Chemical, Petroleum and Environmental Engineeri

Kinetic Studies of Biodiesel Production from Jatropha curcas Oil

Ejiroo Thelma Akhihiero
Department of Chemical Engineering, University of Benin, Benin City, Nigeria
thelma.akhihiero@uniben.edu

Bamidele Victor* Ayodele
Department of Chemical Engineering, University of Benin, Benin City, Nigeria

May Ali Alsaffar
University of Technology Iraq Baghdad, Iraq

T.O.K. Audu
Department of Chemical Engineering, University of Benin, Benin City, Nigeria

E.O. Aluyor
Department of Chemical Engineering, University of Benin, Benin City, Nigeria

ABSTRACT

The world is confronted with the twin crisis of fossil fuel depletion and environmental degradation caused by fossil fuel usage. Biodiesel produced from renewable feedstocks such as *Jatropha* seed oil or animal fats by transesterification offers a solution. Although biodiesel has been produced from various vegetable oils such as *Jatropha* seed oil, the reaction kinetics studies are very few in literature, hence the need for this study. *Jatropha curcas* seed oil was extracted and analyzed to determine its free fatty acid and fatty acid composition. The oil was transesterified with methanol at a molar ratio of methanol to oil 8:1, using 1% sodium hydroxide catalyst, at different temperatures ranging from $32^{o}C$ to $65^{o}C$, at atmospheric pressure. The order of the reactions with respect to the triglyceride's disappearance in the forward reaction at the chosen temperatures was found to be pseudo-first-order and found to be first-order for the reaction at $32^{o}C$. The rate constants of the three consecutive reaction steps at $65^{o}C$, namely, triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol, were found to be 0.422 min^{-1} 0.117 min^{-1}, and 0.037min^{-1}, respectively. Their corresponding activation energies in J/mol were 22.165, 3.136, and 19.770, respectively.
Keywords: Biodiesel; Jatropha curcas; Transesterification; Renewable Energy; Kinetics

<div dir="rtl">

كركاس الجاتروفا زيت من الحيوي الديزل لإنتاج الحركية الدراسات

اليور
، الكيميائية الهندسة قسم
بنين مدينة بنين جامعة ،
نيجيريا

أودو .ت
جامعة ، الكيميائية الهندسة قسم
نيجيريا ، بنين مدينة بنين

الصفار علي مي
العراق التكنولوجية الجامعة
العراق بغداد،

أيوديلي فيكتور باميديل*
الكيميائية الهندسة قسم
بنين مدينة ، بنين جامعة
نيجيريا

أخيهيرو ثيلما إجيرو
الكيميائية الهندسة قسم
بنين مدينة بنين جامعة
نيجيريا

الخلاصة

يواجه العالم الأزمة المزدوجة لاستنفاد الوقود الأحفوري والتدهور البيئي الناجم عن استخدام الوقود الأحفوري. حيث يوفر
وقود الديزل الحيوي المنتج من المواد الأولية المتجددة مثل زيت بذور الجاتروفا أو الدهون الحيوانية عن طريق الأسترة

</div>

التبادلية حلاً لهذه الازمه . على الرغم من أن وقود الديزل الحيوي قد تم إنتاجه من زيوت نباتية مختلفة مثل زيت بذور الجاتروفا ، إلا أن دراسات حركية التفاعل قليلة جدًا في الابحاث، وضهرت الحاجة إلى هذه الدراسة . حيث تم استخلاص زيت بذور الجاتروفا كركاس وتحليلها لتحديد تركيبة الأحماض الدهنية الحرة والأحماض الدهنية . ومن ثم تمت إعادة أسترة الزيت باستخدام ميثانول بنسبة مولارية من الميثانول إلى الزيت 8: 1 ، باستخدام محفز هيدروكسيد الصوديوم بنسبة1 ٪ ، عند درجات حرارة مختلفة تتراوح من 32 درجة مئوية إلى 65 درجة مئوية ، عند الضغط الجوي . حيث يتم سحب نتيجه كل خليط من خليط التفاعل على فترات 15 دقيقة لتحديد تركيزات كل نوع من أنواع التفاعل الموجودة في أي وقت باستخدام كروماتوغرافيا الغاز مع مقياس الطيف الضوئي الشامل (GC MS). ان ترتيب التفاعلات فيما يتعلّق باختفاء الدهون الثلاثية تم العثور على التفاعل الأمامي عند درجات الحرارة المختارة ليكون شبه زائف من الدرجة الأولى ، ووجد أنه من الدرجة الأولى للتفاعل عند 32 درجة مئوية . تم اكتشاف ثوابت المعدل لخطوات التفاعل الثلاث المتتالية عند 65 درجة مئوية وهي كالاتي ؛ تم العثور على الدهون الثلاثية إلى ثنائي الجليسريد ، ثنائي الجليسريد إلى أحادي الجليسريد وأحادي الجلسريد إلى الجلسرين بزمن 0.422 دقيقة ⁻¹، 0.117 دقيقة ⁻¹ و 0.037 دقيقة ⁻¹على التوالي بينما كانت طاقات التنشيط المقابلة في J / مول 22.165 و 3.136 و 19.770 على التوالي.

