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Kinetic Studies of Esterification of Rubber Seed Oil with Homogeneous Acid Catalyst for Biodiesel Production

By

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Abstract

Kinetic studies of the esterification of free fatty acid (FFA) of rubber seed oil (RSO) for biodiesel production was investigated in this work. Esterification of RSO was carried out in batch experiments using a 1 litre round bottom flask placed on a constant temperature magnetic stirrer. The effect of catalyst concentration (1 – 2.5 vol.%), methanol to oil ratio (1:5 – 1:2 v/v) and temperature (45 – 60 °C) on the acid value (AV) of the fatty acid methyl ester (FAME) was investigated. Integral method of kinetic data analysis for constant volume batch reactor systems was used to study the reaction kinetics with the assumption that the reaction was irreversible. The AV of the FAME was found to decrease as the catalyst concentration was increased. It was also observed that methanol to oil volume ratio of 1:2 gave the least AV as time for esterification reaction was increased. At a temperature of 55°C, the least AV was recorded after esterification reaction time of 90 min. The kinetics of esterification revealed a second order reaction in FFA with an average rate constant of 0.267 L/mol min. Activation energy and collision frequency factor were also estimated to be 21.2091 kJ/mol and 671.155 L/mol min respectively.

***Keywords**: Kinetics, Esterification, Rubber seed oil, Biodiesel, Free fatty acid, Acid Value*

1. Introduction

Due to the non-renewable nature of fossil fuels coupled with the increasing demand for energy, researches into alternative sources of energy that are renewable are on the increase. Biofuels such as biogas, bio-ethanol and biodiesel synthesized from agricultural resources are considered excellent alternatives; not just because they are renewable and biodegradable, they are also non-toxic and are free of Sulphur and aromatic compounds, making them more environmentally friendly for use[1]. Biodiesel, one of such biofuels is a mixture of mono alkyl esters of fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats for use in compression ignition engine[2]. Biodiesel also known as fatty acid methyl ester (FAME), though is more expensive than the petroleum-based diesel, when produced to European Standard[3], it is reported to be of higher cetane number than petroleum diesel and can be used in compression ignition

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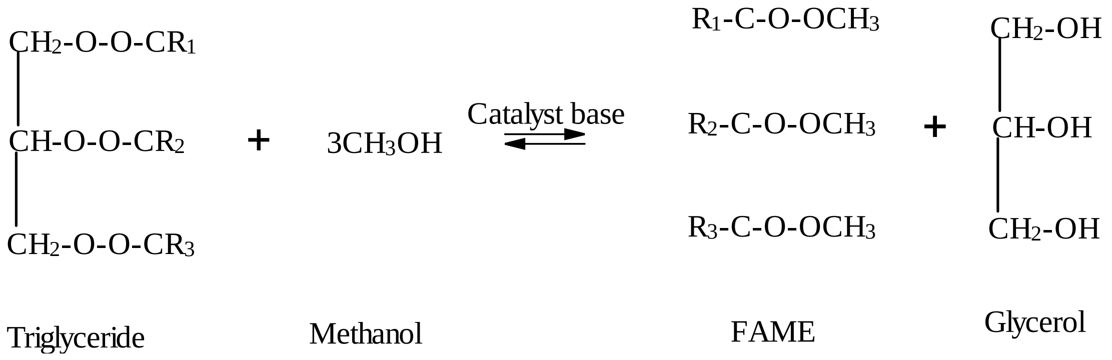
[1] Alenezi, R., Leeke, G. A., Winterbottom, J.M., Santos, R.C.D. and Khan, A.R. (2010). “Esterification kinetics of free fatty acids with supercritical methanol for biodiesel production”, *Energy Conversion and Management* 51: 1055-1059.

[2] Aransiola, E. F. Betiku, E., Ikhuomoregbe, D. I. O. and Ojumu, T. V. (2012). “Production of biodiesel from crude Neem oil feedstock and its emission from internal combustion engines”, *African Journal of Biotechnology* 11(22): 6178-6186.

[3] European Standard, EN 14214 (2008), “Automotive fuels – fatty acid methyl esters (FAME) for biodiesel engines – Requirements and Test Methods”.

engine without modification to the engine.[3] From an economic standing, agricultural resources for biodiesel production should be non-edible to avoid the food versus fuel crises[4]. Amongst the non-edible oils that have been used to produce biodiesel include, Jatropha, Pongamia, Karanja, castor, Neem Linseed, and rubber seed oil[5, 6-7]. Rubber (*Hevea brasiliensis*) is cultivated in abundance in Nigeria primarily for the non-edible latex which is tapped from the stem and the seed of this non-edible commercial crop has been found to be of high oil content[8, 9].

Conventionally, biodiesel is produced from vegetable oils by transesterification reaction provided that the free fatty acid (FFA) content of the oil is less than 1% as can been seen in Eq. 1. For oils having a FFA content of more than 1%, a two – step production process is required[10,11-12]. An acid catalyzed esterification step and an alkali catalyzed transesterification reaction[9, 10, 13].



$$\begin{array}{l} CH_2\text{-O-O-CR}_1 \\ | \\ CH\text{-O-O-CR}_2 \\ | \\ CH_2\text{-O-O-CR}_3 \end{array} + 3CH_3OH \xrightleftharpoons{\text{Catalyst base}} \begin{array}{l} R_1\text{-C-O-OCH}_3 \\ \\ R_2\text{-C-O-OCH}_3 \\ \\ R_3\text{-C-O-OCH}_3 \end{array} + \begin{array}{l} CH_2\text{-OH} \\ | \\ CH\text{-OH} \\ | \\ CH_2\text{-OH} \end{array} \qquad 1$$

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[4] Ahmad, J., Yusuf, S., Bokhari, A. and Kamil, R.N.M. (2014). Study of fuel properties of rubber seed based biodiesel, *Energy Conversion, and Management* 78:266-275.

