Kinetics Study of Balanites Aegyptiaca Oil Transesterification for the Production of Biodiesel

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ABSTRACT:

In this study, transesterification of Balanites aegyptiaca oil employing a homogeneous catalyst (NaOH) was conducted in a reactor with methanol. The transesterification reaction at 6:1 methanol to oil ratio with 1wt% catalyst was studied at 35^oC, 40^oC, 45^oC, 50^oC and 55^oC. An attempt is made to determine the rate of transesterification of Balanites oil by measuring the rate of formation of methyl oleate using GC-MS technique. The concentration of the product (m-oleate) will be monitored by measuring the peak area of GC-MS chromatogram. A kinetic model together with relevant parameters like reaction order, rate constants and Arrhenius parameters would be estimated. It was realized that, first order kinetic model applies with rate constants (k) of $1.41x10^{-1}$, $1.38x10^{-1}$, $3.2x10^{-2}$, $1.28x10^{-1}$ and $1.39x10^{-1}$ moles/sec. for the transesterification process at the prescribed temperatures. A general decrease in the reaction rate with increase in temperature was observed. The transesterification process didn't proceed in accordance with the Arrhenius equation. This means, although the kinetic model and rates of constants were determined, the activation energy (E) and the frequency factor (A) couldn't be estimated for the process.

Keywords: Balanites oil, GC-MS technique, Kinetics, Quantitative determination and Conc-Time Data

INTRODUCTION

Most of the energy consumed in the world today comes from fossil fuels namely; coal, natural gas and oil. These sources are finite and will be exhausted in the near future [1]. Industrialization and population growth at a global level has led to a terrific increase in energy utilization. Combustion of fossil fuels generate emissions that are hazardous and adversely affect human health. Focus is now shifted to the use of renewable energy resources in anticipation of the exhaustibility of fossil fuel reserves and the growing concern for the environment [2, 3]. It is expected that alternative fuels have the potentials to solve the depletion problem of petroleum sources and the concerns towards the environment, global warming and sustainability issues.

Biodiesel with many significant attributes over diesel fuel has gained researchers attention for some time due to being green, non-toxic, biodegradable, renewable and environmentally benign; hence is a fuel for the future that can replace diesel [4]. Conventionally, biodiesel is produced by trans-esterification of triglyceride feedstock usually: vegetable oil, animal fat and used cooking oil. The triglyceride would be treated with methanol/other short chain alcohols with a catalyst. Homogeneous base catalysts are mostly used in industrial biodiesel production because trans-esterification reaction proceeds with fast rate under mild reaction conditions. However, separation of the catalyst and purification of the products require large

amount of water [5, 6]. However, studies on the influence of the triglyceride composition on the biodiesel properties are insufficient [7, 1]. Many authors have reported on trans-esterification reaction employing different homogeneous and heterogeneous catalysts using various types of oils. Both catalysts have their merits and demerits. Heterogeneous catalysts like metal oxides (CaO, MgO and ZnO), hydrotalcites (Mg-Al), Zinc aluminates, Heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$), Organosulphonic acid and Zinc acetate on silica are some of the solids acid/base catalyst employed for trans-esterification. Some of the widely reported Homogeneous catalysts are NaOH, KOH, carbonates and alkoxides like sodium methoxide, ethoxide, propoxide, and acids such as sulphuric, phosphoric and organic sulphonic acids. Homogeneous catalysis route through relatively fast and high conversion [8]. When acid catalysis is employed, oil component of low grade material can be trans-esterified. It is comparatively cheaper than heterogeneous catalysis. However, the latter exhibits moderate conversion and allows catalyst recovery for reuse. Heterogeneous catalysis methodology can be processed using continuous fix bed operation which has limited use with the former [9]. Various researches have been reported on trans-esterification reaction, particularly process optimization with reference to extremely important parameters to enhance reaction rate and product quality. Reaction rate and yield are controlled by some factors viz: catalyst, feedstock, oil/alcohol ratio, presence of FFA's and water, as well as pressure, agitation speed and temperature [10, 11]. The intricacy of dependence of reaction rate and reactant conversion on various factors, arose interest in monitoring trans-esterification to understand biodiesel production process [12].

Table 1: Properties of *Balanites aegyptiaca* oil.