الكلمات الرئيسية :وقود الديزل الحيوي،جاتروفا كركاس، الأسترة ،طاقة متجددة، حركية

1. INTRODUCTION

The interest in renewable energy production has gained wide popularity in the last two-three decades due to the adverse effect of energy from fossil sources (**Burke and Stephens et al. 2018; Gielen et al., 2019**). Thus, bioenergy has received significant attention because of the abundant biomass that can be used as feedstocks (**Chia et al., 2018; Salman et al., 2016**). One such bioenergy is biodiesel which can be produced from various feedstocks such as jatropha, rapeseed, soybean, palm, cottonseed, and peanut oil (**Souza et al., 2018; Humpenöder et al., 2018; Doyle et al., 2016**). Biodiesel is typically produced by the transesterification reaction, which is a chemical reaction between a raw renewable oil consisting mainly of triglycerides molecules such as *Jatropha* seed oil and an alcohol such as methanol or ethanol in the presence of a catalyst such as sodium hydroxide, potassium hydroxide, calcium oxide or zeolite to chemically break the triglyceride molecule in the oil into fatty acid methyl or ethyl esters (biodiesel) with glycerol as a by-product (**Ambat et al., 2018; Veljković et al., 2018**). Biodiesel, unlike petrol diesel, is biodegradable and non-toxic (**Sadaf et al., 2018**) and produces about 60% less net life cycle carbon dioxide emissions, as it is itself produced from atmospheric carbon dioxide through photosynthesis in plants (**Živković et al., 2018; Mohammed and Jabbar, 2016**).

Several studies have been conducted on biodiesel production *Jatropha curcas* oil catalyzed by various homogeneous and heterogeneous catalysts. (**Sudsakorn et al., 2017**) investigated biodiesel production from Jatropha Curcas oil using strontium doped CaO/MgO catalyst. The study revealed that methyl ester content of 99.6% was obtained at 65°C for two hours and the methanol-to-oil molar ratio of 9:1 with the catalyst amount of 5 wt%. (**Kamel et al., 2018**) investigated the optimization and mechanism of Jatropha curcas Linnaeus seed oil for biodiesel production. The study revealed that the optimum operating conditions of the Jatropha curcas oil transesterification process were ascertained as 60 min reaction time, 6:1 methanol to oil molar ratio, 1 wt.% catalyst loading, 400 rpm, and 60°C with a biodiesel production yields of 94 and 96% with calcined jatropha cake and KOH activated jatropha cake catalysts. Kinetic modeling of biodiesel production using non-edible Madhuca Indica oil has been reported by (**Muthukumaran et al. 2017**). The study's kinetic analysis revealed that the apparent activation

energy and pre-exponential factor for transesterification of mahua oil were calculated as 22.306 kJ/mol and 60.51 min [1], respectively. Biodiesel research has mainly focused on the development of cheap, non-edible oils to serve as raw materials. The kinetics of some of these oils must be developed due to differences in the oils' composition. Therefore, this study aimed to investigate the reaction kinetics of biodiesel production from transesterification of ester derived from local *Jatropha* seed oil.

2. MATERIALS AND METHOD

The materials used in this study include *Jatropha* seed oil extracted from fresh *Jatropha* seeds extracted using a crude hydraulic press, methanol of high grade (HPLC grade), and sodium hydroxide purchased from Sigma Aldrich, Germany. Hot plate with a magnetic stirrer, temperature regulation system, an improvised reactor (500ml beaker), a mercury thermometer, cotton wool, and Gas Chromatography-Mass Spectrophotometer (GC MS) were all employed during the kinetic studies.

An equivalent molar ratio of methanol to oil (8:1) was weighed and placed in two beakers labeled A and B. Beaker A containing the oil was heated to 100°C to remove any moisture present in the oil. Prior to the reaction, the oil's free fatty acid was tested and found to be approximately 0.8%, hence suitable for transesterification to occur. One percent sodium hydroxide by weight of oil was dissolved in beaker B containing the methanol. The heated oil was allowed to cool to about 30 °C. The oil was transesterified with the sodium methoxide solution by adding the solution slowly to the oil to avoid clogging while stirring on the hot plate at 450 rpm. The temperature of the hot plate was set as required. The reaction mixture's aliquots were withdrawn at 15 minutes intervals of time for Gas chromatographic analysis to determine the percentage of fatty acid methyl ester (FAME) formed. The reaction was carried out at temperatures ranges from 32 – 65°C under atmospheric pressure. The maximum reaction time for each temperature was 120 min.