[5] Agarwal, A. K. (2006). Biofuels (alcohols and biodiesel) applications as fuel for internal combustion engines. *Progress in Energy and Combustion Science,* doi:10.1016/j.pecs.2006.08.003

[6] Singh, S. P. and Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute for diesel: A review. *Renewable and Sustainable Energy Reviews* 14: 200 - 216

[7] Gui, M. H., Lee, K. T. and Bhatia, S. (2008). Feasibility of edible oil vs. non-edible oil as a biodiesel feedstock. *Energy* 33: 1646 - 1653

[8] Giroh, D.Y., Waizah, Y., Yustus, F.S. and Imarhiagbe, P. (2011), "Cost Analysis of On-farm Adaptive Research (OFAR) as a Strategy for Hevea Technology Transfer in the Rubber Belt of Nigeria", African Journal of Plant Science 5(14) 809-812.

[9] Ramadhas, A.S., Jayaraj, S. and MuraleedharanC. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel* 84 (4): 335–340.

[10] Pisarello, M.L., Dalla, C.B., Mendow, G. and Querini, C.A. (2010) Esterification with ethanol to produce biodiesel from high acidity raw materials – kinetic studies and analysis of secondary reactions", *Fuel Processing Technology* 91:1005-1014.

[11] Van, G.J.H. (2004) Biodiesel processing and production", *Fuel Processing Technology* 86 (10):1097-1107

[12] Mohammed, A.I. and Pillai, B.C. (2011). Optimization of process parameters for biodiesel extraction from rubber seed oil using central composite design. *International Journal of Production Technology and Management Research* 2 (1):23-31.

[13] Thiruvengadaravi, K.V., Nandagopal, J., Bala, V.S.S., Kirupha, S.D., Vijayalakshmi, P. and Sivanesan, S. (2009) Kinetic study of the esterification of free fatty acids in non-edible *Pongamia pinnata* oil using acid catalyst. *Indian Journal of Science and Technology* 2 (12):20-24.

The former may be considered a pretreatment step, because it serves to enhance the latter step by reducing the tendency of alkaline catalyst consumption via soap formation, which in effect complicates product separation when FFA contents of the oil is high as seen in Eq. 2.

$$\underset{\text{FFA}}{\text{R-COOH}} + \underset{\text{Sodium hydroxide}}{\text{NaOH}} \longrightarrow \underset{\text{Soap}}{\text{RCOONa}} + \underset{\text{water}}{H_2O} \qquad 2$$

Esterification is the reaction between a carboxylic acid and an alkanol resulting in the formation of alkyl–alkanoates. For biodiesel production, the carboxylic acids of interest are those with long alky chains found in lipids and the alcohols are those of short chain length usually methanol or ethanol. The esterification step which is a reversible reaction and acid catalyzed may also be considered a biodiesel (FAME) formation process since one of the products is FAME as shown in Eq. 3.[1,14,15].

$$\underset{\text{FFA}}{\text{R-COOH}} + \underset{\text{Methanol}}{CH_3OH} \xrightleftharpoons{H_2SO_4} \underset{\text{FAME}}{RCOOCH_3} + \underset{\text{water}}{H_2O} \qquad 3$$

This latter consideration would be reasonable when the biodiesel produced from esterification is significant and this is obtainable when the lipid feedstock has high FFA content, as may be indicated by high acid value (AV).

This study considers esterification as a pre-treatment step to biodiesel production and so reports AV as the response, rather than biodiesel yield as insisted on by Alenezi *et al.*[1].

Chemical processes are best run at optimum possible conditions and chemical reactors are designed with prior knowledge of the reaction kinetics. Therefore, it is pertinent to optimize the parameters and study the kinetics of esterification of FFA in oils for biodiesel production. Ahmad et al.[4] optimized the esterification of FFA in RSO using central composite design and reported optimum acid value reduction from 42% to 0.82% at 45 °C, 10 wt% catalyst, alcohol to oil molar ratio of 15:1, after 90 min. Also, Mohammed and Pillai (2011) worked with RSO and reported an optimum reduction of acid value from 38.45 to 1.66 mgKOH/g at methanol to oil molar ratio of 6.7 and sulphuric acid concentration of 0.9 w/v after 60 min of reaction at 64 °C. Thiruvengadaravi et al.[13] optimized FFA esterification of *Pongamia pinnata* oil and reported an optimum reduction from 15.96 to 2.42 mgKOH/g at methanol to oil molar ratio of 9:1, catalyst concentration of 1 wt% and temperature of 60°C. Alenezi et al.[1] studied the reaction kinetics with supercritical methanol without catalysis and reported FFA esterification as a reversible second order reaction with activation energy of 72 kJ/mol and a frequency factor of 500,000 L/mol.min for the forward reaction. Song et al.[16] studied the kinetics for esterification of oleic acid via zinc acetate catalysis and reported activation energy of 32 kJ/mol. Pisarello et al.[10] also reported reversible second order kinetics while Thiruvengadaravi et al.[13] studied the kinetics of esterification of FFA in non-edible *P. pinnata* oil using sulphuric acid catalyst and reported reversible pseudo first order kinetics with

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[14] Slinn, M. and Kendall, K. (2009). Developing the reaction kinetics for a biodiesel reactor", *Bioresource Technology* 100:2324-2327

[15] Shu, Q., Gao, J., Liao, Y. and Wang, J. (2011), "Reaction Kinetics of Biodiesel Synthesis from Waste Oil Using a Carbon-based Solid Acid Catalyst", *Chinese Journal of Chemical Engineering* 19(1) 163-168.

