–(5)) [15]. Considering the chemical reaction mechanism, the glycerides are converted to glycerol and yield one ester molecule in each step. Since this reaction is reversible (Eq. (6)–(8)) with Eq. (9) as the summary, excess amount of alcohol is often used to promote the forward reaction and decrease the tendency of soap formation. By implication this approach drives the equilibrium to the right. However, the choice of the catalyst and alcohol type determines the type of initial species and the nature of fatty acid alkyl ester (FAAE) to be produced. Also, a detailed review of various kinetic modeling studies of transesterification has proven that the alcohol/oil molar ratio is always greater than the usual stoichiometric value of 3; hence the irreversible in practice (Eqs. (10)–(12)).

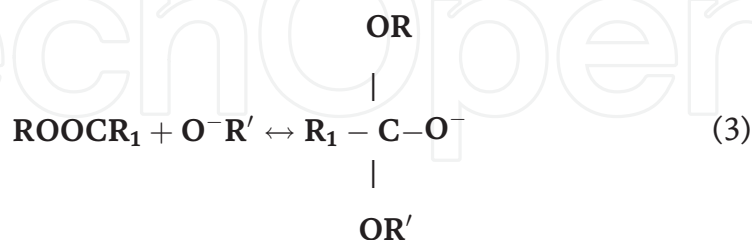
Pre-Step:



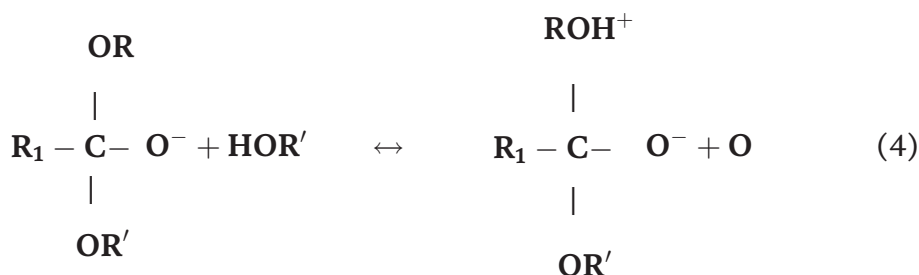
Or



Step 1.



Step 2.

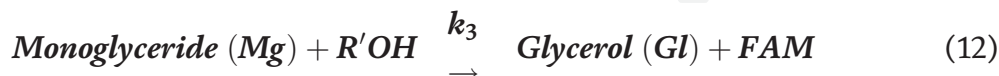
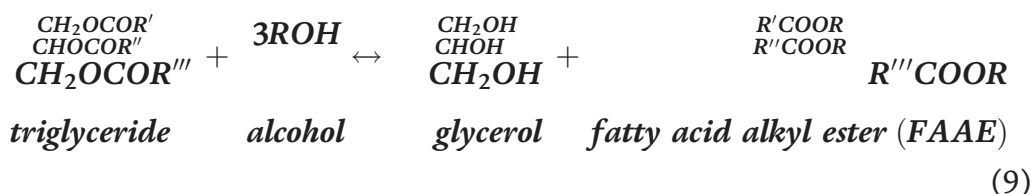


Step 3.



Where R-OH – diglycerides, R₁ – long alkyl group and R' – short alkyl group.

For the mechanism of the transesterification reaction involving an alkaline homogeneous catalyst, the initial step is the attack on the carbonyl carbon atom of the triglycerides molecule by the methoxide ion to produce a tetrahedral intermediate. In the second stage, the tetrahedral intermediate combines with an alcohol (methanol) to form the anion of the alcohol (methoxide ion). In the final stage, rearrangement of the tetrahedral intermediate gives rise to the formation of fatty acid ester and a diglyceride.



Methanol is most commonly used due to its more readily available and cheap while ethanol application results in easy-formation of emulsions which gives rise to end product separation problems. This challenge is more pronounced while using feedstocks with high free fatty acid content. Therefore, the use of homogeneous alkali catalysts like NaOH and KOH at commercial level is highly encouraged because of their high catalytic activity compared to acid catalyst which are more corrosive [1].

Therefore, sustainable production of biodiesel is more feasible with alkali-catalyzed transesterification process using perennial feedstock with lower FFA and edible from agro-waste. The physico-chemical properties of the African star apple

fruit gave an indication of the usefulness of the fruit in brewing industry [16]. The juice of the fruit pulp has potentials as an ingredient of soft drink and can be fermented for wine and other alcohol production with unsaturated fatty acids being



Figure 3. African star apple fruit biomass. (a) Fruit, (b) fruit cut section, (c) ground fruit pulp, (d) dried pulp, (e) the seed with coat, (f) the seed coat, (g) the seed.

the main components of the oil [17]. The fruit contribute to improve health, nutrition, food security and income of the local communities [18]. African star apples are among the under-utilized fruits in Nigeria [16] and seed of this plant have been rarely exploited for production of oil for commercial purposes despite the fact that it contains about 13% of edible oil [19] while most often the seed are thrown away after the consumption of its juicy pulp [20, 21]. Only few attempts on the extraction of oil from *C. albidum* in Nigeria are documented. Ochigbo and Paiko, [20] worked on effect of solvent blending on the characteristics of oil extracted, Sam *et al.*, [22] reported the extraction and classification of lipid from the seeds of *Chrysophyllum albidum*. The study was limited to phytochemical screening and fatty acid profile composition. African star apples are among the under-utilized fruits in Nigeria [16] and seed of this plant have been rarely exploited for production of oil for commercial purposes despite the fact that it contains about 25% of oil [18, 23] while most often the seed are thrown away after the consumption of its juicy pulp [21]. Only few attempts on the extraction of oil from *C. albidum* in Nigeria are documented. The previous results show that star apple fruit can serve for multi-biofuels production for biodiesel and bio-ethanol using the oil from the seed and sugar from the pulp. African star apple fruit biomass is shown in **Figure 3**.

2. Materials and methods

2.1 Materials

The materials used in this research include sodium hydroxide (99%, Sigma-aldrich), potassium hydroxide (loba chemie, 85%), methanol (Merck, Germany, 99.5% purity), carbon tetrachloride (chloroform), Wij's solution (iodine monochloride), potassium iodide solution and phenolphthalein (Merck Germany). The fruit seed biomass was bought from Ochanja market in Onitsha city in Anambra state of Nigeria and the seed oil was extracted by solvent extraction method using hexane.

2.2 Biomass collection and preparation

2.2.1 Sourcing of seeds/seed meal preparation

The ripped fruits of *Chrysophyllum albidum* harvested from Abakaliki city of Nigeria were washed to remove dirt and sands. The pulp was peeled out to release the kernel. The kernels were placed on solar drier for seven (7) days. The kernels were cracked manually to release the milky-colored soft seeds. The seeds were sun dried for another seven(7) days to reduce the moisture content in the seed matrix and to promote effective grinding, Electric milling machine was used to grind the seeds into smaller particles before being sieved using a electric powered mechanical sieve to obtain a finer (300 μm) size of the meal. The residual moisture in the sieved ground meal was removed by further sun drying for a period of five (5) days.

2.3 Oil extraction and degumming

The oil extraction was conducted in accordance with the method previously reported in [24]. The oil from the seed meal from was extracted by n-hexane (95% purity). The solvent extraction process was carried out using 200 ml soxhlet apparatus. About 20 g of the ground meal of a particular particle size (300 μm) was subjected to the solvent extraction for particular time (1 h) duration and temperature of 69 °C. The oil solution was filtered and subjected to distillation using rotary evaporator. The

extracted oil was further subjected to degumming by mixing the raw oil with 3 wt% of warm water and the mixture was stirred using magnetic stirrer for 30 minutes at a temperature of 60 °C to ensure proper separation of the emulsifiers from the oil.