3. RESULTS AND DISCUSSION

The results of the biodiesel components obtained from the gas chromatographic analysis are shown in **Table 1**. The kinetic rate determination for Triglycerides (TG), Diglycerides (DG), and Monoglycerides (MG) are shown in **Tables 2, 3**, and **4**, respectively.

Table 1. Fatty Acid Methyl Ester Content obtained at 32°C.

COMPONENT	(15mins)	(30mins)	(45mins)	(60mins)	(75mins)
Tryglycerides (mol/L)	0.356	0.027	0.017	0.002	0.001
Diglycerides (mol/L)	0.003	0.015	0.024	0.068	0.024
Monoglycerides (mol/L)	0.974	1.573	1.633	2.012	2.385

Glycerol (mol/L)	0.006	0.004	0.017	0.089	0.089
Alcohol (mol/L)	0.006	0.003	0.003	0.002	0.002
Methylester (mol/L)	1.950	2.012	0.974	1.558	1.667
Total (mol/L) (mol/L)	4.934	4.051	1.965	3.220	3.300

Table 2. Fatty Acid Methyl Ester Content obtained at 40°C.

COMPONENT	(15mins)	(30mins)	(45mins)	(60mins)	(75mins)
Tryglycerides (mol/L)	0.093	0.056	0.006	0.048	0.000
Diglycerides (mol/L)	0.004	0.052	0.063	0.074	0.121
Monoglycerides (mol/L)	0.651	1.103	1.709	1.962	2.318
Glycerol (mol/L)	0.002	0.002	0.002	0.003	0.003
Alcohol (mol/L)	0.004	0.006	0.004	0.003	0.003
Methylester (mol/L)	2.286	1.103	0.651	1.962	1.835
Total (mol/L) (mol/L)	4.698	2.270	1.308	3.972	3.543

Table 3. Fatty Acid Methyl Ester Content obtained at 60°C.

COMPONENT	(15mins)	(30mins)	`(45mins)	(60mins)	(75mins)
Tryglycerides (mol/L)	0.024	0.029	0.067	0.206	0.671
Diglycerides (mol/L)	0.005	0.033	0.058	0.083	0.135
Monoglycerides (mol/L)	1.662	2.012	2.025	2.307	2.324
Glycerol (mol/L)	0.012	0.013	0.010	0..013	0.003
Alcohol (mol/L)	0.003	0.002	0.001	0.001	0.003
Methylester (mol/L)	2.025	1.692	2.324	2.012	2.307
Total (mol/L)	4.074	3.425	4.716	4.234	5.287

Table 4. Fatty Acid Methyl Ester Content obtained at 65°C.

COMPONENT	(15mins)	(30mins)	(45mins)	(60mins)	(75mins)
Tryglycerides (mol/L)	0.002	0.025	0.026	0.057	0.114
Diglycerides (mol/L)	0.004	0.008	0.037	0.063	0.214
Monoglycerides (mol/L)	0.530	1.779	2.107	2.304	2.308

Glycerol (mol/L)	0.002	0.002	0.002	0.003	0.002
Alcohol (mol/L)	0.003	0.003	0.002	0.003	0.001
Methylester (mol/L)	2.300	2.107	2.312	1.949	2.385
Total (mol/L) (mol/L)	4.720	4.241	4.758	2.504	4.086

Concentration of triglyceride at time zero (C_{A0}) =2.40mol/l.

3.1 Reaction Kinetics Model Derivation

The biodiesel or transesterification reaction is of the form represented in Eq. (1)

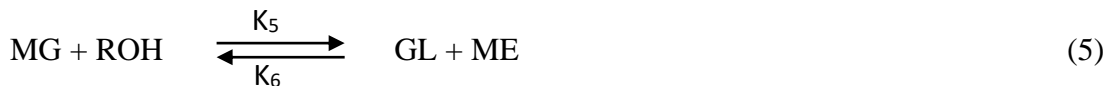$$A + B \; \xrightleftharpoons{\text{Catalyst}} \; C + D \tag{1}$$

where

A = TG, B = alcohol (ROH), C = Glyceride and D = methyl esters (ME)

Therefore, Eq. (1) becomes

$$TG + ROH \; \xrightleftharpoons{\text{Catalyst}} \; Glyceride + ME \tag{2}$$

Where the Glyceride could be either DG, MG or GL.