[16] Song, C., Qi, Y., Deng, T., Hou, X. and Qin, Z. (2010), Kinetic model for the esterification of oleic acid catalyzed by zinc acetate in subcritical methanol. *Renew Energy* 35: 625-628

activation energy of 280.1 J/mol for the forward reaction. Much has not been reported on the parametric optimization and kinetics of esterification of FFA in RSO for biodiesel production; thus, this study aims at optimizing the process conditions and investigating the kinetics of the esterification of FFA in RSO using sulphuric acid catalyst. The process conditions optimized in this study were methanol to oil volume ratio, catalyst concentration and reaction temperature

2. Materials and Methods

Rubber seed oil (RSO) with the physicochemical properties shown in Table 1 was purchased from Rubber Research Institute, Iyanomo, near Benin City, Nigeria Methanol (99.9% pure), potassium hydroxide, benzene, ethanol, sulphuric acid (98%) and phenolphthalein of analytical grade were purchased from Pyrex Nigeria Limited.

2.1. Esterification of Rubber Seed Oil

Esterification reactions were carried out in a 1 L round bottom flask which was placed on a temperature-controlled magnetic stirrer hot plate (Model No. HJ – 3D). The RSO was preheated to the desired temperature (45, 50, 55 and 60^{o}C) before the sulphuric acid catalyst - methanol mixture was added. The reactions were performed using different catalyst concentrations (1 – 2.5 wt %) and methanol to oil volume ratio (1:5 –1:2). The experiments were conducted over different reaction time intervals of 30, 45, 60, 75, 90 and 120 min. After the predetermined time interval, the reaction was stopped and the mixture was transferred into a separating funnel. The lower layer containing water was drained off and the oil rich phase was separated from the alcohol rich phase.

Table 1. Physicochemical Properties of Rubber Seed Oil

Property	Value
Density (27^{o}C)	916.24
Viscosity (27^{o}C)	4.96
FFA (%)	27.25
Acid value (mg KOH/g)	54.98
Saponification value (mg KOH/g)	192.67
Iodine number (g I_2/100g)	119.20
Fatty acids composition (mass %)	
Palmitic (C16:0)	15.4
Palmitoleic (C16:1)	1.98
Stearic (C18:0)	4.45
Oleic (C18:1)	30.48
Linoleic (C18:2)	40.80
Linolenic (C18:3)	1.05
Eicosanoic (C20:0)	4.92
Others	0.92

2.2. Determination of Acid Value, AV

The AV in the samples was determined by titration using the method described by Zhu *et al.*[17]. Briefly, 1g sample was weighed into a conical flask; 12 ml each of ethanol and benzene was added to the sample. The flask was swirled to allow for complete mixing and 2 drops of phenolphthalein were added. The mixture was titrated against a known concentration of potassium hydroxide, KOH, solution. The end point was determined to be the point at which a pink solution appeared and persisted for at least 15 seconds. Blank titration (without the sample) was also carried out and the AVs of samples were estimated using Eq. 4

$$\mathrm{AV(mgKOH/g\ of\ biodiesel)} = \frac{(V_S - V_B)M \times 56.1}{W} \qquad (4)$$

where,
V_S = volume (ml) of KOH solution needed for titration of sample.
V_B = volume (ml) of KOH solution needed for titration of blank.

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[17] Zhu, Y., Xu, J. and Mortimer, P. E. (2011). The influence of seed oil and oil storage on the acid levels of rubber seed oil, derived from *Hevea brasiliensis* grown in Xishuangbanna China. *Energy* 36: 5403 - 5408

M = concentration (moles/dm^3) of KOH solution.
W = weight of the sample (1g)

2.3. Kinetics of Esterification

The kinetics of the esterification reaction was studied at the estimated optimum catalyst concentration and methanol to oil volume ratio. Integral method of kinetic data analysis described for constant volume batch reactor systems by Levenspiel[18] was used to analyze the data, while assuming esterification was irreversible and that triglycerides were inert during the esterification. Eq.3 is the assumed stoichiometry while Eqs. 5 to 7 were considered for the integral analysis for first order in FFA, second order overall (in FFA and methanol) and second order in only FFA respectively.

$$ln\frac{C_{FFA\,0}}{C_{FFA}} = ln\frac{1}{1-X_{FFA}} = kt \tag{5}$$

$$ln\frac{M-X_{FFA\,0}}{M(1-X_{FFA})} = C_{FFA\,0}(M-1)kt = (C_{MeOH\,0} - C_{FFA\,0})kt \tag{6}$$

$$\frac{1}{C_{FFA}} - \frac{1}{C_{FFA\,0}} = \frac{X_{FFA}}{C_{FFA\,0}(1-X_{FFA})} = kt \tag{7}$$

where: $C_{FFA\,0}$ and $C_{MeOH\,0}$ are respectively the initial concentrations of FFA and methanol (at time, t = 0), $C_{FFA}$is the instantaneous concentration of FFA, X_{FFA} is the instantaneous conversion, k is the reaction rate constant and M is the initial reactant ratio ($C_{MeOH\,0}/C_{FFA\,0}$).

