POWER RATE LAW BASED CHEMICAL KINETICS AND THERMODYNAMIC MODELING OF AFRICAN PEAR SEED OIL CONSECUTIVE IRREVERSIBLE BASE METHANOLYSIS FOR BIODIESEL PRODUCTION

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ABSTRACT

Currently the major challenge of biodiesel application as a replacement to petrodiesel is its industrial production sustainability.Consequently, the successful scale-up of laboratory results in transesterification requires so much information obtained through chemical kinetics.This paper presents the kinetics and thermodynamic study of alkali-homogeneous irreversible methanolysis of seed oil derived from African pear. The transesterification process was carried out from 0-100 minutes at temperature range of 55-65°C. The reaction mixture compositions were ascertained using gas chromatography- flame ionization detector (GC-FID) technique. Rate constants of the triglyceride (Tg), diglycerides (Dg) and monoglycerides(Mg) hydrolysis were in the range of 0.0140- 0.07810 wt%/min and increased with increase in temperature. The rate of reaction was found to increase with increase in temperature. Activation energies were found to be 6.14, 20.01 and 28.5kcal/mol at 55, 60 and 65°C respectively. Tg hydrolysis to Dg was observed asthe rate determining step while the reaction agreed with second order principles. A biodiesel yield of 93.02% was obtained with cloud point of 10°C , flash point of 125°C , pour point of 4°C , calorific value of 34.4MJ/kg, and cetane number of 54.90 which satisfy EN14214 and ASTM D 6751 standards. Results presented in this report would serve as idealized conditions for industrial scale up of biodiesel production from African pear seed oil.

Keywords:Kinetics; methanolysis; rate constants; activation energy; African pear seed oil; biodiesel

1.   INTRODUCTION

The challenges on the environment due to the application of fossil diesel have made the application of alkyl esters derived from natural sources indispensable. The physico-chemical characteristics and energy attributes of biodiesel are very similar to those of petrodiesel. Currently, the homogeneous base-catalyzed transesterification using methanol resulting in the corresponding fatty acid methyl esters (FAMEs) is the predominant technique applied for large scale production of biodiesel (Reyero, et al., 2015)). Application of methanol is necessitated by its wide availability and low-cost. The application of homogeneous base catalyst like NaOH and KOH at commercial level is highly encouraged because they possess of higher catalytic capabilitythan acid catalyst which is more corrosive (Wan and Hammed, 2011). The introduction of catalyst neutralization and washing has been among the most important stages of conventional purification steps employed to arrest the challenges of soap formation (Reyero et al., 2015). Also, the challenges of catalyst re-usability and the leaching of support or active sites which causes catalyst loss and decrease of the FAME yield have been serious challenges to heterogeneous catalyst application (Ilgen, 2012).

The major challenge in biodiesel application as a renewable and alternative fuel to petrodiesel is the lack of sustainability of its generation (Wang et al., 2020). The successful scale-up of laboratory results in transesterification requires information obtained through kinetics and optimization 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 (Abdel-Latiff. and Abdallah, 2010). Of great importance is the determination of the rate constants as it is highly required in establishing the value of the reaction rate by

applying its rate equation. Of high industrial importance is the chemical rate equation as it is needed in the kinetics application to establish the important conditions of reaction such as optimal pressure, temperature, feed composition, space velocity, degree of conversion and recycling (Abdel-Latiff. and Abdallah, 2010). Many chemical kinetic models previously proposed have not been able to bridge the gap between laboratory and the industry due to their high complexities and the assumption that the base methanolysis is reversible while the usual application of high methanol/oil molar ratio always shift the reaction to the right. This negates the effect of reversible reactions in transesterification process. Additionally, thorough review of the optimization studies of biodiesel production from literature has reported optimal alcohol/oil molar ration to be above 5:1 and this condition cannot promote reversible transesterification process. 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 3:1; (6:1)(Ilgen, 2012); (Okullo and Temu 2015); (Noureddini and Zhu1, 999), (4:1-14:1)(Zanette. et al., 2011), (15:1)(Wan and Hammed 2011), (6:1,12:1 and 24:1)(Reyero et al., 2015), (9:1)(Zavarukhin, et al., 2013), (6:1, 8:1 and 10:1)(Orifici. et al 2013), (9:1,12:1 and 15:1)(Patil et al., 2011) and (42:1)(Almgrbi et al., 2014). It is noteworthy that the complexity in kinetic models proposed in the above reports based on reversible consecutive mechanism challenges their industrial translation while simplified kinetic models suffice for practical purposes. Consequently, methanolysis reaction has been proposed to constitute three consecutive irreversible stages, especially by the usual condition of using high methanol to oil ratio (>3:1) which shifts the reaction methyl to the right (Ilgen, (2012); Darnoko and Cheryan (2000)

There are some researches that investigated on the reaction kinetics of various vegetable oil transesterification (Menkiti et al 2017) and few on African pear seed oil. The reversible models of kinetics of African pear seed oil on the basis of heterogeneous catalysis [Onukwuli and Ude 2018), its esterification and transesterification (Esonye. et al 2018) have been reported but this study presents the kinetics of methyl ester production from non-conventional non-edible tropical seed of African pear on the basis of irreversible consecutive mechanisms. Most seed oil transesterification kinetics presented earlier dealt on complex three-step. Before now, the seed oil from African pear is treated as a waste after consuming its

fatty and juicy pulp (Bull and George, 2015). Also, African pear is a perennial plant with high seed oil content in the seed with good productivity per hectare (Ogunsuyi, 2015; Bull and George2015) and thus satisfies the EU stipulations for biodiesel feedstock. Consequently, this research proposes the evaluation Aof the kinetics of biodiesel production from African pear seed oil (APSO) on the basis of irreversible consecutive mechanism.