Eq. (2) is an equilibrium reaction that occurs in three consecutive steps forming intermediates. Stoichiometrically, 3 moles of alcohol are required to react with 1 mole of TG to 3 moles or esters and 1 mole of glycerol. Therefore, we have

$$TG + ROH \; \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \; DG + ME \tag{3}$$

$$DG + ROH \; \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \; MG + ME \tag{4}$$

$$MG + ROH \; \underset{K_6}{\overset{K_5}{\rightleftharpoons}} \; GL + ME \tag{5}$$

Overall reaction is therefore

$$TG + 3\,ROH \; \rightleftharpoons \; GL + 3\,ME \tag{6}$$

From Eq. (3)

$$TG + ROH \; \xrightarrow{K_1} \; DG + ME \tag{7}$$

$$K_2$$

And DG + ME $\longrightarrow$ TG + ROH   (8)

From Eq. (4)

DG + ROH $\xrightarrow{K_3}$ MG + ME   (9)

and MG + ME $\xrightarrow{K_4}$ DG + ROH   (10)

from Eq. (5)

MG + ROH $\xrightarrow{K_5}$ GL + ME   (11)

and GL + ME $\xrightarrow{K_6}$ MG + ROH   (12)

The overall order proposed for the forward reactions in Equations (7), (9) and (11) have been reported to be a second order for transesterification of waste cooking oil (**Krishnan and Dass, 2012**). There are conflicting reports from different authors on different vegetable oils (**Turner, 2005**). Sometimes same vegetable oil but different reaction conditions may also have different report (**Wang et al., 2020**). This would be proven by the data obtained from the experiment in this study. The way the reactions above were initiated and terminated are as follows. Formation of alkoxide from methanol and sodium hydroxide.

ROH + OH^{--} $\rightleftarrows$ RO^{--} + H_2O (13)

Alcohol   catalyst   alkoxides   water

The alkoxide ion attacks the glycerides molecules to form methyl esters and glycerol, as shown from Eq. (14) to (19).
Transesterification

TG + RO^{--} $\rightleftarrows$ DG^{--} + ME   (14)

DG^{--} + ROH $\rightleftarrows$ DG + RO   (15)

DG + RO^{--} $\rightleftarrows$ MG^{--} + ME   (16)

MG^{--} + ROH $\rightarrow$ MG + RO^{--} (17)

MG + RO^{--} $\rightarrow$ GL^{--} + ME   (18)

GL^{--} + ROH $\rightarrow$ G L+ RO^{--} (19)

In a saponification reaction, an almost inevitable side reaction associated with transesterification when using a homogeneous catalyst such as sodium hydroxide (NaOH) can take place. The following reaction represented in Eq. (20) to (23) would be observed.

ME + OH^{--} $\rightarrow$ ROH + Soap   (20)

TG + OH^{--} $\rightarrow$ DG + Soap   (21)

DG + OH^{--} $\rightarrow$ MG + Soap   (22)

MG + OH^{--} $\rightarrow$ GL + Soap   (23)

Saponification reactions of Eq. (20) to (23) become prominent during transesterification when using vegetable oil with high free fatty acids and high moisture content. Therefore,

transesterification of high free fatty acid vegetable oil (e.g., *Jatropha* seed oil) with sodium hydroxide catalyst would result in a lot of soap formation with little or no biodiesel formation. Hence it is recommended that if sodium hydroxide catalyst must be used in *Jatropha* seed oil transesterification, the free fatty acid of the oil must be lower than 3% or 1%, and the oil must be dried or free from moisture.

In the present study, the free fatty acid of *Jatropha* seed oil used was 0.8%, and the oil was preheated at a temperature of over 100°C for about 5 – 10 minutes to eliminate moisture. The molar ratio of methanol to the oil used was 8:1. The reactions were carried out at 32°C, 40°C, 60°C, and 65°C. At each reaction temperature, aliquots of the reaction mixture were withdrawn at every 15 minutes of time for 75 minutes. The reactions above are assumed to be elementary thus obeying, the law of mass action (**Turner 2005, Freedman et al., 1986)**

3.1.1 Assumptions of the kinetic model

   i.   The concentration of free fatty acid of the oil used was negligible.
  ii.   All the reactions and intermediates formed proceed at the same rate, with the same mechanism.
 iii.   Transesterification is catalysed by OH ⁻ or RO ⁻ (alkoxide) ions.
 iv.   Saponification reaction is negligible.
  v.   The concentration of alcohol is constant due to the high molar ratio of alcohol to triglyceride; hence reaction rate depends solely on the disappearance of the triglycerides.
 vi.   All reactions go to completion.
 vii.   The reactions are elementary and thus obey the law of mass action.
viii.   The reverse reactions are negligible due to the high molar ratio of methanol to triglycerides used, causing equilibrium to shift to the right (Le Chartelier's Principles).