To determine the activation energy, the rate constants at respective temperatures were fitted into Arrhenius equation[19]. Eq. 8 is the Arrhenius equation while Eq. 9 is the linearized form of it.

$$k = Ae^{-\frac{E_a}{RT}} \tag{8}$$

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T} \tag{9}$$

Where: k is the reaction rate constant, A is the collision frequency factor also called the pre-exponential factor, E$_a$ is the activation energy, R is gas constant and T is temperature.

3. Results and Discussion

3.1 Effect of Catalyst Concentration on the Acid Value of FAME

The effect of catalyst concentration on the AV of the esterified RSO is shown in Fig. 1. The catalyst concentration was varied from 1 to 2.5 vol. %, while keeping the reaction temperature and methanol to oil volume ratio constant at 60^{o}C and 1:5 respectively. Catalyst concentration of 1vol..% gave a distinctively high acid value (the least conversion) all through while 2 vol.% concentration gave the highest conversion beyond 75 min. The lowest AV obtained was 1.96 mg KOH/g at 90 min. It was observed that the AV of the esterified RSO remains constant beyond

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[18] Levenspiel, O. (1999), “Chemical Reaction Engineering”, John Wiley and Sons, 3rd edition, 38 – 82.

[19] Missen, R. W., Mims, C. A. and Saville, B. A. (1999). Introduction to chemical reaction engineering and kinetics. John Wiley and Sons, Inc. 1st edition

reaction time of 90 min. Generally, it was observed that increasing catalyst concentration reduces the AV of the esterified RSO.

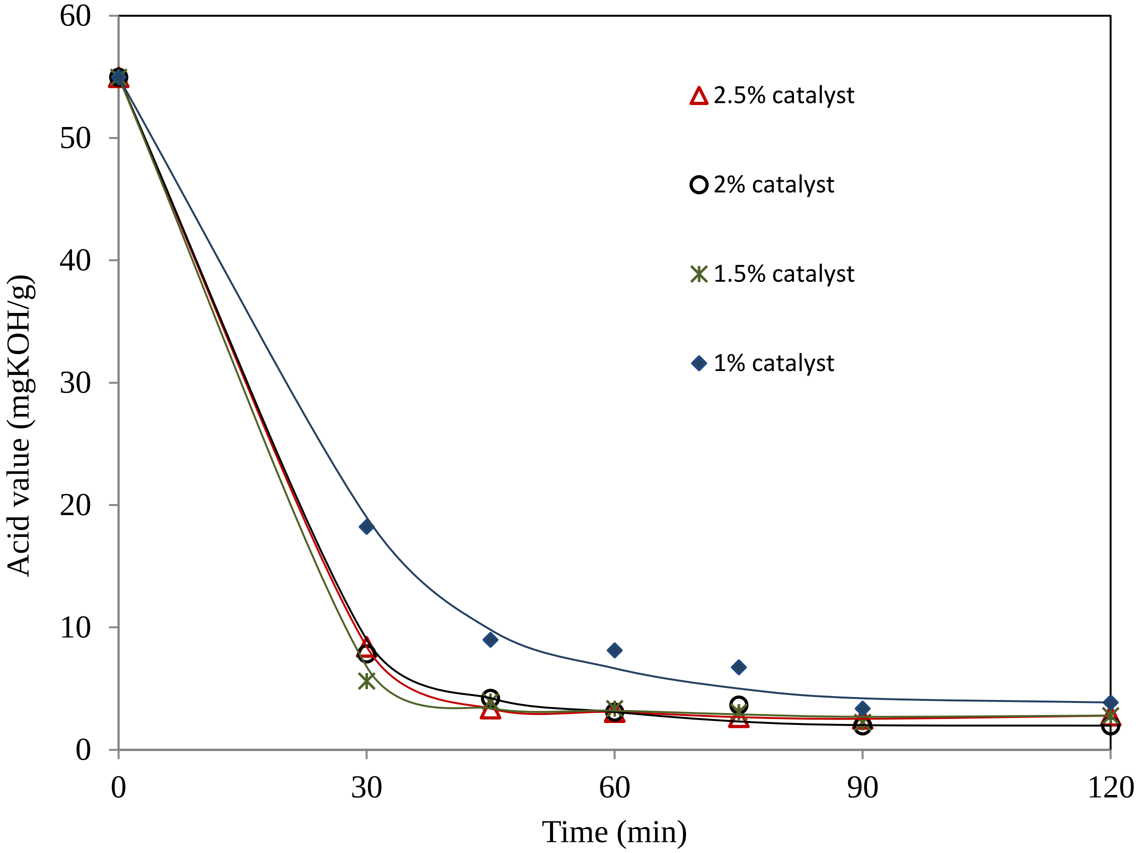

Fig. 1 Effect of Catalyst Concentration on the AV of Esterified RSO

Effect of Methanol to Oil Volume ratio on the Acid Value of FAME

Fig. 2 shows the effect of methanol to oil volume ratio on the AV of the esterified RSO at a reaction temperature of 60°C and catalyst concentration of 2 vol. %. The figure shows that methanol to oil volume ratio of 1:5 and 1:2 gave the highest and lowest AV respectively during the course of the experiments. The AV of the esterified RSO tends to attain a constant value beyond a reaction time of 75 min. The least AV (1.12 mgKOH/g) was obtained at 90 min using a methanol to oil volume ratio of 1:3