Parameters	*Balanites* oil
Moisture (%)	0.54±0.01
Density (g/cm^3) @ 20°C	0.92±0.00
Sap. value (mgKOH)	167.60±1.88
Free fatty acids (%)	0.65±0.01
Kin. Viscosity @40°C (cSt)	36.10±0.15
Pour point (^{o}C)	-2.5±0.44
Ash content (%)	0.22±0.03
Iodine value (gI$_2$/100g)	105.65±3.54

The study of fuel potentials of perennial crops like palm, olive, palm kernel, ziziphus and jatropha oilseeds instead of the annually harvested crops such as pumpkin, rape, soy and cotton seeds etc., marked an obvious shift from the annually replanted crops to the perennial ones [13]. There is a need for renewable energy supplies that will not compete with the food crops. Biofuels would be of greater benefits only if their biomass feedstock were reproducible with low agricultural input such as less energy, fertilizer and pesticide and could be produced on land with low agricultural value (marginal land,

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wild crops [14]. *Balanites aegyptiaca* L. (Desert date) belongs to the family *Zygophyllaceae*; highly adapted to the drier parts of Africa and south Asia. The tree is distributed in most arid desert environments and is always green even in the worst drought, with wide ecological distribution [15]. A Desert date tree is an underutilized specie which produces up to 10,000 yellow date-like fruits annually on a mature tree in good condition. So far the planting of the tree is not reported but is found in ample. Each fruit consists of an epicarp, pulp, an endocarp and a kernel. The kernel yields a highly stable oil up to 44-48% [16]. As reported by[17]; more than 4,000,000 ton of Desert date fruits are naturally and widely produced in Sudan and most of this is available for oil extraction. Properties of *Balanites* oil are listed in **Table 1**. Although many authors investigated the kinetics of homogeneous catalyzed alcoholysis of triglycerides taking several process variables (oil/alcohol ratio, catalyst, agitation speed, temperature, etc.) simultaneously; since these information are necessary at arriving on standard operating conditions to achieve maximum yields [18]. The objective of this work is to investigate the kinetics of transesterification of *Balanites aegyptiaca* oil into biodiesel at various temperature range of $35^{o}C$ to $55^{o}C$ to obtain an optimal value for maximum alkyl ester yield. An additional goal of the study is to measure the associated reaction rate constants at the temperatures mentioned and estimate the transesterification route as first or second order rate-law compliant.

MATERIALS AND METHODS

Materials

Methanol, Hydrochloric and Ethyl acetate (BDH Poole), NaOH (Fisons, UK), pure Oleic acid (Qualikems), distilled water and *Balanites* oil. Chemicals used in the experiment were of analytical reagent (AR) grade.

Equipment

A $50cm^{3}$ borosil glass reactor, GC-MS machine (6890N, Agilent), centrifuge machine-800 (400r/min), water-bath with stirrer to control and monitor mixing as well maintain constant temperature (Equitron, GD-100 Grant; USA), Vortex mixer (SA8; 1000r/min Stuart, Germany) Density/Specific gravity meter (DA 500; Japan), vials ($10cm^{3}$, spodex) $5cm^{3}$ and $1\mu L$ syringes, ice-bath and refrigerator.

Reaction Conditions

Trans-esterification of *Balanites* oil was carried out under the following conditions: 6:1 M methanol/oil, 400 rpm stirring, 0.33g NaOH per 27.6g of oil, and $35^{o}C$ to $55^{o}C$ reaction temperature.

Experimental Procedure

Methods reported by [19, 20], were adapted with slight modifications in this test. To obtain 6:1 M ratio of methanol to *Balanites* oil, $7.6cm^{3}$ of methanol was reacted with $30cm^{3}$ oil. The reactor (a $50cm^{3}$ volumetric flask) was charged with oil ($30cm^{3}$), stoppered with cork fitted with a stirrer and placed in circulation water bath at $35^{o}C$. CH_3OH and NaOH were mixed and heated separately to $35^{o}C$ and added to the reactor. The stirrer and stopwatch started immediately and reaction monitored by measuring methyl ester formed using GC-MS. For the estimation of methyl ester produced as a function of time, $2cm^{3}$ of reaction sample was collected at intervals of 10minutes for a period 60 minutes using a $5cm^{3}$ pre-cooled syringe.

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The sample aliquot was placed immediately in a pre-cooled test-tube and few drops of 0.5MHCl were added to the solution, closed and placed in ice-bath kept below 0^oC to quench the reaction. Mixture was washed severally with distilled water, shaken vigorously and kept until the aqueous and organic phases separated. Upon washing; glycerol, CH_3OH and remaining NaOH or HCl solutions were transferred to the water phase which was discarded. The organic phase which contained the ester was centrifuged to ensure thorough separation and then transferred to a vial which was closed, labelled and kept below 0^oC in a refrigerator for subsequent analysis using GC-MS. This process was repeated for each reaction sample collected at interval of 10 minutes; thus six methyl ester samples were collected over the 60 minutes period with the reactor temperature kept at 35^oC. Each of the six methyl ester samples was analysed using GC-MS to generate time versus concentration data at 35^oC. For the same oil, above procedure was repeated at 40, 45, 50 and 55^oC.