2. MATERIALS AND METHODS
2.1 Materials.
The materials used in this research include sodium hydroxide (99%, Sigma-aldrich), potassium hydroxide (lobachemie, 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 Physico-chemical characterization of the seed oil and the biodiesel
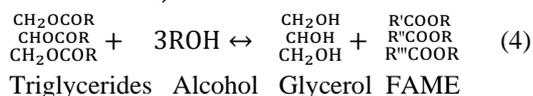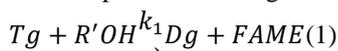This stage of the experiment has been conducted and reported previously (Esonye et al., (2018). The properties of the African pear seed oil were determined in accordance with Association of Official Analytical Chemists method (AOAC, 1990), the acid value by AOAC Ca5a-40, saponification value by AOAC 920:160; iodine value by AOAC 920:158 and peroxide value by AOAC 965.33) while the viscosity was determined by using Oswald viscometer apparatus, the density by using density bottle and moisture content by the Rotary evaporator oven (BTOV 1423). The ash content was evaluated by heating to dryness in Veisfar muffle furnace and the refractive index was measured using Abbe refractometer (Model: WAY-25, Search tech. Instruments). The fuel properties of the synthesized biodiesel were determined by ASTM standards: the kinematic viscosity was determined by ASTM D-445 method, the density was determined by ASTM D-1298 method, and the pour point determination was made using ASTM D-97 methods. The flash point of the fuel was determined as ASTM D-93, the value of cloud point was estimated according to ASTMD-2500, and acid value was measured following the ASTM D-664 method. The calorific value and cetane number were calculated according to the correlation developed by Bull and George, (2015).

2.3 Kinetic Study

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

2.4 Equation of transesterification reaction

Darnoko and Cheryan, (2000) have reported that transesterification reaction mechanism includes three consecutive irreversible reactions that yield fatty acid diglycerides and monoglycerides as intermediates. Equation (4) is the summary of Equation (1) to (3), which represents the stages of the reaction.

$$Tg + R'OH \xrightarrow{k_1} Dg + FAME \quad (1)$$

$$Dg + R'OH \xrightarrow{k_2} Mg + FAME \quad (2)$$

$$Mg + R'OH \xrightarrow{k_3} Gl + FAME \quad (3)$$

$$\begin{matrix} CH_2OCOR \\ CHOCOR \\ CH_2OCOR \end{matrix} + 3ROH \leftrightarrow \begin{matrix} CH_2OH \\ CHOH \\ CH_2OH \end{matrix} + \begin{matrix} R'COOR \\ R''COOR \\ R'''COOR \end{matrix} \quad (4)$$

Triglycerides Alcohol Glycerol FAME
  Where FAME is fatty acid methyl ester

2.5 Irreversible model assumptions

Since simplified kinetic models suffice for practical purposes, experimental data were processed under the following assumptions (Ilgen, 2012; ,Patil et al., 2011; Darnoko and Cheryan, 2000):

1. The methanolysis reaction is constituted by three consecutive stages but assumed irreversible because of the excessive presence of methanol in the reaction.

2. The free fatty acid neutralization was insignificant since the free fatty acid was negligible.

3. The saponification reaction was considered insignificant because of low acid value of the oil.

2.6 Experimental procedure

Experiments were designed to determine the reaction rate constants. A 6:1 molar ratio of methanol to oil was used in all the experiments. To examine the temperature dependency of the reaction rate constants, reactions at 55, 60 and 65°C were studied. The oil obtained from the esterification the seed oil as previously reported by the authors (Esonye et al., 2019) was used in this experiment. All reactions were carried out at atmospheric pressure with 0.20wt% sodium hydroxide as catalyst, methanol/oil molar ratio of 6:1 at a stirring speed of 140rpm. As reaction progresses, 2ml aliquot sample was withdrawn with a disposable pipette through an opening on the top of the reactor. The samples were collected in 10ml 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 GC operating specifications are given in Table 1. The diglycerides and monoglycerides contents were minimal ($< 3\%$), while the amounts of triglycerides were above 94%.

Table 1: Operating conditions of gas chromatography analysis .

SN	Item	Condition
1	Column	5"x1/4" internal diameter (i.d), glass column packed with 10% silica 10°C on 80-100mesh chromasorb HP at a temperature of 180°C
2	Detector	Flame Ionization Detector (FID),
3	Column Temperature	185°C (set point = 150°C , increment = 35°C)
4	Nitrogen flowrate	30 ml/min.
5	Hydrogen flowrate	20lb/in^2
6	Air Pressure	12lb/in^2
7	Sample size	0.3μl
8	Attenuation	2x10^4
9	Backing off range	x100

2.7 Second –order irreversible model

The best kinetic model for an irreversible model has been proposed to be a second-order based on Tg hydrolysis especially during the early stages of the reaction (Darnoko and Cheryan, 2000). To test the above report, a model developed based on Tg hydrolysis and the second-order reaction rate for Tg would be as shown in Equation (5) (Darnoko and Cheryan 2000, Levenspiel, 1999)

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$$\frac{-d[Tg]}{dt} = k[Tg]^2 \qquad (5)$$

Integrating and rearranging of Equation (5) by integration yields Equation (6).

$$k_{Tg}t = \frac{1}{[Tg]} - \frac{1}{[Tg0]} \qquad (6)$$

Where k is the overall rate constant, t is the reaction time, Tg_0 is the initial triglyceride concentration.

A plot of reaction time (t) against $\frac{1}{[Tg]}$ will give a straight line if the model is valid.

Where k is the overall rate constant, t is the reaction time; Tg_0 is the initial triglyceride concentration. A plot of reaction time (t) against $\frac{1}{[Tg]}$ will give a straight line if the model is valid. Similar approach was applied on the monoglycerides and diglycerides hydrolysis to get Equations (7) and (8).

$$k_{Dg}\, t = \frac{1}{[Dg]} - \frac{1}{[Dg_0]} \qquad (7)$$

$$k_{Mg}\, t = \frac{1}{[Mg]} - \frac{1}{[Mg_0]} \qquad (8)$$

2.7   First-order irreversible model
To determine the kinetics of the reaction based, the effect of reaction temperature and time were measured.
It was assumed that the catalyst was used in sufficient amount with respect to oil to shift the reaction equilibrium towards the formation of fatty acid methyl esters. Thus, the reverse reaction could be ignored and change in concentration of the catalyst during the course of reaction can be assumed to be negligible [Esonye, C, et al (2019)]. Also, since the concentrations of both Dg and Mg were found to be very low (Dg<2.9wt%, Mg<1.45wt %) compared to those of Tg (Tg>94wt%) in the crude vegetable oils used in this research, the reaction could be assumed to be a single-step transesterification (Levenspiel, 1999). Therefore, the rate law of the transesterification reaction for forward reaction can be expressed by Equation (9) (Zhang et al 2010).