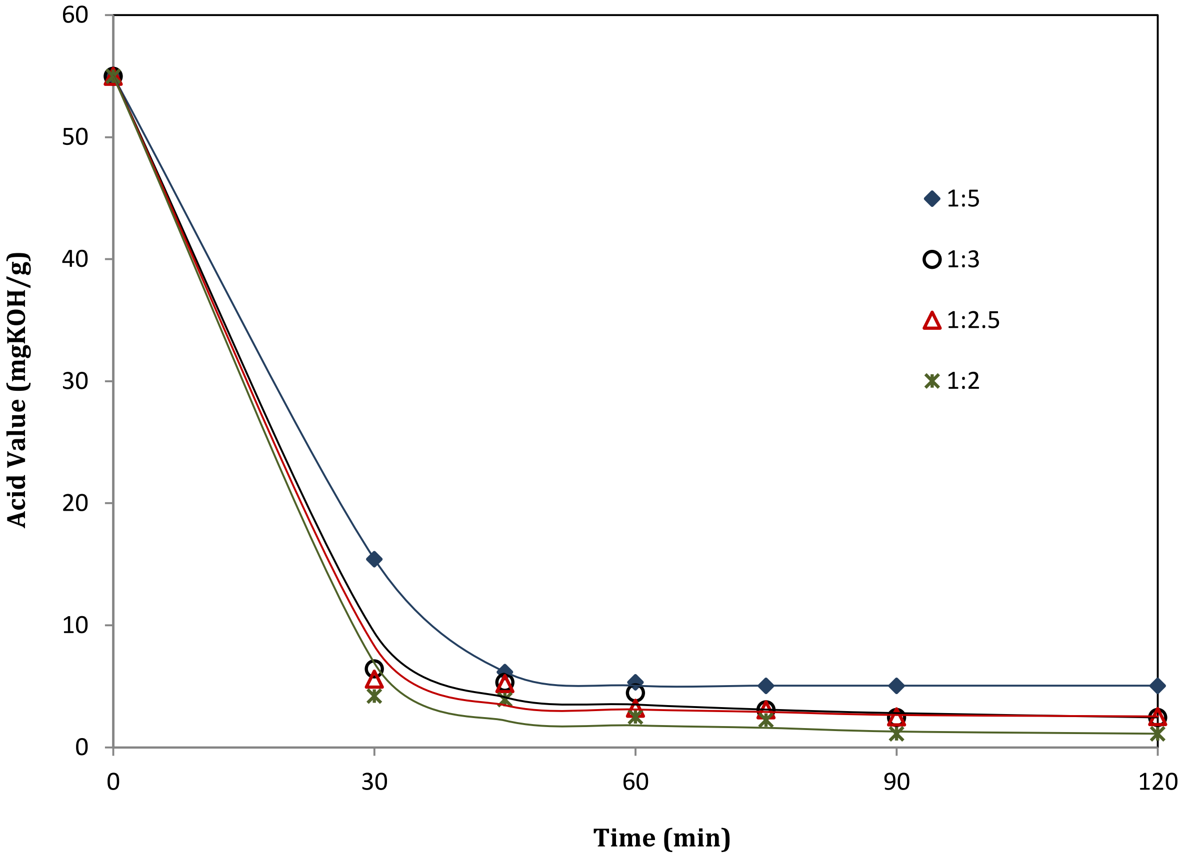

Fig. 2. Effect of Methanol to Oil Volume Ratio of AV of Esterified RSO

3.2 Effect of Temperature on the Acid Value of FAME

The effect of temperature variation on the AV of esterified RSO is shown in Fig. 3. Both the catalyst concentration and methanol to oil ratio were kept constant at 2 vol. % and 1:3 v/v respectively. It was observed that at a temperature of 55°C, the least AV was obtained, which was followed by that carried out at 60°C. It has been reported by Levenspiel[18] that increase in temperature increases reaction rate, but conversion does not necessarily increase with temperature. It was also observed that the highest AV for the esterified RSO was obtained at a temperature of 50°C.