3.1.2 Determination of the Rates and Order of the Reactions

From Eq. (7) to (12), the rates of the reactions according to LMA are obtain as follows:

$$r_{TG} = \frac{dC_{TG}}{dt} = K_1 C_{TG} C_{ROH} + K_2 C_{DG} C_{ME} \tag{24}$$

$$r_{DG} = \frac{dC_{DG}}{dt} = K_1 C_{TG} C_{ROH} = K_2 C_{DG} C_{ME} - K_3 C_{DG} C_{ROH} + K_4 C_{MA} C_{ME} \tag{25}$$

$$r_{MG} = \frac{dC_{MG}}{dt} = K_1 C_{DG} C_{ROH} = K_4 C_{MG} C_{ME} - K_5 C_{MA} C_{ROH} + K_6 C_G C_{ME} \tag{26}$$

$$r_G = \frac{dC_G}{dt} = K_5 C_{MG} C_{ROH} - K_6 C_G C_{ME} \tag{27}$$

$$r_{ME} = \frac{dC_{ME}}{dt} = K_1 C_{TG} C_{ROH} - K_2 C_{DG} C_{ME} - K_3 C_{DG} C_{ROH} - K_4 C_{MG} C_{ME} + K_5 C_{MA} C_{ROH} +$$

$$K_6 C_G C_{ME} \tag{28}$$

$$r_{ROH} = \frac{dC_{ROH}}{dt} = - \frac{dC_{ME}}{dt} \tag{29}$$

Where C_{TG}, C_{DG}, C_{ME}, C_{GL}, C_{ROH}, and C_{ME} are mole concentrations of TG, DG, MG, G, ROH, and ME, respectively in the reaction mixture. Eq. (24) to (29) holds when the reactions are non-

elementary. But when the reactions are assumed to be elementary due to the high molar ratio of methanol to oil (**Freedman et al., 1986, Krishnan and Das, 2012**), then from Eq. (1) and (2),

$$A + B \quad \rightleftarrows \quad C + D$$
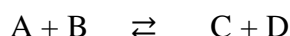
Assuming the reaction is a first-order reaction.

Then for a first-order reaction in a batch reactor,

$$-r_A = KC_A \tag{30}$$

where

$-\frac{dC_A}{dt}$ (rate of disappearance of reactant A), K is the rate constant, and C_A is the concentration of reactant A at any given time, t.

$$-\frac{dC_A}{dt} = KC_A \tag{31}$$

$$\frac{dC_A}{C_A} = Kdt \tag{32}$$

Integrating Eq. (32), we have

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = K \int_0^t dt \tag{33}$$

Equation (33) becomes

$$\ln \frac{C_A}{C_{Ao}} = Kt \tag{35}$$

The value of K in Eq. (35) can be determined by plotting $ln\frac{C_A}{C_{Ao}}$ versus t as shown in **Fig. (1)**. The fittings of the kinetic data obtained at 32ºC into Eq. (35) gave a straight line which is an indication that the transesterification reaction is a first-order reaction with a rate constant of 0.112min⁻¹. However, the kinetic data obtained at reaction temperatures of 40ºC, 60ºC, and 65ºC could not fit into the first-order reaction mechanism. Hence, they were subsequently tested in a second-order reaction represented in Eq. (36).

$$\frac{1}{C_A} - \frac{1}{C_A} = Kt \tag{36}$$

From Eq. (36), a plot of 1/C_A versus time would give a straight line to indicate a second-order reaction. The second-order reaction mechanism did not fit for reactions at 40ºC, 60ºC, and 65 ºC; hence an nth order determination was considered. A plot of C_A versus time and dC_A/dt versus ln C_A was used to determine the values of K as in **Table 5**. The order of the triglyceride disappearance was found to be pseudo-first-order. A plot of In K versus 1/T for the three consecutive reaction steps shows that the TG disappearance involves high activation energy. In contrast, the energy of conversion of MG to GL involves very low activation energy. In fact, the third step, which is the MG conversion to GL and ester, is the rate-determining step.

From **Fig. 1** it can be seen that the reaction is typical of first-order at 32 ºC. (**Wang et al., 2020**) reported that the triglyceride disappearance in the forward reaction appears to be pseudo-first-order or second-order depending upon conditions used. (**Khrishnan and Dass, 2012**) reported a second-order mechanism for the transesterification of waste cooking oil. (**Al-Zuhair, 2007**),

in his work on kinetics of lipase catalysed methanolysis of palm oil did not follow second order kinetics as indicated by **(Freedman et al., 1986)**. **(Noureddini and Zhu, 1997)** found that the rate of reaction is temperature-dependent. **(Turner's, 2005)** reported on modeling and simulation of reaction kinetics for biodiesel production shows that there are conflicting findings as to the order of reaction and estimates of reaction rate constants vary widely in biodiesel reaction kinetics.