$$-r_{Tg} = \frac{-d[Tg]}{dt} = k'.[Tg].[ROH]^3 \quad (9)$$

Where [Tg] is the concentration of triglycerides and [ROH] that of methanol and k′ is the equilibrium rate constant. 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. Hence, the reaction would obey pseudo-first order kinetics (Zhang, et al., 2010) and finally, the rate expression can be written as in Equation (10).

$$-r_{Tg} = \frac{-d[Tg]}{dt} = k.[Tg] \qquad (10)$$

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 $[Tg_t]$. The integration of Equation (10) from t = 0, [Tg]= $[Tg_0]$ to t = t, [Tg] =$[Tg_t]$ gives Equation (11)[14]:

$$-\ln[Tg] + \ln[Tg_0] = kt \qquad (11)$$

Based on the above considerations, the rate data from the seed oil of African pear transesterification reaction was fit into Equation (11) to test this rate equation. Hence, -ln[Tg] was plotted against time. In this procedure, the weight percentage of Tg was used as concentration because $[Tg]_0/[TG]$ is a concentration ratio and its value is independent of units, provided that the same units are used for both $[Tg]_0$ and [Tg]. 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 (Eqn. 12).

$$\log_{10}k = \frac{-Ea/2.303R}{T} + A \qquad (12)$$

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

3.   RESULTS AND DISCUSSIONS
3.1   Seed oil and biodiesel characterization

The physico-chemical parameters of the APSO and APSOME are shown in Table 2. The oil content is a key factor influencing the choice of plant seeds as potential feedstock for biodiesel and other industrial products. The percentage oil yield from African pear is very encouraging for biodiesel purposes when compared with most oil feedstocks. It is observed that the seed has high oil yield (>56%), though with high free fatty acid (FFA). High FFA in oils results in losing the oil to soap rather than to biodiesel (Mushtaq et al., 2014). The high FFA

(9)

gave the need to apply two - step transesterification which brought down the FFA to 0.16, at 65 °C reaction temperature and 100 minutes esterification time, in order to prevent soap formation which lowers the biodiesel yield (Esonye et al 2019). The results of moisture content obtained for APSO is quite low and would therefore promote high yield of biodiesel, prevent oxidation rancidity and sustain its shelf life (Menkiti et al., 2017). APSOME showed slight decrease in the iodine values obtained from the parent seed oil. The iodine value according to EN 14214 (European committee for standardization) should be less than 120 g I$_2$/100 g sample for the seed oil to be suitable as feedstock for biodiesel production while oils having high unsaturation of fatty acids, when heated are prone to polymerization of the glycerides, causing formation of deposits and thereby compromising oxidative stability (Birla et al 2012). Peroxide value is an index of rancidity and hence provides information on oil quality and stability. The value obtained clearly suggests that the seed oil is stable and may not readily become rancid during storage.The specific gravity value is close to the range of 0.87 – 0.90 for biodiesel. It is expected to promote effective functioning of the injection engines through maintaining the optimal air to fuel ratio required for efficient combustion and low particulate matter emissions. The viscosity result is consistent with 3.70 cp for APSO as reported in (Ogunsuyi 2015). Viscosity is important in determining optimum handling, storage and operational conditions because biodiesel fuel need to have suitable flow characteristics to ensure that adequate

supply reaches injectors at different operating temperatures. The values obtained is very optimal and would prevent fuel filters clogging, formation of droplets on injection which causes poor atomization and provide sufficient lubrication for precision fill of the fuel injection pumps (Atabani , et al., 2012). Moreover, the viscosities of the seed oil decreased considerably after transesterification. The seed oil and the methyl ester have favorable values for smoke point, titre, flash point and cloud point and this would translate to high biodiesel potentials. The cold flow properties of the methyl esters were measured by determination of cloud point (CP) and pour point (PP). Specifications for CP and PP are not in the biodiesel standards of DIN 14214 though ASTM D6757 requires that CP be reported probably because each country has different climatic conditions. As reported here, APSOME has values which are quite within ASTM D6757 standards and this shows that the produced FAME would perform well in very cold and temperate regions.The ash content of the methyl ester is lower than the values obtained from the corresponding vegetable seed oil sample showing improved fuel quality because of the transesterification process. The calorific value is below diesel fuel ASTM D 975 standards but within the limit of EN DIN14214 standard. The cetane number (CN) is above the standard set for petrol diesel. This could be explained to be due to higher oxygen content which is typical of biodiesel fuel. The quality of the oil and biodiesel compared well with result of other studies in the literature (Ogunsuyi, 2015).

Table 2: Physico-chemical parameters of APSO and its biodiesel in relation with standards

Parameters			Standards		
	APSO	APSOME	ASTM D 9751	ASTMD 6751	EN 14214
Yield (wt%)	56.30	93.025	-	-	-
Colour	Pale yellow	Light brown	-	-	-
Specific gravity	0.8875	0.8570	0.850	0.880	0.86 -0.90
Moisture content (%)	0.53	0.030	-	-	-
Refractive Index	1.4369	1.4279	-	-	-
Acid value (mgKOH/g)	13.98	0.32	0.062	0.50	0.50
Free fatty acid (wt%)	7.89	0.16	0.31	0.25	0.25
Iodine value (mgKOH/g)	51.96	45.21	42-46	-	120 max
Peroxide value (milli eq. oxy/kg)	1.79	-	-	-	-
Saponification value (mgKOH/g oil)	254.72	243.51	-	-	-
Ash content (%)	1.65	0.11	0.01	0.02	0.02
Viscosity (mm^2/s)	5.82	2.34	2.6	1.9-6.0	3.5-5.0
Smoke point (°C)	30	24	-	-	-

Parameters	APSO	APSOME	Standards		
			ASTM D 9751	**ASTMD 6751**	**EN 14214**
Titre value (ºC)	35	-	-	-	-
Fire point (ºC)	40	27	-	-	-
Flash point (ºC)	147	125	60-80	100-170	120
Cloud point (ºC)	10	10	-20	-3 to 12	-
Pour point (ºC)	-6	4	-35	-15 to -16	-
Calorific value (KJ/Kg)	-	34,391.50	42-46	-	35
Conductivity (Us/CM)	-	0.87	-	-	-
Cetane index	-	56.98	-	-	-
Cetane number	-	54.90	40-55	47 min	51 min