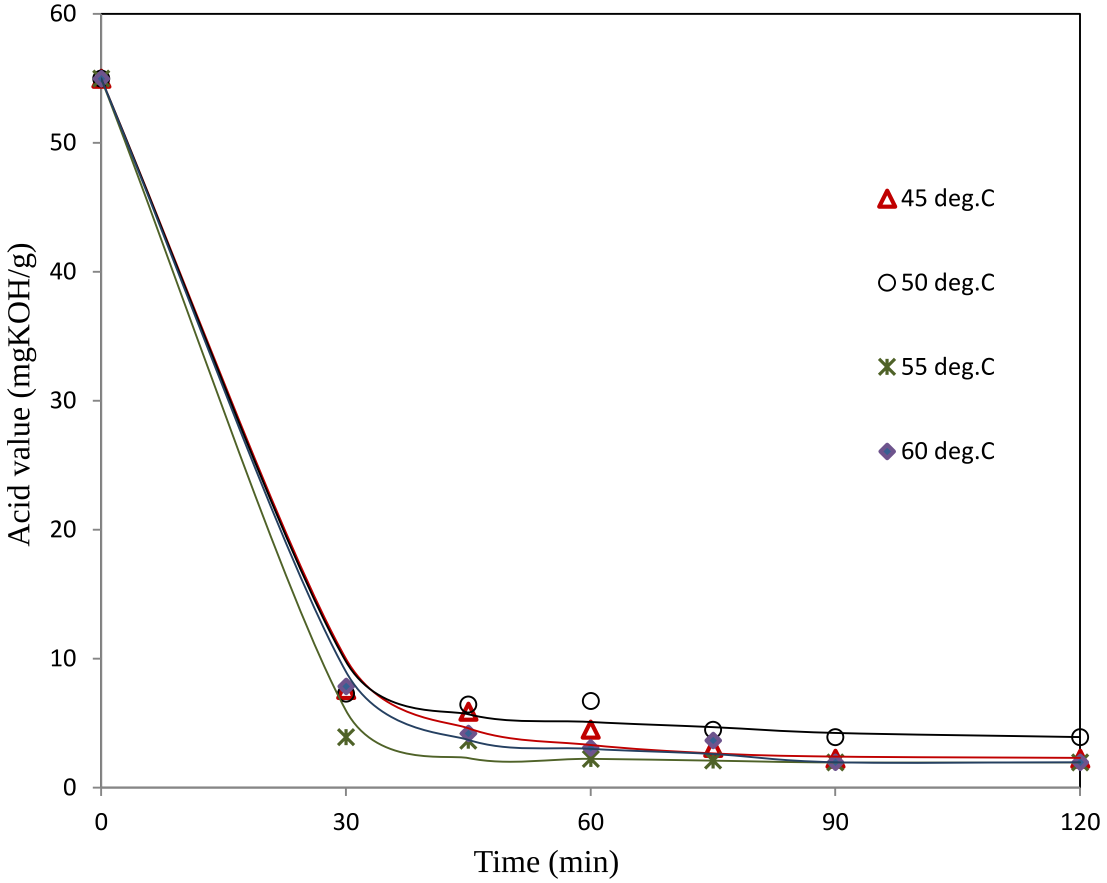

Fig. 3 Effect of Temperature on the AV of Esterified RSO

3.3 Optimum Process Parameters for Esterification of RSO

Based on the results obtained from the effect of the different variables on the AV of the esterified RSO, the optimum process parameters for the esterification of the RSO were taken as: catalyst concentration of 2 vol.%, reaction temperature of 55 ^{o}C and methanol to oil volume ratio of 1:2 At the chosen optimum conditions, a minimum AV of 1.12 mgKOH/g of oil was attained after 90 min as shown in Fig.3. In a similar study, Mohammed and Pillai [12] reported an optimum reduction of AV from 38.45 to 1.66 mgKOH/g at methanol to oil molar ratio of 6.7 and sulphuric acid concentration of 0.9 w/v after 60 min of reaction at 64 ^{o}C. Thiruvengadaravi *et al*.[13] reported an optimum reduction from 15.96 to 2.42 mgKOH/g at methanol to oil molar ratio of 9:1, catalyst concentration of 1 wt% and temperature of 60^{o}C, while Ahmad *et al*.[4] reported an optimum acid value reduction from 42% to 0.82% at 45 ^{o}C, 10 wt% catalyst, alcohol to oil molar ratio of 15:1, after 90 min.

3.4 Kinetic Studies of Esterification of RSO

The experimental data at varied temperature were fitted into Eqs.5 to 7, in search of the best fit, as the integral method of kinetic data analysis involves trial and error. Figs 4 - 6 show typical plots of the data at 45 ^{o}C. In the same manner, the kinetic data at other temperatures were analyzed and the results are shown in Table 2.