2.4 Alkali-homogeneous methyl ester synthesis

The process follows the approach previously applied in [24] with some modifications. The temperature of the refined *Chrysophyllum albidum* seed oil (100 ml) was first raised to 80 °C for 30 min followed by the addition of sodium methoxide. The application of sodium methoxide is preferred over direct mixing of sodium hydroxide since it more effective than of due to the fact that direct mixing of NaOH with methanol produces water through hydrolysis which negatively affects the methyl ester yield. Then the *Chrysophyllum albidum* seed oil was added to the sodium methoxide at methanol/oil molar ratio of 6:1 was kept at 65 °C for 65 min. This process was conducted in a 500 ml reflux condenser fitted with heater and stirrer under atmospheric pressure and at an agitation speed of 140 rpm. The biodiesel mixed with glycerin was separated, biodiesel washing and drying was done in accordance with previous methods in the literature [25]. The fatty acid methyl ester yield in weight percent was calculated by using Eq. (13).

$$FAME\ yield(wt\%) = \frac{W_{FAME}}{W_{seed\ oil}} \times 100 \quad (13)$$

Where W_{FAME} =weight of fatty acid methyl ester after methanolysis.

$W_{seedoil}$ =weight of seedoil used for the base methanolysis

2.5 Physico-chemical characterization of the seed oil and the methyl ester

This stage of the experiment has been conducted and reported previously [24]. The quality of the *Chrysophyllum albidum* was determined in accordance with Association of Official Analytical Chemist method [24]. Other properties such as moisture, viscosity and density content were ascertained by using oven method, Oswald viscometer apparatus and density bottle respectively. The ash content and the refractive index were also measured with Veisfar muffle furnace and Abbe refractometer respectively [26]: The necessary fuel related physico-chemical properties of the biodiesel produced were determined using ASTM and AOAC standard methods [24]. ASTM D standards were used to determine the kinematic viscosity, density, pour, cloud, flash points, acid value and calorific values while AOAC methods were used to determine specific gravity, iodine value and refractive index. ASTM D-445 method, the density was determined by ASTM D-1298 method. The pour, flash and cloud points determinations were done using ASTM D-97, ASTM D-93, ASTM D-2500b methods respectively while acid value was measured by ASTM D-664 method. The refractive index was determined using AOAC 921.08. The specific gravity was ascertained using AOAC 920.212 and iodine value using AOAC 920:159 while moisture content was obtained using air-oven method. The cetane index (CI), cetane number (CN) and higher heating values were ascertained using standard correlations previously applied in [25].

2.6 Chemical analysis of seed oil and its methyl ester

2.6.1 Determination of the oil and biodiesel functional groups using FTIR

Fourier Transform Infra red (FT-IR) analysis was performed to ascertain the functional groups present in *Chrysophyllum albidum* seed oil using IR Affinity-1

Shimadzu, model No: 3116465. The FT-IR has an SN class ratio of 30,000:1, 1 minute accumulator in the neighborhood of $2,100\text{ cm}^{-1}$ peak to peak with a maximum resolution of 0.5 cm^{-1} in the region of 400 cm^{-1} – 4000 cm^{-1} . Microlab software is attached as supporting software. *Chrysophyllum albidum* seed oil sample was introduction through sample cell while cleaning of the cell was done with trisolvent mixture of acetone-toluene-methanol prior to background collection. About 0.5 ml of the sample (oil) was taken using the sample cell and introduced into the cell unit of the system. The scan results were obtained on the incorporated computer system as spectra. The peaks of the spectra obtained were identified and interpreted to identify the functional groups in the molecules of the *Chrysophyllum albidum* seed oil in accordance with [27].

2.6.2 Gas chromatographic-mass spectroscopic (GC–MS) analysis

The fatty acid composition of the biodiesel samples were ascertained using AOAC official method Ce2–66 using GCMS-QP2010 plus, Shimadzu. GC–MS was preferred in this study because it is faster than the GC, provides molecular weight information and requires an aliquot sample. The GC–MS fragments the analyte to be identified on the basis of its mass and the column was calibrated by introducing methyl ester standards while dilution of the sample in a little quantity of ethyl acetate was done to achieve excellent separations. Hydrogen served as the carrier gas and its flowrate was controlled at 41.27 ml/min while the flowrate of the column was set at 1.82 ml/min. The oven temperature was fixed at $80\text{ }^{\circ}\text{C}$ before increasing up at $6\text{ }^{\circ}\text{C}/\text{min}$ and then up till $340\text{ }^{\circ}\text{C}$. The Peaks identification was carried out by comparing their retention time and mass spectra with Mass Spectra Library [28].

2.7 Kinetic study

The rate of reaction and its mechanism as regards the transesterification process of the seed oil were investigated by considering irreversible conditions.

2.7.1 Assumptions

It is reported that transesterification reaction mechanism includes three consecutive irreversible reactions that yield fatty acid diglycerides and monoglycerides as intermediates which represents the stages of the reaction [29]. Moreover, simplified kinetic models suffice for practical purposes, experimental data were processed under the following assumptions [30, 31]:

1. The methanolysis reaction is constituted by three consecutive stages.
2. The three (3) stages above are assumed irreversible because higher methanol/oil molar ratio (greater than 3:1) was applied.
3. The saponification reaction was neglected since the free fatty acid content of *Chrysophyllum albidum* was negligible (about 1.4%).

2.7.2 Experimental procedure

The design of experiments to determine the reaction rate constants involved 6:1 methanol to oil molar ratio in all the experiments. Results obtained at different temperatures of 55, 60 and $65\text{ }^{\circ}\text{C}$ were used to study the effect of temperature on the reaction process. All reactions were carried out at atmospheric pressure with 0.20 wt% sodium hydroxide as catalyst, methanol/oil molar ratio of 6:1 at a stirring

speed of 140 rpm. As reaction progresses, 2 ml aliquot sample was withdrawn with a disposable pipette through an opening on the top of the reactor. The samples were collected in 10 ml test tubes and kept in an ice bath at 5 °C prior to use to quench the reaction. Samples were withdrawn at specified time intervals (0, 0.3, 0.5, 2, 4, 6, 10, 20, 40, 60, 80 and 100 minutes). The composition of sample was determined by gas chromatography (GC) on Perkin Elmer Claurus 600 model FID to ascertain the amount of triglycerides, diglycerides, monoglycerides, total methyl esters and glycerol content in the biodiesel production batch reaction system.. The diglycerides and monoglycerides contents were minimal (< 3%), while the amounts of triglycerides were above 94%.

2.7.3 Second-order irreversible model

Second-order irreversible model for triglyceride hydrolysis has been proposed previously [29]. Therefore, a model developed based on *Chrysophyllum albidum* seed oil hydrolysis based on the second-order reaction rate for Tg would appear as in Eq. (13) [29, 32].

$$\frac{-d[\text{Tg}]}{dt} = k[\text{Tg}]^2 \quad (14)$$

Integrating and rearranging of Eq. (13) by integration yields Eq. (14).

$$k_{\text{Tg}}t = \frac{1}{[\text{Tg}]} - \frac{1}{[\text{Tg}_0]} \quad (15)$$

Where k is the overall rate constant, t is the process duration or reaction time; Tg₀ is the initial concentration of the *Chrysophyllum albidum* seed oil triglyceride.

The validity of the model is tested on the bases that a plot of reaction time (t) against $\frac{1}{[\text{Tg}]}$ will give a straight line plot. Similar trend was expected in cases of the hydrolysis of monoglycerides and diglycerides as the intermediates to get Eqs. (15) and (16).

$$k_{\text{Dg}}t = \frac{1}{[\text{Dg}]} - \frac{1}{[\text{Dg}_0]} \quad (16)$$

$$k_{\text{Mg}}t = \frac{1}{[\text{Mg}]} - \frac{1}{[\text{Mg}_0]} \quad (17)$$

2.7.4 First-order irreversible model

Assumptions:

1. The catalyst was used in sufficient amount with respect to oil to shift the reaction equilibrium towards the formation of fatty acid methyl esters.
2. The reverse reaction could be ignored and change in concentration of the catalyst during the course of reaction can be assumed to be negligible [33].
3. The concentrations of both Dg and Mg were found to be very low (Dg < 2.9 wt %, Mg < 1.45 wt %) compared to those of Tg (Tg > 94 wt%) in the crude *Chrysophyllum albidum* seed oil therefore, the reaction could be assumed to be a single-step transesterification [34].