3.2   Chemical Kinetics Result

Fig. 1(A-C) shows the progress of the transesterification reaction of African pear seed oil for reaction temperatures of 50°C, 60°C and 65°C. The catalyst concentration was 0.2wt % of NaOH and methanol/ oil ratio of 6:1 at mixing speed of 140rpm. The initial stage of the reaction produced fatty acid methyl esters (FAMEs) rapidly. The rate then reduced and finally reached almost equilibrium in about 80 minutes for all the temperatures. It is observed in Fig.1 that the glycerol concentration increased with increase in FAME but was not in relative proportion (without a constant factor). This could be as a result of the intermediate products (Dg and Mg). Also, the triglycerides concentration reduced as the reaction progresses. The Tg concentration after 60 minutes was less than 15% for all the temperatures. The highest concentration of Dg and Mg were observed in the first 2 minutes for APSO after which they started decreasing until after 80 minutes when they started being almost at equilibrium. The values of Tg was greater than Dg and Dg was greater than Mg values for all the temperature. It was observed in Fig 1 that the higher the temperature, the lower the values of Tg, Dg and Mg for respective reaction times but the higher the temperature, the higher the values of FAME (Fig. 2). This could be probably because as the temperature moves from 55°C towards the 65°C, the closer it gets to the boiling point of methanol (68°C) which could give better reaction condition for higher conversion of glycerides (Fig. 1).
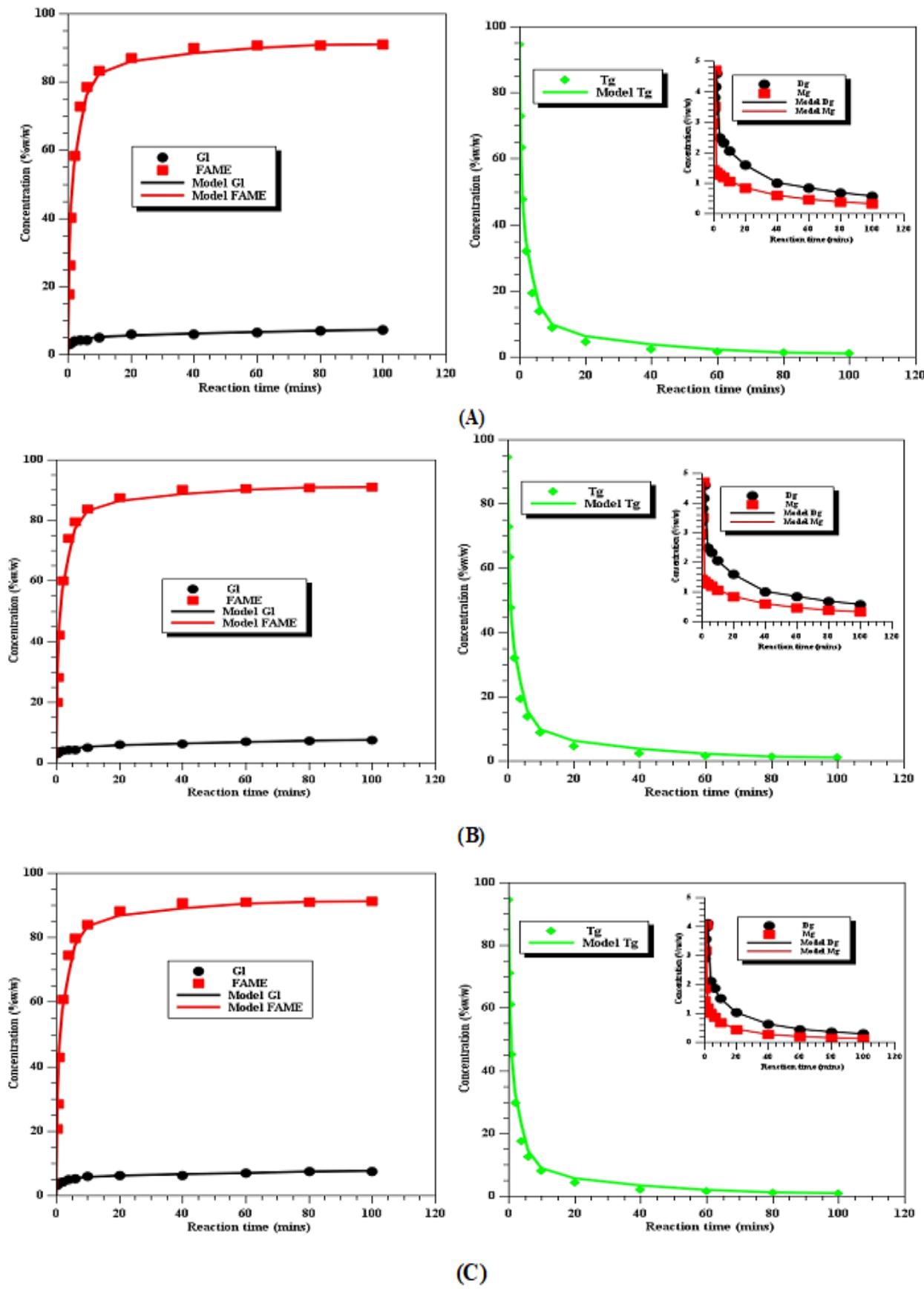
(A)

(B)

(C)