However, a first-order reaction kinetics obtained for the reaction at 32 °C in this study is in agreement with Hymore and Audu's report on the kinetics of alcoholysis of rubber seed oil. This report also agrees with Mittelbach's report, which says that the rate of reaction is temperature-dependent. This is true and in agreement with what is obtained in this study. As soon the reaction temperature was raised from room temperature of 32 °C to 40 °C and above, the rate of reaction changed. The reaction order could no longer fit into the first-order reaction mechanism nor the second-order mechanism. An nth order mechanism was proposed for reactions at 40°C, 60°C and 65°C. Pseudo first-order kinetics was obtained. These results agree with the report of **(Freedman et al., 1986)** mechanism; hence a further attempt was made to fit the data into second-order reaction expression. The fittings of the data into second-order reaction expressions are represented in **Fig. 3**.
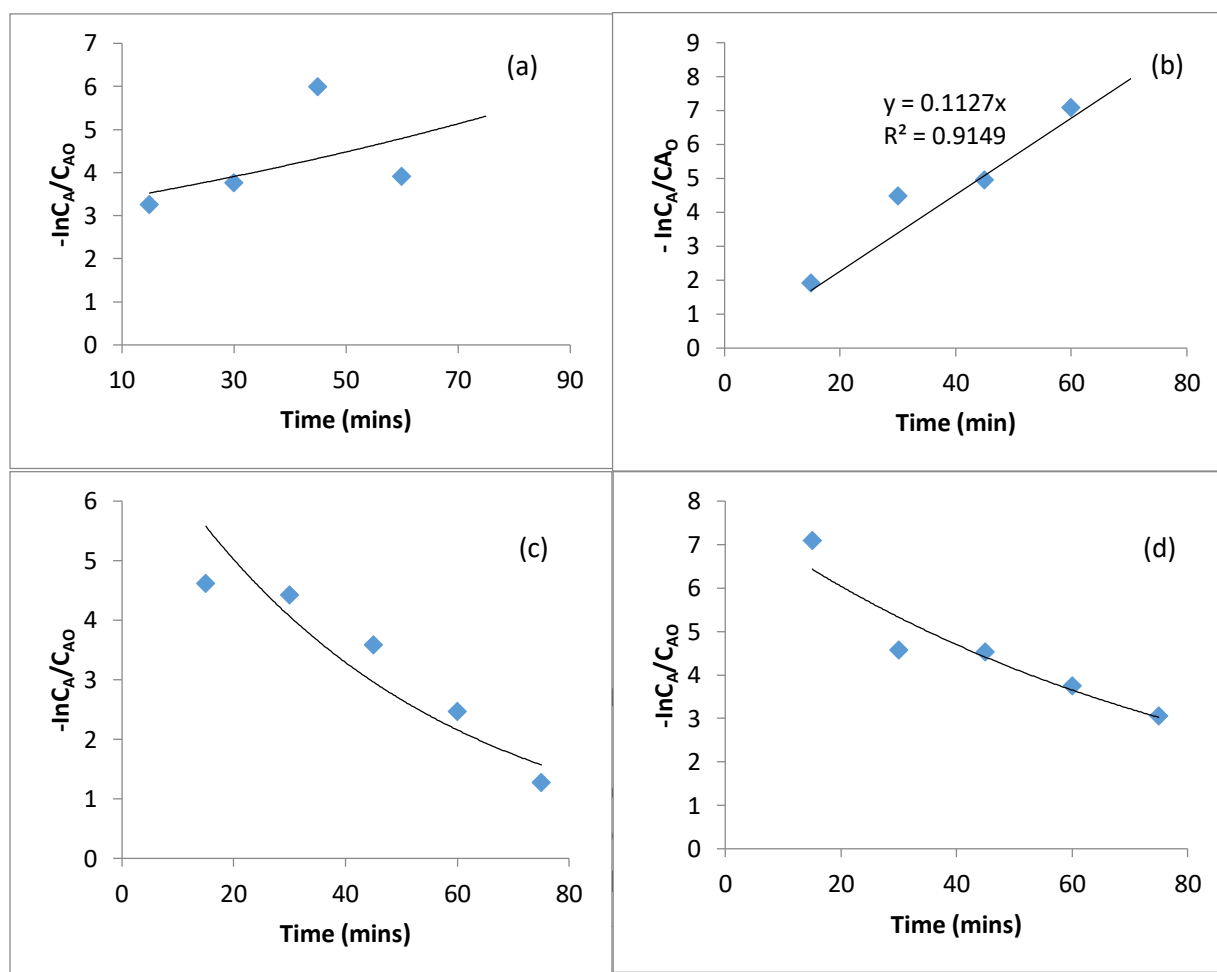

Figure 1. First order Kinetics Plot at (a) 32°C (b) 40 °C (c) 60 °C (d) 65 °C.

and 65°C are pseudo-first-order. The DG disappearances are also pseudo-first-order. These results are in agreement with the report of **(Freedman et al., 1986)**.