Consequently, the rate equation of the NaOH alkali-based methanolysis reaction for forward reaction can be expressed by Eq. (17) [35].

$$-r_{Tg} = \frac{-d[Tg]}{dt} = k' \cdot [Tg] \cdot [ROH]^3 \quad (18)$$

Where $[Tg]$ is the triglycerides concentration, $[ROH]$ is the concentration of methanol and k' is the equilibrium rate constant. This overall reaction follows a second-order reaction rate law. However, due to the high molar ratio of methanol to oil, the change in methanol concentration can be considered as constant during reaction. This means that by taking methanol in excess, its concentration does not change the reaction order and it behaves as a first-order chemical reaction. Therefore, the *Chrysophyllum albidum* seed oil transesterification reaction would obey pseudo-first order kinetics [22] and finally, the rate expression can be written as in Eq. (18).

$$-r_{Tg} = \frac{-d[Tg]}{dt} = k \cdot [Tg] \quad (19)$$

Where k is modified rate constant and $k = k'[ROH]^3$. Assuming that the initial triglyceride concentration was $[Tg_0]$ at time $t = 0$, and at time t it falls down $[Tg_t]$. Integration of Eq. (11) from $t = 0$, $[Tg] = [Tg_0]$ to $t = t$, $[Tg] = [Tg_t]$ yields the Eq. (19):

$$-\ln [Tg] + \ln [Tg_0] = kt \quad (20)$$

Relying on the above conditions, the rate data from the seed oil of *Chrysophyllum albidum* seed oil transesterification reaction would fit to Eq. (11). In order test fitness, $-\ln[Tg]$ was plotted against reaction time using the weight percentage of Tg as concentration since $[Tg]_0/[Tg]$ is a concentration ratio and its value is not depended on units, provided that the same units are used for both $[Tg]_0$ and $[Tg]$. Consequently, Least-square approximation was applied in fitting a straight line to the experimental data, and in each case the coefficient of determination (R^2) was determined.

2.8 Thermodynamic properties determination

Activation energies of the reaction taking place were estimated using the calculated rate constants and temperatures at which they were observed in Arrhenius equation (Eq. (20)).

$$\log_{10} k = \frac{-E_a/2.303R}{T} + A \quad (21)$$

Where E_a = Activation energy, R = Gas constant and A = Arrhenius constant or frequency factor

3. Results and discussion

3.1 FTIR result of ASASO and ASASOME in comparison

Table 1 contains the functional groups of ASASO and ASASOME. It is observed that the 640.52 cm^{-1} for ASASO and 640.20 cm^{-1} for ASASOME vibrations respectively are bending and out of plane and indicate the presence of $-(CH_2)$

functional groups. The 764.04 cm⁻¹ for ASASO is ascribed to the rocking vibrations of alkenes and methylene groups (=C-H and-(CH₂)n) while 763.56 cm⁻¹ for ASASOME represents same functional groups but with bending of alkenes and overlapping of rocking vibrations of methylene. The peaks between 949.32–1134.60 cm⁻¹ represents the C-O stretching vibrations for ASASO while 979.44–1133.64 cm⁻¹ represents bending vibrations of the same carbonyl groups for ASASOME. The stretching vibrations of the C-O-C groups could be ascribed to the wave numbers of 1261.98 cm⁻¹ (ASASO) and 1257.00 (ASASOME) while there is the appearance of bending vibrations of -CH₂ at 1362.34 cm⁻¹ for ASASO and 1318.68 cm⁻¹ for ASASOME. Peak 1474.28 cm⁻¹ for ASASO contains -CH₂ group with bending vibrations while 1442.04 cm⁻¹ contains -CH₂ bending and rocking vibrations. The methylene group (C=C) appeared at peaks of 1655.70 cm⁻¹ for ASASO and 1657.92 cm⁻¹ for ASASOME with stretching and bending vibrations respectively. The stretching vibrations of C-O ester group was observed at 1740.62–1875.72 cm⁻¹ for ASASO and 1835.25 cm⁻¹ for ASASOME while at high energy bands of 3384.96–3539.38 cm⁻¹ for ASASO and 3384.96–3539.16 cm⁻¹ for ASASOME appeared the hydrogen group (O-H).

The FT-IR spectra have been used to identify the functional groups and the peaks corresponding to various stretching and bending vibrations in the vegetable oil and their biodiesel. It is observed that the esters have two characteristically strong absorption bands arising from C=O around 1721.32–1875.72 cm⁻¹ and that of C-O at 1138.64–1196.40 cm⁻¹ [25]. The C=O group indicates the presence of carbonyl functional groups that show the conversion of triglycerides in the seed oils to methyl esters [36]. The stretching and bending vibrations of CH₃, CH₂ and CH group in the biodiesel samples lie in the reported ranges: 1318.68–1566.92 similar to results observed by other researchers [36]. The single bond functional group O-H was observed to be prevalent in all the samples with both stretch and hydrogen bonding. The change in wave number of the functional groups between the seed oils and their methyl esters as they appeared on their spectra indicates that the fatty acids reacted to form ester. These results reflect the conversion of the triglycerides to methyl esters. The presence of C-H indicates prevalence of properties such as pour and cloud points that affect the performance of biodiesel during cold weather

ASASO			ASASOME		
Wave number (cm ⁻¹)	Type of vibration	Functional group	Wave number (cm ⁻¹)	Type of vibration	Functional group
640.52	Bending	– (CH ₂)	640.20	Bending	– (CH ₂)
764.04	Rocking	C-H	763.56	Bending	=C-H
949.32	Stretching	C-O	979.44	Bending	C-O
1134.60	Stretching	C- O	1133.64	Bending	C-O
1261.98	Stretching	C-O-C	1257.00	Stretching	C-O-C
1362.34	Bending	CH ₂	1318.68	Bending	CH ₂
1474.28	Bending	CH ₂	1442.04	Bending	CH ₂
1655.70	Bending	=CH,C=C	1657.92	Bending	=CH,C=C
1740.62	Stretching	C=O			
1875.72	Stretching	C=O	1835.25	Stretching	C=O
3384.96–3539.38	Stretching	O-H	3384.96–3539.16	Stretching	O-H

Table 1.
FT-IR main characteristic band positions for ASASO and its biodiesel.

engine operation. The presence of carbon to carbon (C=C) can cause the biodiesel samples to remain in liquid state but may be liable to possible oxidation during storage. However, all the observed absorptions corresponding to C=O stretches show that the biodiesel products from the three seed oils contain ester functional groups described in any biodiesel type.