Fig. 1: Composition of Transesterification reaction products at 65°C (A), 60°C (B) and 55°C (C).
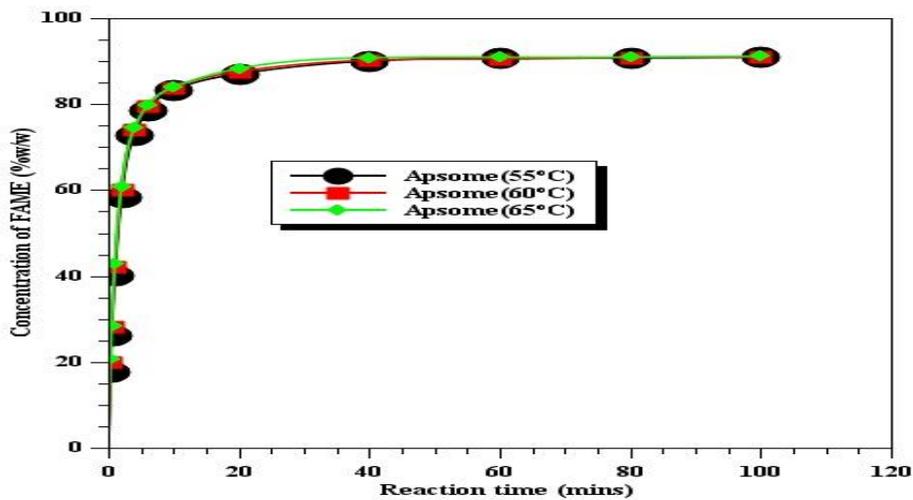
Fig. 2: Effect of reaction temperature on the transesterification reaction.

Fig. 3 shows a clearer reaction trend of the Dg and Mg at the initial stages of the reaction time (0-10 minutes). The trends show an agreement with a typical progress trend observed in consecutive reaction systems on the intermediates. It was observed that the concentration of the intermediates (Mg and Dg) increased as the concentration of triglycerides (Tg) decreased. This continued until about 2.0 minutes of reaction time when maximum intermediate concentrations were reached. After this the decomposition of the intermediates becomes more rapid than their formation and their concentration drops. The maximum points of last intermediates (Dg) were found to be 4.59, 4.20 and 4.10 wt% at 55°C, 60°C and 65°C respectively which correspond to the point of inflection of final product (FAME) of 58.32, 60.15 and 60.84wt% for 55°C, 60°C and 65°C respectively at 2.0 minutes.

The plot of the inverse of triglyceride oncentration against time for the three temperatures is shown in Fig. 4. The slope is k_{Tg} (wt%$^{-1}$min). The same trends observed in Figure 3 were observed in the case of the intermediates. It is observed that k increased with temperature. The plots equally validate the second order model proposed considering the fact that at all the temperatures the plots agreed with the proposed model equation. This is supported by the high coefficient of determination (all were above 0.97). Fig. 5 shows the Arrhenius plots for the three temperatures to determine the activation energies. It contains the plots of the logarithm of rate constants against the inverse of temperature in Kelvin. The results of the activation energies and rate constants are presented in Table 3.
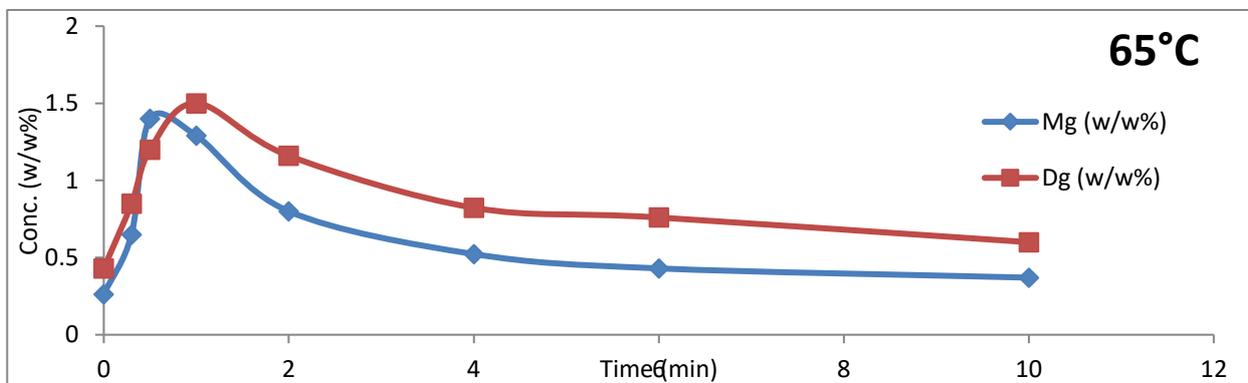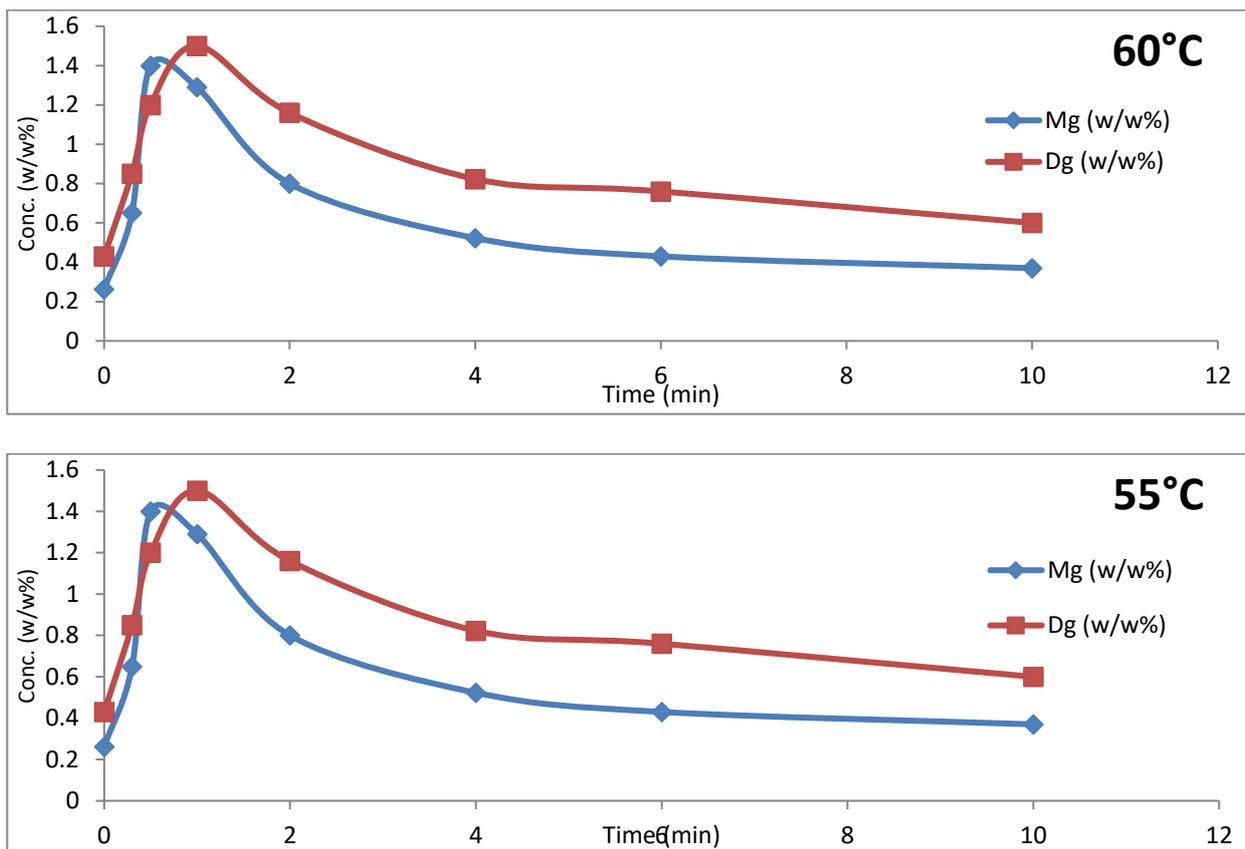
Fig. 3: Progress of intermediates at various temperatures at the initial stage.