Determination of the Activation Energy of Reactions

To determine the activation energies of the reactions, we use the Arrhenius law. The Arrhenius law is stated in Eq. (41) below.

$$\text{In } k = -E_a/RT + \text{In } A \tag{41}$$

Where   K is the reaction rate constant

     R is gas constant given as 0.082 liter atm.mol^{-1}deg^{-1} in this case

     T is temperature of reaction

     A is frequency or pre-exponential factor and

     E_a = activation energy of reaction.

A plot of In K versus 1/T yield a straight line whose slope equals $-E_a/R$.

Therefore the activation energy in joules/mol is obtained as:

Activation energy (E_a) = - slope x gas constant

The graph intercept = In A.

Table 5. Activation Energy (Ea) Values for TG, DG, and MG.

	E_a values	In A
TG	22.1646	4.225
DG	3.13568	-1.794
MG	-19.7702	-9.313

Further testing of the kinetic models revealed that the reaction order of the TG disappearing to DG are pseudo-first-order. Only the reaction at 60 °C may be approximated to the second order. All the DG disappearing to MG, are all pseudo-first-order reactions. As for the MG disappearing to esters and glycerol, the orders are also pseudo-first-order except for the reactions at 32 °C and 60 °C, which are 3rd order and 4th order, respectively. These results agree with those obtained by **(Freedman et al., 1986)** in the kinetics of soybean oil transesterification with methanol. According to Freedman, all the forward reactions were pseudo-first-order. The values of the rate constants obtained are also in agreement with what **(Krishnan and Dass, 2012)** obtained for the kinetics of waste cooking oil transesterification with methanol.

The activation energies of the TG, DG and MG disappear are 22.165, 3.136, and – 19.77, respectively. The MG disappearance's k values have the least activation energy showing that the monoglycerides' disappearance to glycerol and esters is the rate-limiting step. The high activation energy accompanying the TG disappearance typify that energy is absorbed as the TG breaks down to DG and them to MG. The activation energy for the TG obtained in this study is close to that reported by **(Freedman et al., 1986)** for soybean oil. According to Freedman's report, the activation energies for all the reaction steps namely TG, DG and MG for both forward and reverse reactions ranges between 8 – 20 cal/mol. **(Krishnan and Dass, 2012)** reported activation energies of between 2 – 4 kcal/mol for all the reaction steps in waste

cooking oil transesterification with methanol .since different oils have different molecular weight and composition, it is possible that reaction order and the activation energy of the reaction may not exactly be the same. The values of activation energy obtained in this study for DG agrees with (**Krishnan and Dass, 2012**). A common observation from Freedman work and that of **Krishnan and Dass** is that of the MG transformation's activation energy to ester being the lowest of the three. This shows that the MG transformation to GL and ester is the rate-determining step.

A summary of all the rate constants in weight percent per minute at different temperatures for the glycerides transformation are shown in **Table 6.**

Table 6 . Summary of rate constants at different temperatures.

Glycerides	Temperatures	Reaction rate constant (wt% min^{-1})	R^2
T G $\longrightarrow$ DG	32	0.112	0.914
	40	0.0067	0.698
	60	0.309	0.760
	65	0.422	0.716
DG $\longrightarrow$ MG	32	0.0103	0.730
	40	1.000	0.686
	60	0.0267	0.823
	65	0.117	0.705
MG $\longrightarrow$ GL	32	0.0639	0.680
	40	0.0409	0.651
	60	0.1689	0.783
	65	0.037	0.683

4. CONCLUSIONS

The kinetics of biodiesel production from *Jatropha curcas* seed oil by transesterification reaction has been investigated. The disappearance of the triglycerides molecules in the forward reaction was found to follow a first-order reaction mechanism at 32°C with a rate constant of 0.112 min^{-1} and R^2 of 0.914 for the kinetic prediction. The activation energy of the TG disappearance is 22.165 kJ/mol, which indicates that the reaction at the beginning is temperature-sensitive, but as the reaction proceeds, the second step of diglyceride breaking down to monoglyceride and then to esters and glycerol are temperature-insensitive as both have low activation energies. Considering the very low activation energy of the monoglyceride disappearance to methyl esters and glycerol, little or no energy of activation is required at this step due to its very low value.