3.2 The biodiesel fatty acid composition

The fatty acid composition of African star apple seed oil methyl esters were analyzed by gas chromatography coupled with mass spectrometer. The identification of peaks was done by comparison of their retention time and mass spectra with mass spectra library (NIST05s LIB.) [34]. The profile is contained in **Table 2**. Twenty one (21) peaks were recorded which showed different fatty acid methyl esters present. Other researchers have identified such number of peaks while using GC–MS to analyze methyl esters. Sharmila and Jeyanthi [37] identified 31 peaks representing different organic compounds including fatty acids in *Cladophora vagabunda* methyl esters. Among the saturated fatty acids methyl esters in the sample are caprylic, capric, palmitic, stearic, behenic, lauric, myristic, lignoceric, eicosenic and arachidic, while the monounsaturated fatty acids identified were erucic, oleic, and palmitoleic. The polyunsaturated fatty acids present are linoleic, α-linolenic and γ-linolenic. ASASOME contains 27.71% saturated fatty acids, 53.30%

Peak	Retention time	Fatty acid	Amount(%)
1.	3.774	Eicosenic	2.14
2.	3.936	Erucic	0.09
3.	4.208	Oleic	50.50
4.	5.198	Palmitic	20.66
5.	5.576	Linoleic	13.97
6.	6.850	Stearic	1.01
7.	8.186	α-linolenic	0.21
8.	10.087	Caprylic	0.95
9.	12.182	Behenic	0.59
10.	13.966	Myristic	1.23
11.	15.511	Lignoceric	1.65
12.	16.578	Palmitoleic	0.09
13.	18.125	Butyric	1.44
14.	18.195	Arachidic	1.01
15.	19.273	Oxalic	0.22
16.	20.363	Phthalic	2.00
17.	21.601	Lauric	0.70
18.	23.149	Capric	0.31
19.	24.526	Elaidic	0.40
20.	25.602	γ-linolenic	0.43
21.	26.493	Gadoleic	0.40

Table 2.
Fatty acid profile of ASASOME using GC–MS.

monounsaturated fatty, acids and 18.99% polyunsaturated fatty acids (**Table 2**). Its oleic acid content (50.5%) is the highest fatty acid content, followed by palmitic acid (20.66%) and linoleic acid (13.97%). The oleic acid component of ASASOME (50.5%) compares with those of sesame seed oil (52.8%) and peanut kernel oil (48.3%) reported previously as good feedstocks for biodiesel production [37, 38].

3.3 Physico-chemical characterization result

The fuel quality of the biodiesel and its parent oil obtained from this study are presented in **Table 3**. The properties of the biodiesel compared well with the required standards in accordance with American standards (ASTMD 6751), Euro-
pean specification (EN 14214) and other feedstocks recently studied and

Parameters	African star apple seed oil	African star apple seed oil Biodiesel	Standards		
			ASTM D 9751	ASTMD 6751	EN 14214
Oil/biodiesel yield (%)	27.04	86.49	—	—	—
Density (kg/m ³)	834.10	819.5	850	880	860– 900
Moisture content (%)	0.79	0.026	—	—	—
Refractive index	1.4515	1.4438	—	—	—
Acid value (mgKOH/g)	201.66	0.32	0.062	0.50	0.50
Free fatty acid (%)	1.44	0.16	0.31	0.25	0.25
Iodine value (mgKOH/g)	37.57	32.86	42–46	—	120max.
Saponification value (mgKOH/g)	201.66	189.03	—	—	—
Ash content (%)	1.22	0.01	0.01	0.02	0.02
Kinematic viscosity (mm ² /s)	5.50	2.19	2.6	1–9–6.0	3.5–5.0
Smoke point (°C)	35	25	—	—	—
Fire point (°C)	—	36	—	—	—
Flash point (°C)	135	126	60–80	100–170	120
Cloud point (°C)	–3	–3	–20	–3 to 12	—
Pour point (°C)	—	–8	–35	–15 to 16	—
Calorific value (KJ/Kg)	—	32,828.50	42–46	—	35
Conductivity (Us/CM)	—	0.52	—	—	—
Cetane index	—	67.16	—	—	—
Cetane number	—	64.57.60	40–55	47 min.	51 min.
Higher heating value(HHV) ^a (MJ/kg)	—	34.52	—	—	—
Higher heating value(HHV) ^b (MJ/kg)	—	40.46	—	—	—
Higher heating value(HHV) ^c (MJ/kg)	—	63.75	—	—	—
<i>a</i> -based on flash point, <i>b</i> -based on viscosity, <i>c</i> -based on density, min-minimum, max-maximum					

Table 3.
Physico-chemical properties of the African star apple seed oil and its FAME.

recommended for fatty acid methyl ester synthesis [39]. The kinematic viscosity of the biodiesel compared well with standards and other similar feedstocks. This is very important for the efficiency of its engine applications. Many diesel engines use injection pumps that do not accept high viscous liquid fuels that block the fuel filtration units. Therefore, the value of the viscosity of the biodiesel produced with *Chrysophyllum albidum* seed oil would serve effectively and efficiently in this purpose. Also, the African star apple seed oil biodiesel had a good cetane number and compared well with standard specifications. The low value of the biodiesel iodine value indicates less unsaturation. It equally shows that the biodiesel will be comparatively less prone to oxidation instability and glyceride polymerization that normally leads to formation of deposits. The flash point, cloud point and pour point imply that the biodiesel will be less challenging in distribution considering its flammability and hazardous status. Also, it will be less suitable for winter season operations considering its cold flow properties. The parent oil characteristics of African star apple showed improved fuel qualities upon transesterification [1].

Figure 4a–c show the progress of the transesterification of *Chrysophyllum albidum* seed oil at reaction temperatures of 50, 60 and 65 °C using 0.1 wt % of NaOH and methanol/oil ratio of 6:1 at agitation rate of 140 rpm. The early stage of the reaction produced rapidly the biodiesel rapidly. It is observed that the glycerol concentration increased with increase in biodiesel yield but was not in relative proportion. Additionally, the triglycerides concentration reduced as the reaction progresses. The triglycerides concentration after 60 minutes was less than 8 wt% for all the temperatures. The highest concentration of diglycerides and monoglycerides were observed in the first 2 minutes after which they started reducing until after 75 minutes when they started being almost at equilibrium. The value of triglycerides was greater than diglycerides and diglycerides were greater than monoglycerides values for all the temperature at respective times.

The higher the temperature, the higher the rate of triglyceride conversion at respective times (**Figure 4**). The effect of temperature within the range (55–65 °C) studied was insignificant. This could be due to the smaller range of difference between them. However, the effect of the range of temperature on the rate of transesterification studied here shows no initial lag period as previously reported on soybean methanolysis [31]. The possible reason for the absence of lag period is formation of methyl esters, which acted as a solvent for the reactants, and consequently, made the reaction mixture a homogeneous single phase.

The effect of mixing rate or stirring speed on the conversion of *Chrysophyllum albidum* seed oil is shown in **Figure 5**. Increase in stirring speed (200, 400 and 800 rpm) favored conversion of the triglycerides. The intermolecular forces are broken down mixing, making the oil/methanol solution homogeneous without phase formation. A constant high temperature of 60 °C was applied. It was observed that after 40 minutes reaction duration, increasing the stirring speed was irrelevant since the methyl ester produced is soluble in oil and methanol and it could have acted as a co-solvent. Therefore, the system becomes homogenous and only chemical reaction controls the kinetics at this state. Large differences were not observed in triglycerides conversion to methyl ester between 200 rpm and 400 rpm. Also, 800 rpm showed highest conversion all through the reaction time. The results obtained are similar to those previously reported [36, 38] while the slight variations are as a result of the difference in mixing intensities worked on. Previously 150, 300, 600, 700 and 800 rpm were studied and reported [40, 41]. Initially when the reaction rate were set at 140 rpm, at 60 °C and 6 minutes reaction time, only about 79.38 wt% conversion was obtained but at 800 rpm, 90.21 wt% was obtained. Optimal mixing rate was not observed and the highest stirring speed of 800 rpm was the most favorable among the mixing rate studied (**Figure 6**).