Table 3: Summary of the kinetics result for second-order irreversible reaction

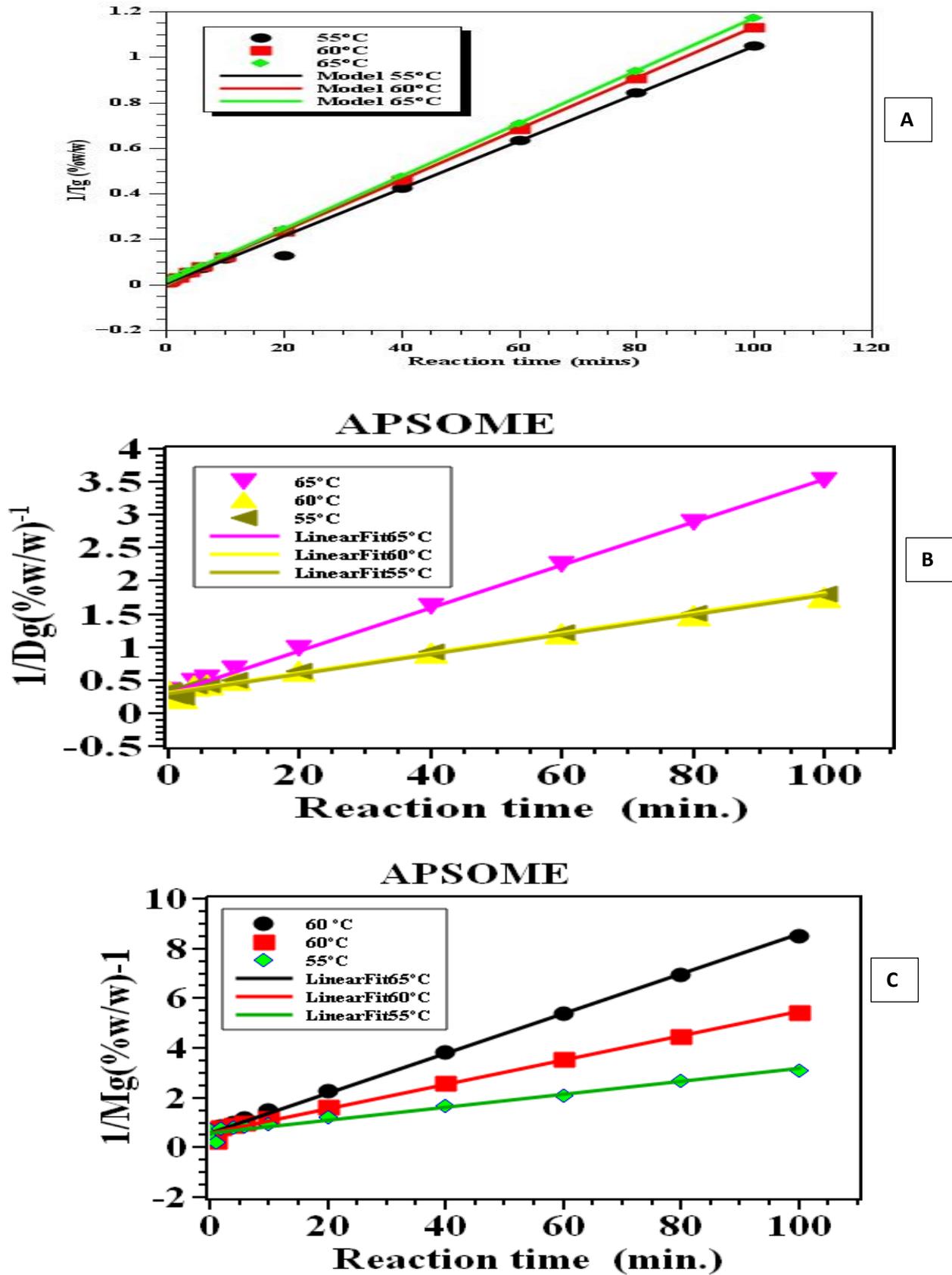| Glyceride	Temperature(T)			Rate constant, k (wt%/min)	Log k	Activation energy (Kcal/mol.)
	(°C)	(K)	$1/T \times 10^3 (K^{-1})$			
Tg ⟶ Dg	55	328	3.05	0.01040	-1.98	6.14
	60	333	3.00	0.01120	-1.95	
	65	338	2.96	0.01160	-1.93	
Dg ⟶ Mg	55	328	3.05	0.01404	-1.85	20.01
	60	333	3.00	0.01460	-1.83	
	65	338	2.96	0.03170	-1.50	
Mg ⟶ Gl	55	328	3.05	0.02470	-1-61	28.50
	60	333	3.00	0.04730	-1.32	
	65	338	2.96	0.07810	-1.11	