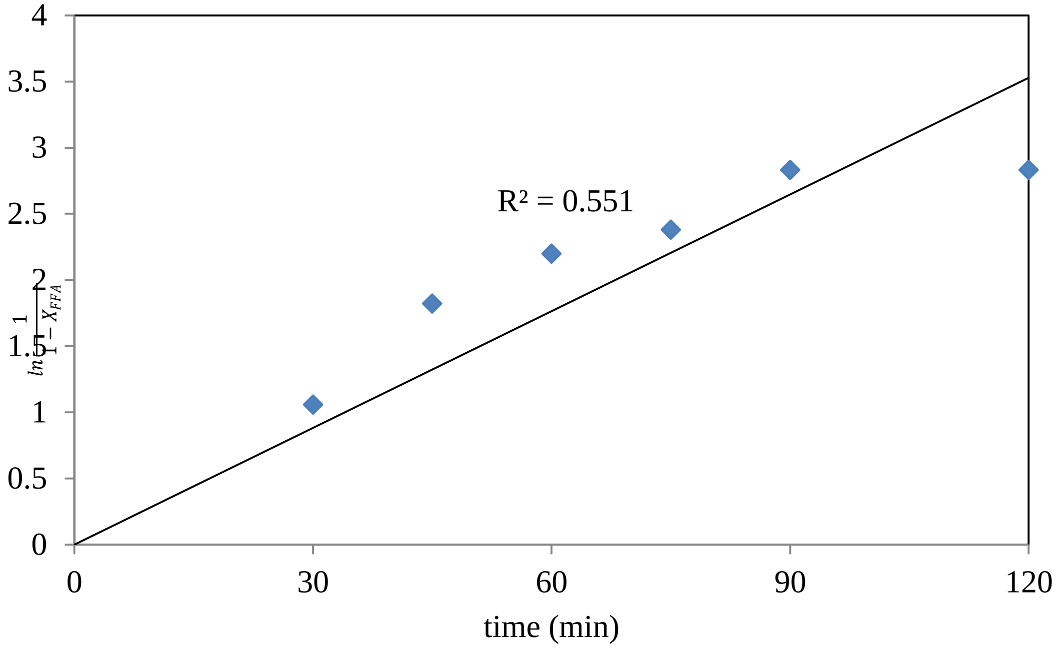

Fig. 4 Fitting of Kinetic data at 45°C to First Order Kinetics

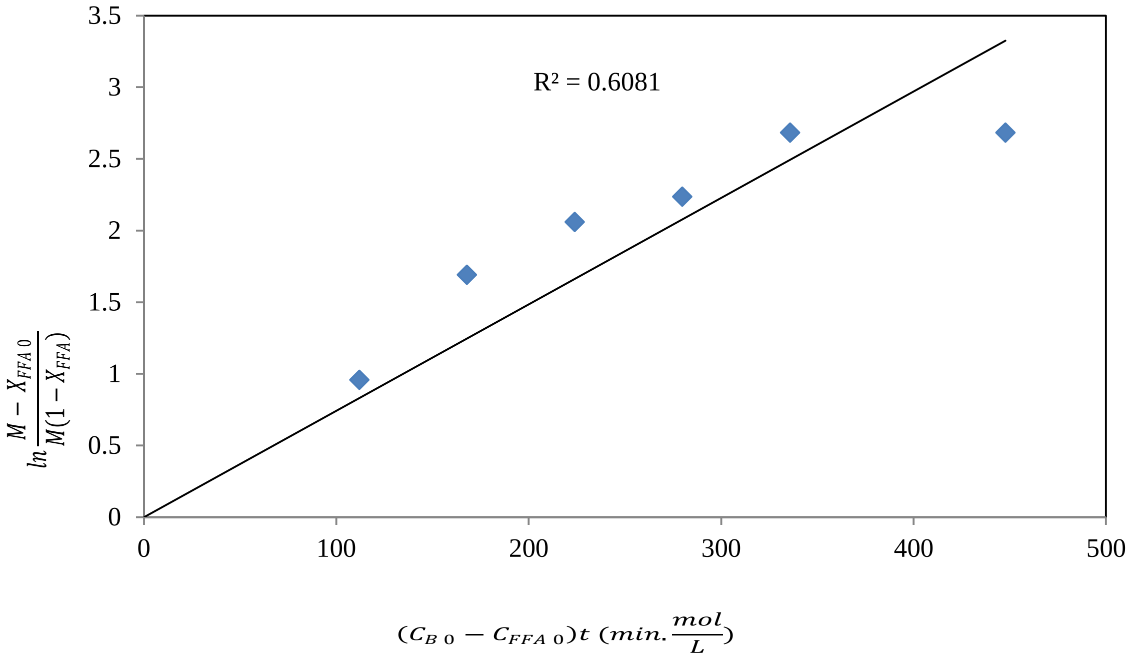

Fig. 5 Kinetic data plot at 45 °C to a 2nd order with respect to FFA and Methanol

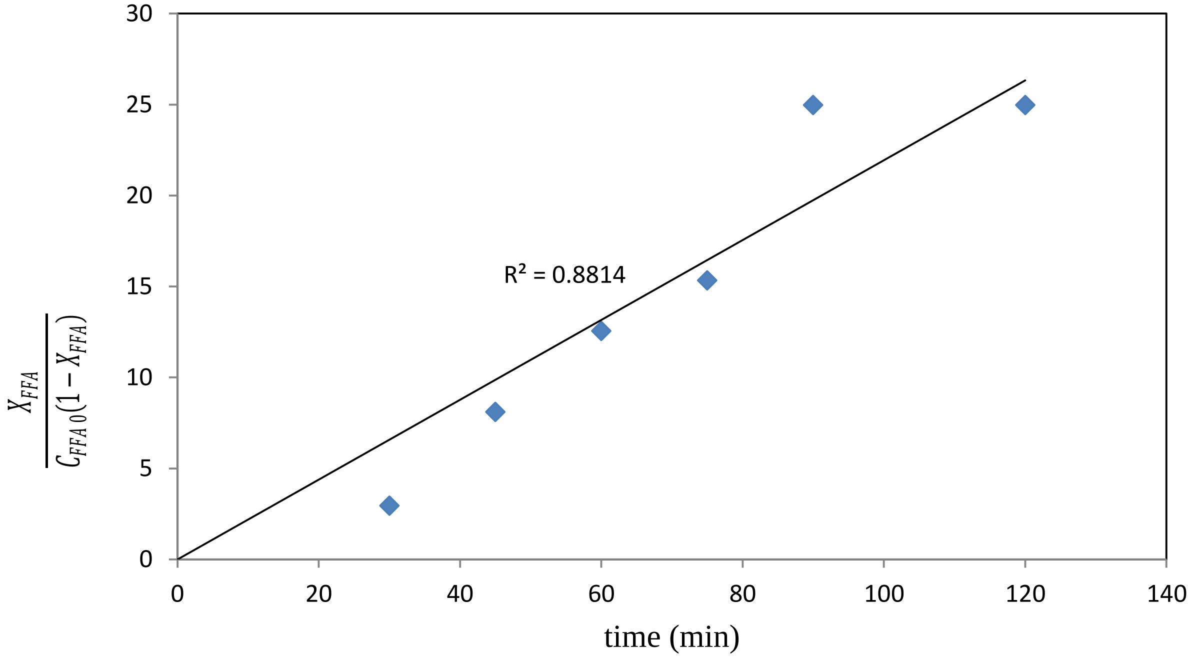

Fig. 6. Kinetic data plot at 45 °C to a 2nd order with respect to FFA

It can be deduced from the table that changes in temperature did not significantly affect the reaction rate constants (k) for first order in FFA and second order in FFA and methanol, besides their poor correlation coefficient(R^2) values indicate lack of fit. The reaction rate constant values for second order kinetics in FFA were not just of better fit (greater R^2 values), but they also followed an increasing trend with increasing temperature. The average R^2value obtained was 0.946 based on the second order in FFA content. As a result, second order kinetics in FFA was chosen and utilized to estimate the thermodynamic constants in Arrhenius equation to enable the prediction of kinetics at any temperature.