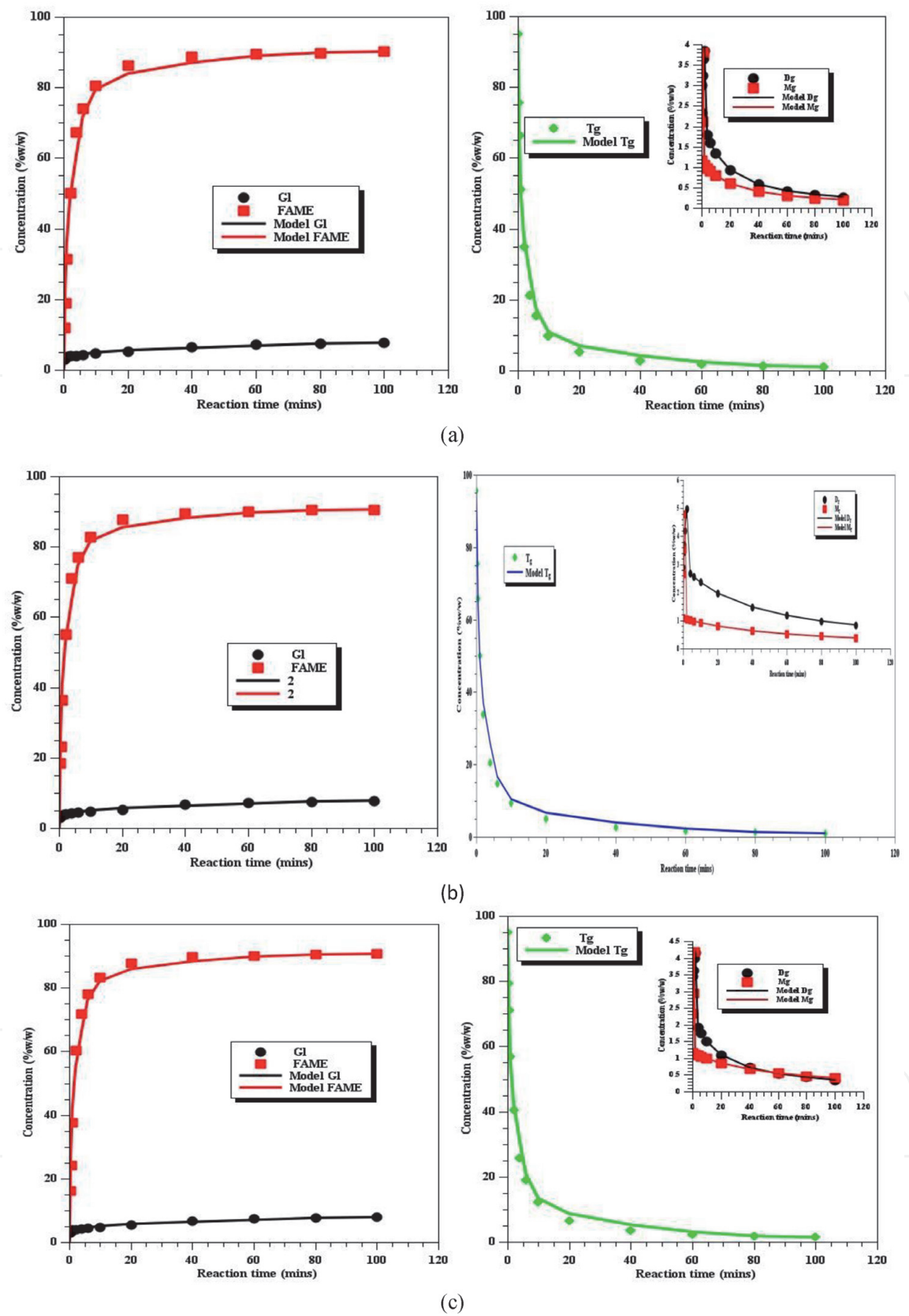


Figure 4.
Composition of reaction (a) at 50 °C, (b) at 60 °C and (c) at 65 °C.

3.3.1 Second order model

The Least-square approximation was applied, in fitting a straight line to the experimental data according to a model developed based on TG hydrolysis and the second-order reaction rate as shown in Eq. (20) [29, 32]. In each case the coefficient of determination (R^2) was determined.

$$\frac{-d[{\text{TG}}]}{dt} = k[{\text{TG}}]^2 \tag{22}$$

Integration of Eq. (20) gives Eq. (21).

$$k_{\text{Tg}}t = \frac{1}{[{\text{TG}}]} - \frac{1}{[{\text{TG}}_0]} \tag{23}$$

Where *k* is the overall pseudo-rate constant, *t* is the reaction time, TG₀ is the initial triglyceride concentration.

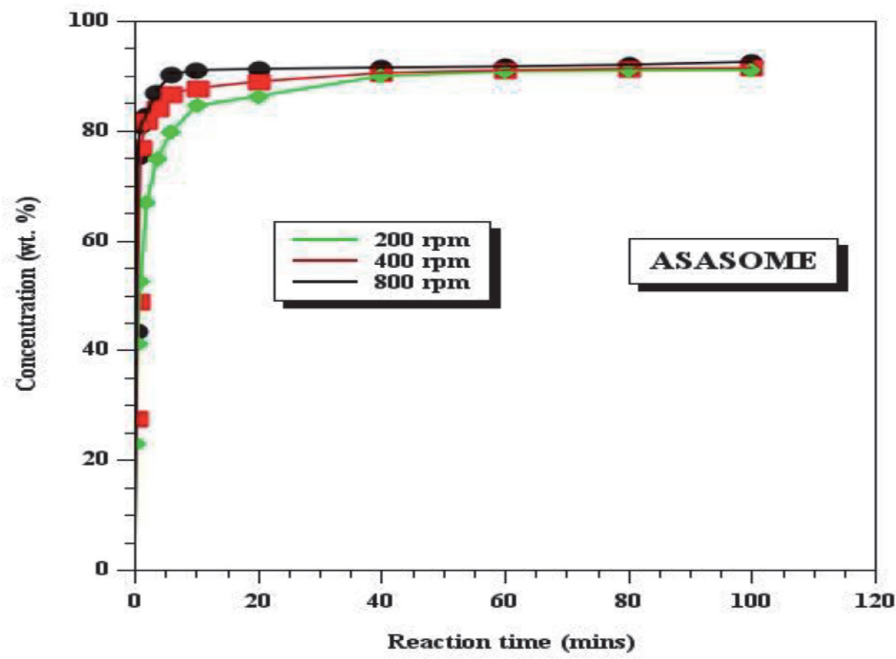


Figure 5.
Effect of mixing on ASASOME triglyceride conversion.

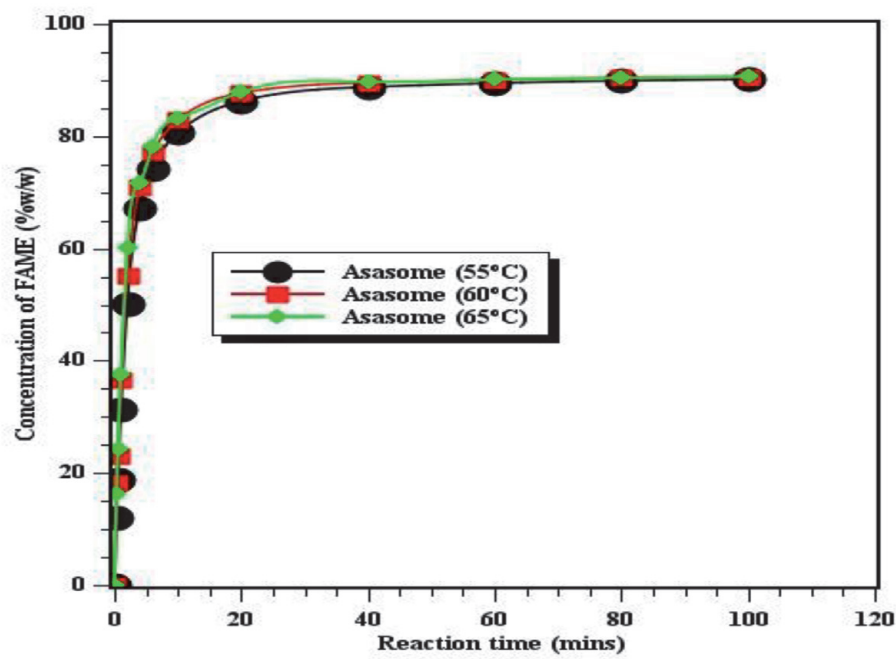


Figure 6.
The effects of temperature on ASASOME yield at 55 °C, 60 °C and 65 °C.