Fig. 4: Second – order reaction irreversible model of triglycerides (A), diglycerides (B) and monoglycerides (C) hydrolysis
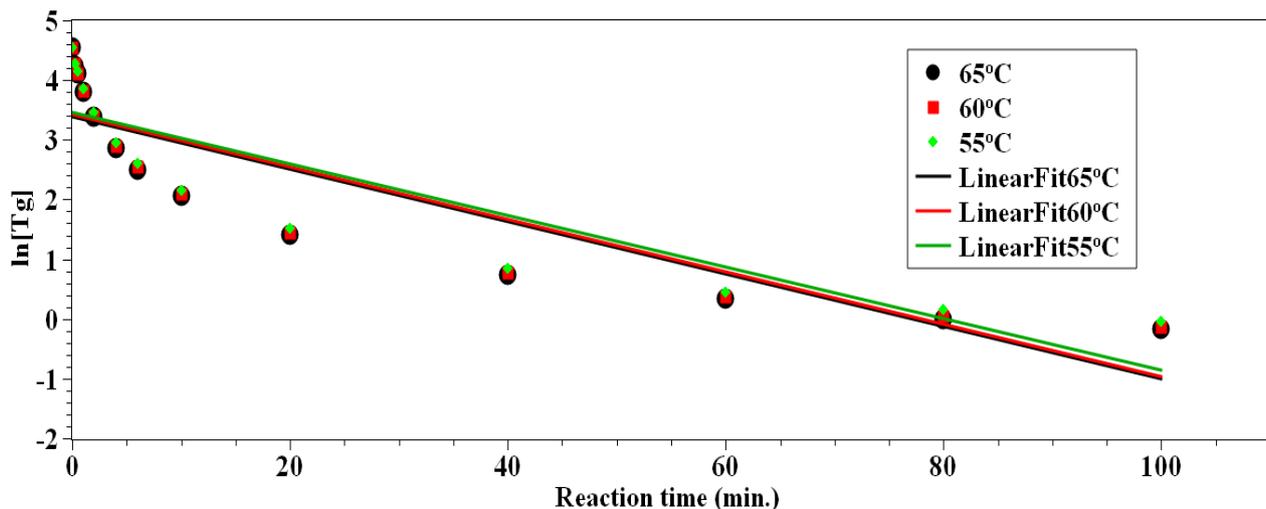
Fig. 5: First – order reaction irreversible model of triglycerideshydrolysis
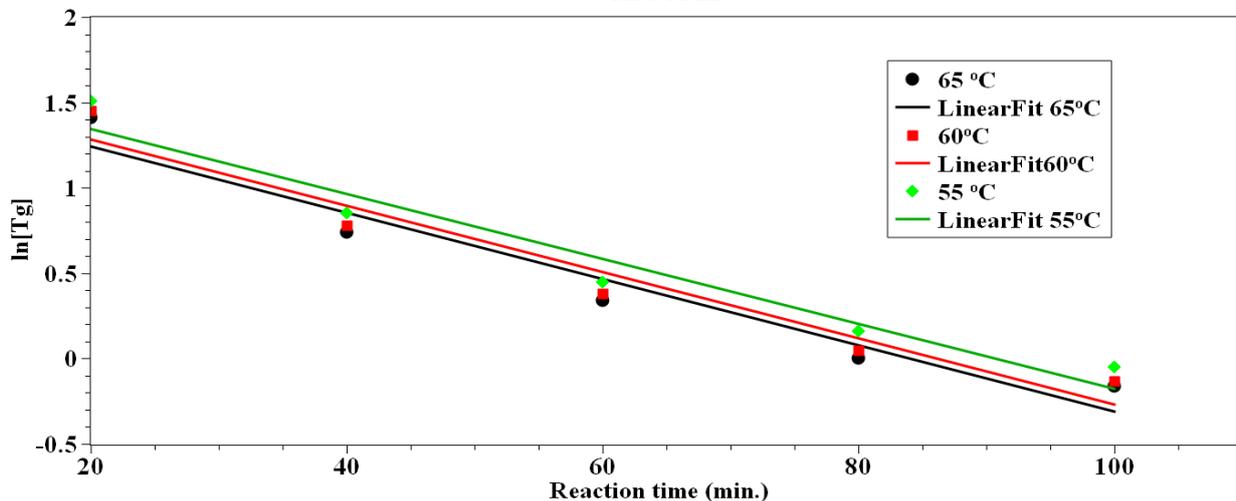

Fig. 6: First – order reaction irreversible model of triglycerides of later stage hydrolysis.
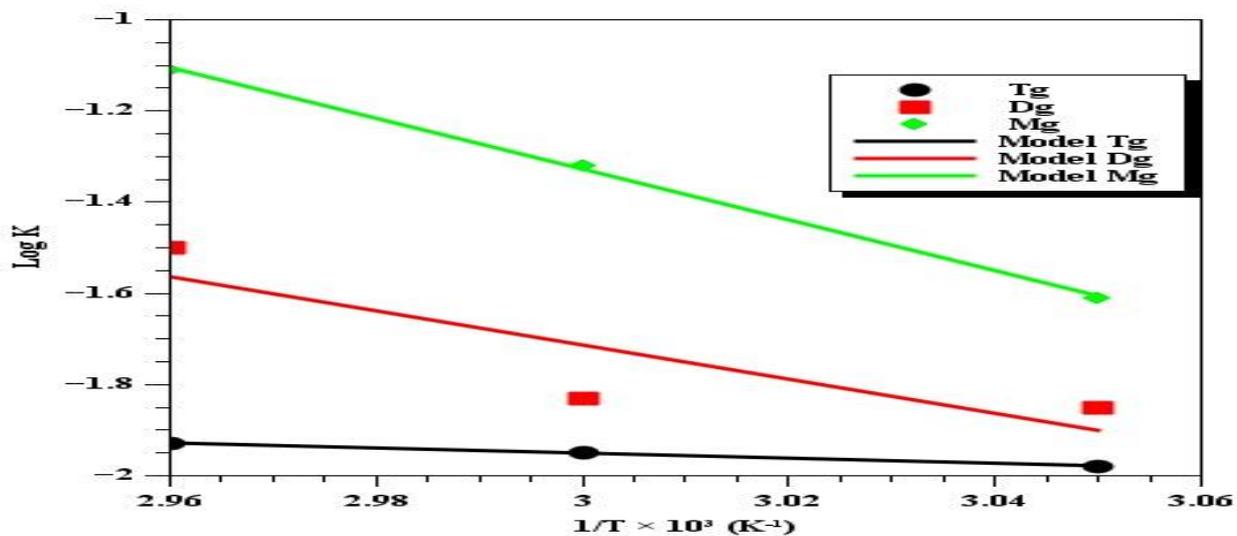

Fig. 7: Arrhenius plot of second order irreversible model reaction rate versus temperature.