Table 2. Results from the integral analysis of kinetic data

		1st Order in FFA		2nd Order in FFA and CH_3OH		2nd Order in FFA	
T (°C)	1/T (K^{-1})	k (min^{-1})	R^2	k (L/mol.min)	R^2	k (L/mol.min)	R^2
45	0.003145	0.029	0.551	0.007	0.608	0.219	0.881
50	0.003096	0.031	0.204	0.007	0.310	0.256	0.961
55	0.003049	0.036	0.187	0.009	0.315	0.267	0.965
60	0.003003	0.038	0.036	0.008	0.173	0.323	0.976

The temperature dependence on the reaction rate constant was also verified by applying Arrhenius equation (Eq. 9). The effect of temperature on the rate constant of esterification of RSO is shown in Fig.7.The high R^2 value of 0.95 is an indication that the result is in accordance with Arrhenius' findings. An activation energy of 21.209 kJ/mol and pre-exponential or collision frequency factor of 671.155 L/mol.min were calculated.

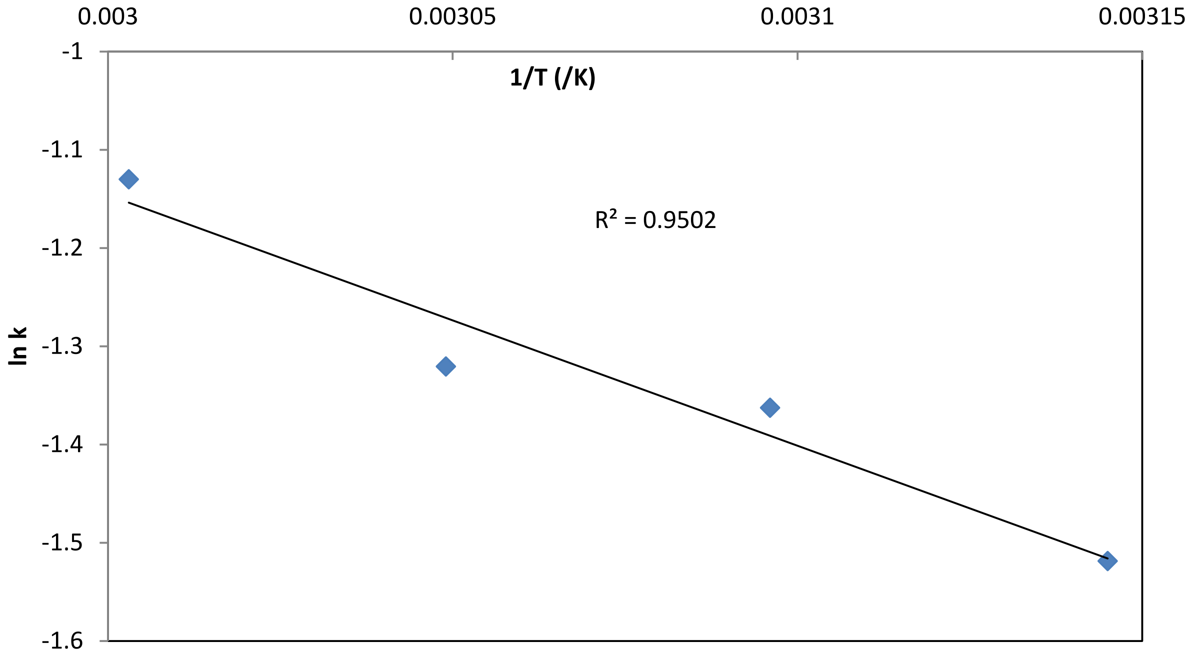

Fig. 7 Effect of Temperature on the Rate constant of Esterification Reaction of RSO

Furthermore, when compared with literature values, Song et al.[16] reported, 32 kJ/mol for esterification of oleic acid via zinc acetate catalysis, Alenezi et al.[1] used supercritical methanol without catalysis and reported FFA esterification as a reversible second order reaction with a forward reaction activation energy of 72 kJ/mol and a frequency factor of 500,000 L/mol.min. Pisarello et al.[10] using various oils and homogeneous acid catalyst also reported reversible second order kinetics but Thiruvengadaravi et al. [13] reported reversible pseudo first order kinetics with activation energy of 280.1 J/mol for the forward reaction. This study reported a higher value of activation energy of 21.2091 kJ/mol for the forward reaction while assuming the reaction to be irreversible, since excess methanol was used.

Finally, the idea of activation energy tells how much work needs to be done to achieve a chemical change, the smaller the value, the less the work and catalysts act to reduce this energy barrier. Therefore, higher literature values of activation energy reviewed, could be an indication of a less effective catalyst than that used in this study or an entirely more stable system.

4. Conclusion

Homogeneous esterification of RSO with methanol using sulphuric acid catalyst was carried out at various temperatures, catalyst concentrations, methanol to oil ratios and reaction times. The best response (least acid value) value was attained at the highest methanol to oil volume ratio of 1: 2, catalyst concentration of 2 vol. % and at a temperature of 55°C. The kinetics of the reaction was studied and it was found to be a second order in FFA having an average R^2 of 0.946. Activation energy for the esterification of RSO was 21.209 kJ/mol. Results obtained from this research show that high methanol to oil volume ratio favours FFA conversion and esterification of FFA in RSO follows a second order kinetics in FFA.