REFERENCES

- Ambat, I., Srivastava, V., and Sillanpää, M., 2018. Recent advancement in biodiesel production methodologies using various feedstock: A review. *Renewable and Sustainable Energy Reviews*, *90*, pp., 356-369.

- Al-Zuhair, S., Ling, F. W., and Jun, L. S., 2007. Proposed kinetic mechanism of the production of biodiesel from palm oil using lipase. Process Biochemistry, 42(6), pp., 951-960.

- Burke, M. J., and Stephens, J. C., 2018. Political power and renewable energy futures: A critical review. *Energy Research & Social Science*, *35*, pp., 78-93.

- Chia, S. R., Ong, H. C., Chew, K. W., Show, P. L., Phang, S. M., Ling, T. C., ... and Chang, J. S., 2018. Sustainable approaches for algae utilisation in bioenergy production. *Renewable energy*, *129*, pp., 838-852.

- Dhanasekaran K. and Dharmendira K.M.D., 2012. A kinetic study of biodiesel in waste cooking oil. *African Journal of Biotechnology*,11 (41), pp. 9791 – 9804.

- Doyle, A. M., Albayati, T. M., Abbas, A. S., and Alismaeel, Z. T., 2016. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. *Renewable energy*, *97*, pp., 19-23.

- Freedman B, Butterfield RO, Pryde EH., 1986. Transesterification Kinetics of Soybean *Oil Journal of American Oil and Chemist Society*; 63(10), pp., 1375.

- Freedman B, Pryde E.H, Mounts T.L.,1984. Variables Affecting the Yield of Fatty Esters from Transesterified Vegetable Oils. *Journal of American Oil and Chemist Society*, 61(10), pp., 1638.

- Gielen, D., Boshell, F., Saygin, D., Bazilian, M. D., Wagner, N., and Gorini, R., 2019. The role of renewable energy in the global energy transformation. *Energy Strategy Reviews*, *24*, pp., 38-50.

- Humpenöder, F., Popp, A., Bodirsky, B. L., Weindl, I, Biewald, A., Lotze-Campen, H., and Rolinski, S., 2018. Large-scale bioenergy production: how to resolve sustainability trade-offs?. *Environmental Research Letters*, *13*(2), pp., 024011.

- Kamel, D. A., Farag, H. A., Amin, N. K., Zatout, A. A., and Ali, R. M., 2018. Smart utilization of jatropha (Jatropha curcas Linnaeus) seeds for biodiesel production: Optimization and mechanism. *Industrial Crops and Products*, 111, pp., 407-413.

- Mohammed, W. T., and Jabbar, M. F. A., 2016. Zirconium Sulfate as Catalyst for Biodiesel Production by Using Reactive Distillation. *Journal of Engineering*, 22(1), pp., 68-82.

- Muthukumaran, C., Praniesh, R., Navamani, P., Swathi, R., Sharmila, G., and Kumar, N. M., 2017. Process optimization and kinetic modeling of biodiesel production using non-edible Madhuca Indica oil. *Fuel*, *195*, pp., 217-225.

- Sadaf, S., Iqbal, J., Ullah, I., Bhatti, H. N., Nouren, S., Nisar, J., and Iqbal, M., 2018. Biodiesel production from waste cooking oil: an efficient technique to convert waste into biodiesel. *Sustainable Cities and Society*, *41*, pp., 220-226.

- Salman, S. M., Mohammed, M. M., and Mohammed, F. L., 2016. Production of methyl ester (Biodiesel) from used cooking oils via trans-esterification process. *Journal of Engineering*, 22(5), pp., 74-88.

- Sudsakorn, K., Saiwuttikul, S., Palitsakun, S., Seubsai, A., and Limtrakul, J., 2017. Biodiesel production from Jatropha Curcas oil using strontium-doped CaO/MgO catalyst. Journal of environmental chemical engineering, 5(3), pp., 2845-2852

- Wang, Y., Li, D., Zhao, D., Fan, Y., Bi, J., Shan, R., and Huhe, T., 2020. Calcium-Loaded Municipal Sludge-Biochar as an Efficient and Stable Catalyst for Biodiesel Production from Vegetable Oil. ACS omega, 5(28), pp., 17471-17478.

- Veljković, V. B., Biberdžić, M. O., Banković-Ilić, I. B., Djalović, I. G., Tasić, M. B., Nježić, Z. B., and Stamenković, O. S., 2018. Biodiesel production from corn oil: A review. *Renewable and Sustainable Energy Reviews*, *91*, pp., 531-548.

- Živković, S., and Veljković, M., 2018. Environmental impacts the of production and use of biodiesel. *Environmental Science and Pollution Research*, *25*(1), pp., 191-199.