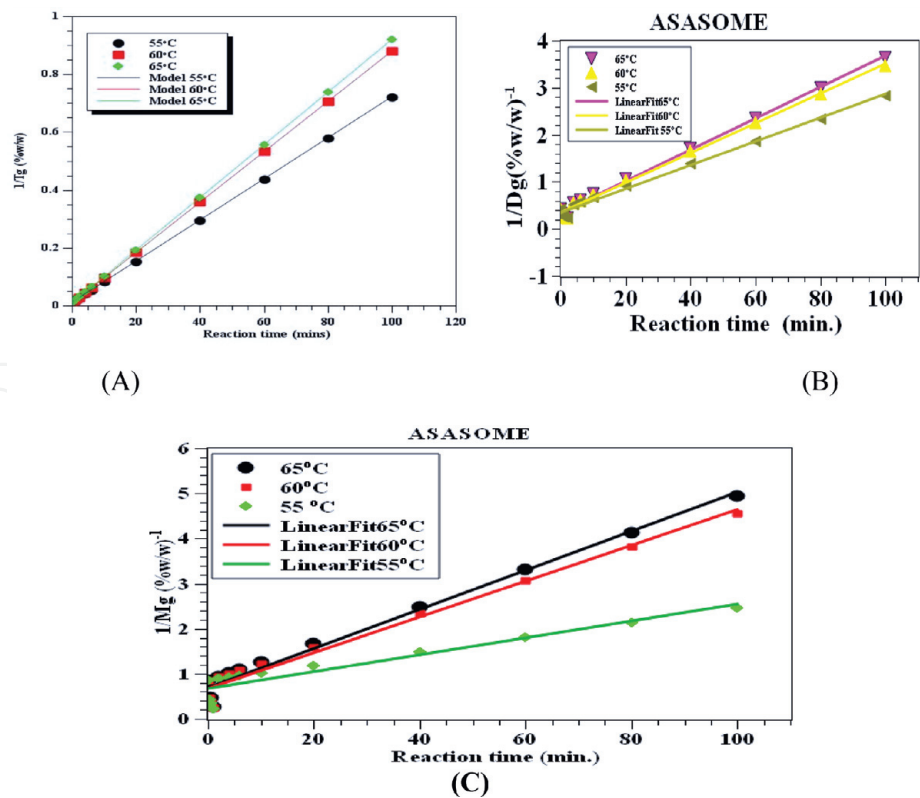


Figure 7. Second – Order reaction irreversible model of triglycerides (A), diglycerides (B) and monoglycerides (C) hydrolysis.

Glycerides	Second order model			First order model
	(°C)	k (wt%/min)	E _a (Kcal/mol.)	k (min ⁻¹)
Tg → Dg	55	0.00710 (R ² = 0.98)	2.707	0.0408 (R ² = 0.82)
	60	0.00870 (R ² = 0.97)		0.0420 (R ² = 0.81)
	65	0.00910 (R ² = 0.97)		0.0428 (R ² = 0.81)
Dg → Mg	55	0.02390 (R ² = 0.99)	7.30	—
	60	0.03040 (R ² = 0.99)		
	65	0.03210 (R ² = 0.98)		
Mg → Gl	55	0.01600 (R ² = 0.97)	23.33	—
	60	0.03710 (R ² = 0.97)		
	65	0.04090 (R ² = 0.99)		

Table 4. Summary of the kinetics result for second-order irreversible reactions for ASASOME.

A plot of reaction time (t) against $\frac{1}{[TG]}$ gave a straight line graph as shown in **Figure 7a** with high values of coefficient (R^2) (**Table 4**) to show that the model is valid. The plot for the three temperatures (55, 60 and 65 °C) is shown in **Figure 7a**, the slope is k_{TG} (wt%⁻¹min). It is observed that k fairly increased with temperature. Finally, activation energies of the reaction taking place were estimated using the calculated rate constants and temperatures at which they were observed in Arrhenius equation (Eq. (15)).

The diglycerides and monoglycerides vary with time in the same trend (**Figure 7b** and **c**) with that of triglycerides. A close similarity is observed in the

values of activation energy obtained in this study to the previous works [29] more especially in the Tg and Dg hydrolysis. Also, the rate constants were found to be four (4) times higher and two (2) times lower than those reported previously on palm oil base methanolysis [29] and on sun flower base-ethanolysis [42]. The choice of feedstocks, alcohol and other factors like temperature could have resulted in the variations. Moreso, the rate constants increase with temperature follows a trend of $k_{TG} < k_{DG} < k_{MG}$ in values. After 60mins reaction time, the highest conversion was above 90% and it is found to be in the same range with what many the authors have reported [1]. The hydrolysis of triglycerides to diglycerides is observed to be the rate determining step since it has the smallest rate constant while the diglycerides hydrolysis to glycerol is most favored by high temperature. The positive activation energy possessed by the steps is in supports of the endothermic characteristics of conventional transesterification process [1].

3.3.2 Pseudo first-order model

Neglecting the intermediate reactions of diglyceride and monoglyceride, the three stagess were combined in a single reaction stage [43]. However, due to the high molar ratio of methanol to oil, the change in methanol concentration can be considered as constant during reaction. It implies that by taking applying methanol in excess, its concentration does not alter the reaction order and it behaves as a first order chemical reaction [33]. The overall pseudo rate constants obtained from the slopes of the straight line plots of $\ln [TG]$ against t as presented in **Figure 8** are presented in **Table 4** for the methyl ester. It is clearly shown from **Figure 9**, in the reactions conducted at the three (3) different temperatures, there was a reduction in the coefficient of determination for the pseudo first-order kinetic model. **Figure 9** shows that the reaction at these temperatures does not fit the pseudo first-order reaction kinetic model better. This is supported by the lower values of coefficient of determination obtained from the first-order fitted plots ($R^2 < 0.80$) against high coefficient of determination obtained on the second-order irreversible kinetic model ($R^2 > 0.96$). Similar reported exists on the kinetics of hydrolysis of *Nigella sativa* (black cumin) seed oil catalyzed by native lipase in ground seed where pseudo first-order rate equation at 20, 30 and 40 °C; and the pseudo second-order equation at 50, 60 and 70 °C [44]. Therefore, it implies that hydrolysis of some oils follows first-order irreversible kinetic models at low temperature ranges (20–40 °C). The low temperature ranges is reported to favor the activity of native lipase better than at higher temperatures and this resulted in different mechanisms. But such low

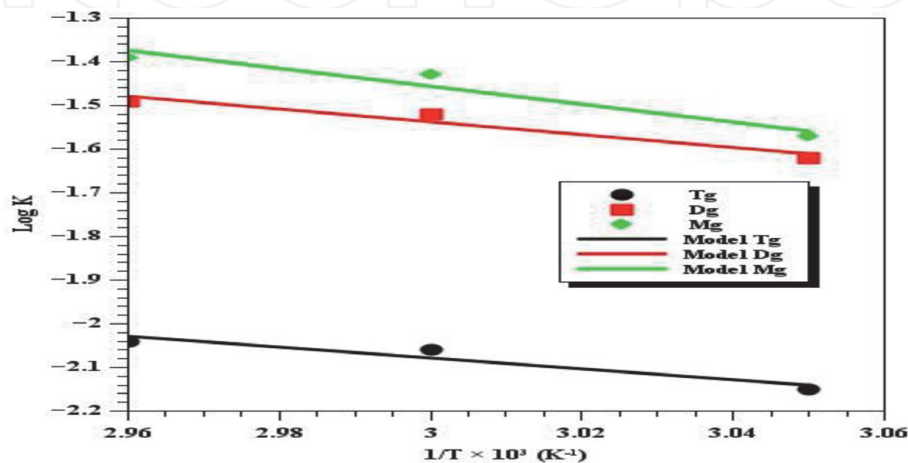


Figure 8.
Arrhenius plot of second order irreversible model.