Although, the kinetics of base-catalyzed transesterification of African pear seed oil is not widely documented in the literature, the results obtained in this study is comparable withprevious works on other feedstocks. The values 14.7 and 14.2 kcal/min obtained for Tg and Dg hydrolysis of palm oil has been reported in literature (Darnoko and Cheryan 2000) at same temperature. The values of rate constants for the Tg hydrolysis obtained in this research is about 4 times higher than that determined in (Darnoko and Cheryan, 2000) for palm oil at same conditions and about 2 times lower than the values reported in (Reyero et al., 2015) on the kinetics of NaOH catalyzed transesterification of sun flower oil with ethanol.

Also, the percentage conversion of Tg recorded for the seed oils ranged from 89-91% and this is agreement with 91% obtained by Zhang et al., (2010) and 98% obtained in (Darnoko and Cheryan 2000) after 1hour. The model predicts that maximum monoglycerides yield decreases as the reaction temperature increases. This could be due to the fact that the conversion of monoglycerides into glycerol has the highest activation energy among the three transesterification steps. The results show that kinetic constants of the first step (hydrolysis of Tg into Dg and biodiesel) has the smallest values. It is therefore slowest and the rate determining step. It is observed that k increased with temperature. The values of rate constants were used to determine the Arrhenius activation energy from the plots of reaction rate constant (k) versus the reciprocal of absolute temperature (T). Dg and Mg relationship with time followed the same trend with that of Tg. The lower activation energies obtained for the triglycerides hydrolysis indicate that temperature has a profound impact on the reaction according to kinetic theory. Then the higher activation obtained for monoglycerides hydrolysis clearly shows that higher temperature favours the reaction step more than the other steps with lower activation (for multiple reaction). The positive value of the activation energy supports the exothermic nature of transesterification process (Reyero, et al., (2015). The increase in k with temperature follows the magnitude of $k_{Mg}>k_{Dg}>k_{Tg}$ and in agreement with reports of Darnoko and Cheryan (2000). It was observed that triglycerides are the major constituents of the three tropical oil ($T_g>94.0\%$). Similar results have been reported by Kumar *et al.,* (2011), who obtained 92-93% of Tg for mahua oil and 90-92% for *jatropha* oil. However, the results are in contrast to the composition of pongamia oil with Tg, Dg and Mg found to be in the ratio of 42:26:11 (Mushtaq et al., (2014).

3.3   First-order irreversible model

By ignoring the intermediate reactions of diglyceride and monoglyceride, the three steps have been combined in a single step (Birla et al., 2012). 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 (Zhang, et al 2010). 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. The overall pseudo rate constants determined from the slopes of the straight line plots of ln [Tg] against t shown in Figure 7 are presented in Tables 4. As can be seen from Figure 6, in the reactions conducted at 55, 60 and 65°C, there was a decrease in the coefficient of determination for the pseudo first-order kinetic model. The coefficient of determination is especially important because the value of R^2 x100 represents the percentage of original uncertainty as explained by the linear model. Figure 5 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 ($R^2 > 0.97$). Similar results have been reported 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 (Dandikand Aksoy, 1992). Therefore, it could be that hydrolysis of some oils to methyl esters follows first-order irreversible kinetic models at low temperature ranges (20-40°C). The low temperature ranges is reported to favour the activity of native lipase better than at higher temperatures and this resulted in different mechanisms. But such low temperatures would not favour maximum ester yield in this study because they are far below the reported optimum temperature (Darnoko and Cheryan 2000). Darnoko and Cheryan (2000), has observed that at latter reaction stages (beyond 30 mins) of palm oil hydrolysis to methyl ester, the first-order or zero-order reaction model is the best fitted. Similar observation was made on this study where as from 20 minutes reaction, the reaction follows first-order model with high coefficient of determination ($R^2 > 0.94$). This is shown in Figure 6. These stages showed low reaction rate due to reduction in the reactants concentration. It implies that at low temperatures and

latter stages of methanolysis of the vegeatble oilsprogesses very slowly and follow first-order kinetic model.

Table 4: First-order model reaction rate constant for APSOME.

Glyceride	Temperature (°C)	Reaction rate constant (min^{-1})	R^2
Triglyceride	55	0.0431	0.80
	60	0.0437	0.80
	65	0.0439	0.80

CONCLUSION

Chemical Kinetic model has been developed for the NaOH – catalyzed methanolysis of African pear seed oils. The second order model describes very well the effects of temperature on the oil conversion and yields of final (biodiesel and intermediate Tg and Mg) transesterification products on irreversible basis. The

NOTATIONS

[Al]	Alcohol concentration
Al	Alcohol
APSO	African pear seed oil
APSOME	African pear seed oil methyl ester
A	Arrhenius constant
Dg	Diglycerides
[Dg]	Diglycerides concentration
E_a	Activation energy (kcal/min)
FAAE	Fatty acid alkyl ester
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
Gl	Glycerol
[Gl]	Glycerol concentration
k_1-k_3	Rate constants (wt%/.min)
Mg	Monoglycerides
[Mg]	Monoglycerides concentration
T	Temperature (K or °C)
t	Time (minutes)
Tg	Triglyceride
[Tg]	Triglyceride concentration

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kinetics of base-catalyzed methanolysis of APSO studied at three different temperatures (65°C, 60°C and 55°C) showed no initial lag phase (usually attributed to mass transfer) in the conversion of Tg. The seed oil conversion increased with increase in temperature. The initial time of reaction recorded high conversion. At about 40 minutes, complete conversion was achieved. The rate constants for APSO methanolysis showed highest values for Mg hydrolysis. However, there was obvious increase in rate constants with increase in temperature.

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