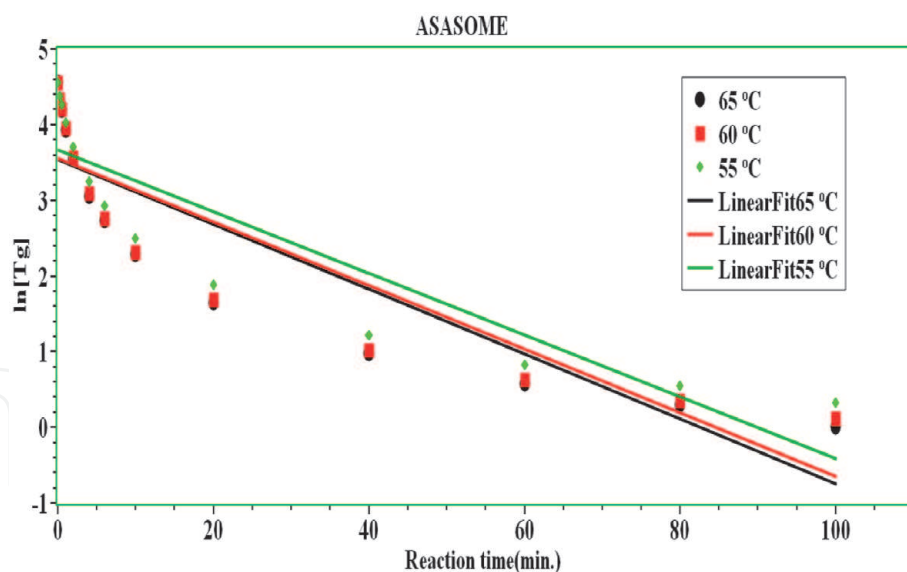


Figure 9.
First – Order reaction irreversible model of triglycerides hydrolysis.

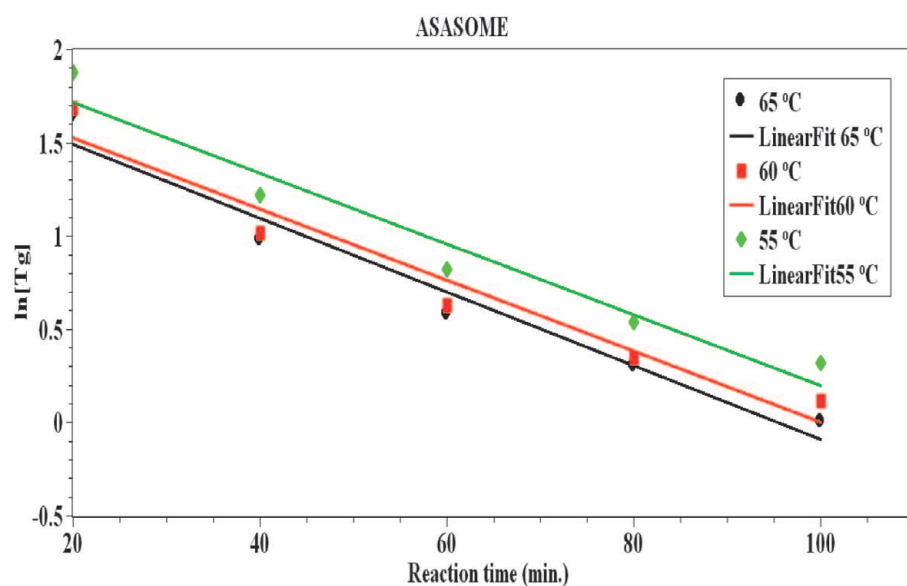


Figure 10.
First – Order reaction irreversible model of triglycerides of later stage hydrolysis.

temperatures would not favor maximum ester yield in this study because they are far below the reported optimum temperature [28]. Some authors, has observed that at latter reaction stages (beyond 30 mins) of palm oil hydrolysis to, the first-order or zero-order reaction model is the best fitted [29]. Comparable results are obtained on this study where as from 20 minutes reaction, the reaction follows first-order model with high coefficient of determination ($R^2 > 0.94$) (**Figure 10**). These stages presented low reaction rate owing to the reduction in the reactants concentration. It shows that at low temperatures and late stages of vegetable oils methanolysis, it progresses very slowly and follow pseudo first-order kinetic model.

4. Conclusion

The successful application of NaOH catalyst and methanol for synthesis of fatty acid methyl ester from the highly underutilized seed oil of *Chrysophyllum albidum* has investigated and reported. Power rate law approach modeling of the process and

irreversible consecutive transesterification showed that second order model was the best fitted kinetic model. It was observe the thermodynamic results agrees with endothermic reaction principles. The approach used in this study were simpler than most highly complicated reversible consecutive mechanisms and would promote easy translation into industrial scale. The seed oil of *Chrysophyllum albidum* is therefore a viable feedstock for biodiesel production and for alternative source of petrodiesel with its renewable characteristics and advantages.

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References

- [1] Esonye, C., Onukwuli, O. D and Ofoefule, A. U. (2019) Chemical Kinetics of a Two-step Transesterification of *Dyacrodes Edulis* Seed Oil Using Acid-Alkali Catalyst. *Chemical Engineering Research and Design*, 145, 245–257. <http://dx.doi.org/10.1016/j.cherd.2019.03.010>
- [2] Leung, D. Y. C. and Guo, Y. (2010). Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Process Technol.* 87: 883–890.
- [3] Atabani, A. E., Silitonga, A.S., Irfan, A.B., Mahlia, T.M. I., Masjuki, H. H. and Mekhilef, S A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable energy review*, **2012**, 16: 2070–2093.
- [4] Sani, Y. M., David, W. M. A. W. and Abdul Aziz, A. Z. (2013). Biodiesel Feedstock and Production Technologies Successes, Challenges and Prospects. In *Intech-Open*, <http://dx.doi.org/10.5772/52>.
- [5] Esonye, C. (2019). Optimization, Engine Performance and Kinetic Studies of Base Methanolysis of Selected Seed Oils for Biodiesel Production- Ph.D Thesis: Nnamdi Azikiwe University Awka, Nigeria
- [6] Meka, V. G. Pillai, S. K., and Sakoulas, G.. (2004). Linezolid resistance in sequential *Staphylococcus aureus* isolates associated with a T2500A mutation in the rRNA gene and loss of a single copy of rRNA. *Journal of Infectious Diseases* 190, 311–317.
- [7] Ataya, F. Dube, M. A. and Terman, M. (2007) Acid catalysed transesterification of canola oil to biodiesel under single-and-two-phase reaction conditions. *Energy Fuels* 21: 2450–2459.
- [8] Rashid, U., Anwar, F., Ashraf, M., Saleem, M. & Yusuf, S. (2011). Application of response surface methodology for optimization tranesterification of *Moringa oleifera* oil, biodiesel production. *Energy Conversion Management*, 52, 3034–3042.
- [9] Meher, L., Sagar, D. and Nack, S. (2006). Technical aspects of biodiesel production by transesterification - A review. *Renewable and Sustainable Energy Reviews*, 10, 248–268.
- [10] Freedman, B.; Butterfield, R. O.; and Pryde, E. H. Transesterification Kinetics of Soybean Oil. *J. Am. Oil Chem. Soc.* **1986**, 63, 1375–1380.
- [11] Vicente, G., Martinez, M. and Aracil, J. (2004). Integrated Biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresource Technology*, Vol. 92, No. 3, (May 2004), p. p. 297–305, ISSN 0960–8524.
- [12] Williams, J. W., Jackson, S. T. and Kutzbach, J. E. (2007). Projected distributions of novel and disappearing climates by 2100AD. Schneider, S. H. (Ed.). *PNAS* April, 104 (14) 5738–5742; <https://doi.org/10.1073/pnas.0606292104>.
- [13] Wang, Y; Seo, B; Wang, B; Zamel, N; Jiao, K. and Adroher, X, C. Fundamentals, materials and machine learning of polymer electrolyte membrane fuel cell technology. *Energy and AI*, (2020). 1: 100014. [Doi.org/10.1016/j.jegyai..](https://doi.org/10.1016/j.jegyai..)
- [14] Agu, C. M. and Agulanna, A, C., (2020) Kinetics and Thermodynamics of Oil Extracted from Amaranth, in *Nutritional Value of Amaranth*, Intech Open, DOI: <http://dx.doi.org/10.5772/intechopen.88344>

- [15] Ma, F.; Hanna, M. A. Biodiesel Production: A Review. *Bioresource Technology*, **1999**, 70, 1–15.
- [16] Olufumilola, A. A., and Oladapo, A. S. Physico-chemical properties of African star apple (*Chrysophyllum albidum*) components. *Nutrition and Food Science*, (2011). 41(1), 8–11.
- [17] Ureigho, U. N., and Ekeke, B. A. Nutrient values of *Chrysophyllum albidum* linn (African star apple) as a domestic income plantation species. *African Research Review*, (2010). 4(2), 50–56.
- [18] Houesson, L. G., Lougbegnon, T. O., Gbesso, F. G. H., Anagorau, L. E. S., and Sinsin, B. Ethno-botanical study of the African star apple (*Chrysophyllum albidum* G. Don) in the Southern Benin. *West Africa Journal of Ethnobiology and Ethnomedicine*, (2012). 8, 40 1–10.
- [19] Musa, U., Isa, A.G., Mohammed, J. A., Mohammed, U. G., Usman, Z. & Alharsan, B. (2015). Extraction of *Chrysophyllum albidum* seed oil, optimization and characterization. *Chemical and Process Engineering Research*, 30, 1–8.
- [20] Ochigbo, S. S. & Paiko, Y. B. (2011). Effects of solvent blending on the characteristics of oils extracted from the seeds of *Chrysophyllum albidum*. *I.J.S.N*, 2(2), 352–358.
- [21] Audu, T. O. K., Aluyor, E.O. Egualeoma, S., Momoh, S. S. Extraction and characterization of *Chrysophyllum albidum* and *Luffa cylindrical* seed oils. *Petroleum Technology Development Journal*, (2013). 3(1), 1–7.
- [22] Sam, S. M., Akonye, L.A., Mensah, S.I., & Esenowo, G. J. (2008). Extraction and classification of lipids from seeds of *Persea Americana* Miller and *Chysophyllum albidum* G. Don. *Scientia Africans*, 7 (2), 35–38.
- [23] Ajiwe, V. I. E., Okeke, C. A., Nnabuike, B., Ogunleye, G. A., Elebo, E. Application of oils from African star apple (*Chrysophyllum africanum*), horseeye bean (*Mucuna sloanu*) and African pear (*Dacyodes edulis*) seeds. *Bioresource Technology*, (1997). 59, 259–261.
- [24] Esonye, C., Onukwuli, O. D., Ofoefule, A. U. Optimization of Production from *Prunus Amygdalus* Seed Oil Using Response Surface Methodology and Artificial Neural Networks. *Renewable Energy*, (2019). 130, 62–71. <http://dx.doi.org/10.1016/j.renene.2018.06.036>.
- [25] Ofoefule, A. U., Esonye, C., Onukwuli, O. D., Nwaeze, E., Ume, C. S. Modeling and optimization of African pear seed oil esterification and transesterification using artificial neural network and response surface methodology comparative analysis. *Industrial Crops and products*, (2000) 140,111707, doi:10.1016/j.indcrop.2019.111707.
- [26] AOAC Official methods of analysis, (13th Edition), Association of Official Analytical Chemists, Washington, DC.
- [27] Furnish, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R. Vogel's textbook of practical organic chemistry, 5th ed., Longman group, UK, (1989), 1412–1422.
- [28] Fu, Y. J., Zu. Y. G., Wang. L. L., Zhang, N. J., Liu. W., Li, S. M. Zhang, S. Determination of fatty acid s in biodiesel produced from yellow horn oil by RP-LC-RID. *Chromatographia*, (2008). 67, 9–14.
- [29] Darnoko, D.; Cheryan, M (2000) Kinetics of palm oil transesterification in a batch reactor, *J. Am. Oil Chem. Soc.* 77, 1263–1267.
- [30] Ilgen, O. (2012). Reaction kinetics of dolomite catalyzed transesterification

of conola oil and methanol. Fuel Processing Technology 95, 62–66.

[31] Patil, P., Gude, V.G., Pinappu, S and Deng, S(2011). Transesterification kinetics of *Camelina sativa* oil on metal oxide catalyst under conventional and microwave heating conditions. Chemical Engineering Journal. 168: 1296–1300.

[32] Levenspiel,, O. (1999) Chemical Reaction Engineering, 3rd edition, McGraw-Hill.

[33] Zhang, L., Sheng, B., Xin, Z., Liu, Q., and Sun, S., (2010). Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst. Bioresource. Technol. 101, 8144–8150.

[34] Kumar, G. R.; Ravi, R.; Chadh, A. (2011) Kinetic Studies of Base-catalyzed transesterification reaction of non edible oils to prepare Biodiesel; The effect of co-solvent and temperature, Energy and Fuels 25, 2826–2832.

[35] Vujicic, D., Comic, D., Zarubica, A., Micic, R., & Boskovi, G., 2010. Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst. Fuel 89, 2054–2061.

[36] Mushtaq, A, Shazia, S., Lee, K.T., Ahmed, Z.A., Haleema, S., Muhammed, Z., Taibi Ben, H., Muhammed, A.A.& Rasool, B.T.(2014). Distaff Thistle Oil: A possible new non-edible feedstock for biogas energy. International Journal of Green Energy, 10: 1–27.

[37] Mittelbach, M.(1996). Diesel fuel derived from vegetable oils: specification and quality control of biodiesel. Bioresource Technol. 56, 7–11.

[38] Almgrbi, A. M., Hatami, T., Glisic, S. B. and Orloric, A. M. (2014). Determination of kinetic parameters for complex tranesterification reaction by

standard optimization methods. Hem. Ind. 68(2): 149–159.

[39] Patel, V. (1999). Cetane Number of New Zealand diesel, Report, office of Chief Gas Engineer, Energy Inspection Group. Ministry of Commerce Press, Wellington, New Zealand.

[40] Nouredini, H.; Zhu, D. Kinetics of Transesterification of Soybean Oil. J. Am. Oil Chem. Soc. **1997**, 74 (11), 1457–1461.

[41] Okullo, A. A.; Temu, A. K. Modelling the Kinetics of Jatropha Oil Transesterification. Energy and Power Engineering, **2015**, 7, 135–143.

[42] Reyero, J. G.; Arzamendi, S.; Zabala, M. L.; Gandia, P. Kinetics of NaOH-catalyzed transesterification of sun flower oil with ethanol to produce biodiesel, Fuel Processing Technology, **2015**, 129, 147–155.

[43] Birla, A., Singh, B., Upadhyay, S. and Sharma, Y. (2012). Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. Bioresource Technol., 106: 95–100.

[44] Dandik, L. and Aksoy, H. A. (1992). The kinetics of hydrolysis of *Nigella sativa* (Black Cumin) seed oil catalyzed by native lipase in ground seed. JAOCS, 69, (12), 1239–1240.