Background Theory

The mechanism proposed for trans-esterification of *Balanites* oil is composed of a series of reversible decompositions of TG to DG, DG to MG, and MG to GL. Each step consuming 1mole of A and producing 1 mole of E as in the following equations [20].

$$TG + A \rightleftharpoons DG + E$$

$$DG + A \rightleftharpoons MG + E$$

$$MG + A \rightleftharpoons GL + E$$
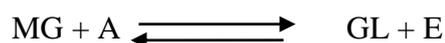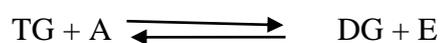
The overall reaction is given as:

$$TG + 3A \rightleftharpoons GL + 3E \text{ ----------- (\#1)}$$

Where TG is triglyceride, DG is diglyceride, MG is monoglycerides, A is alcohol E is ester

and GL is glycerol. Equation #1 shows that the rate of trans-esterification reaction could be determined by either measuring the disappearance of TG or formation of GL or E. In this work, an attempt is made to determine the rate of trans-esterification of *Balanites* oil by measuring rate of formation of methyl-oleate using GCMS technique. The concentration of methyl-oleate will be monitored by measuring the peak area of GCMS chromatogram. Generally, quantitative analysis in chromatography is based on measurement of the Peak Area of chromatographic peak which is proportional to the quantity of given component in the linear response area. This is achieved by addition of an internal standard to the solution of the unknown sample. The response factor is measured using standard measure and the quantity of unknown component is calculated using the following equation [21].

$$X = \frac{S.Ax}{F.As} \text{ --------------------------------\#2.}$$

Where, A_x is the peak area of the analyte sample;

A_s is the peak area of the internal standard, S is the concentration of the internal standard, X is the concentration of the analyte and F is the response factor. However, in this work a different approach is attempted which is based on the calibration curve method as employed in Flame Photometry and Atomic Absorption methods. Thus, a calibration curve will be produced by derivitization of Analar grade Oleic Acid to produce Methyl oleate which will be monitored using GCMS. In this case, the Peak Areas of 2,4,6,8 and 10% Methyl oleate will be plotted against the concentration (in percentage), a relatively good straight line would confirm the proportionality of the peak area to the concentration of the methyl oleate. The concentration data will then be used for kinetic analysis for the trans esterification of the

oils. From equation #1, the rate of trans-esterification could be written as:

Rate of production of Methyl Oleate

$$= \frac{1}{3}\frac{dc}{dt} = KC^n$$

Where C = concentration of methyl ester, K = rate constant, n = reaction order

On separation of variables and integration we get:

$$\int_{c1}^{c2} \frac{dc}{c^n} = 3k \int_{t=1}^{t=2} dt \text{- ----------#3}$$

For First Order (n=1), integration of equation #3 gives:

$$LnC_2 — Lnc_1 = 3k (t_2 — t_1) \text{ ---------#4,}$$

So that the rate constant (k_1) for First Order is given by

$$k_1 = \frac{(LnC_2 - LnC_1)}{3(t_2 - t_1)} \text{- --------------#5.}$$

For Second Order (n=2), integration of equation #3 gives:

$$\frac{1}{C_1} - \frac{1}{C_2} = 3k_2(t_2 - t_1) \text{ ------------#6,}$$

So that the rate constant (k_2) for Second Order is given by

$$k_2 = \frac{C_2 - C_1}{3C_1C_2(t_2 - t_1)} \text{ --------------------#7.}$$

Equations 5 and 7 will be used separately to compute the rate constants for trans-esterification of the *Balanites* oil at given time intervals for given temperature. If the rate constants remain the same for the considered intervals for any of the equations, that equation is considered as indicative of the mechanism. Thereafter, the rate constants will be used to calculate the activation energy (E) of the reaction using the Arrhenius equation:

$$k = Ae^{-E/RT} \text{------------#10.}$$

This is normally recast into the logarithmic form as follows:

$$Ln\, k = Ln\, A - \frac{E}{RT} \text{ -------------#11,}$$

Where k = rate constant; A = pre-exponential factor, E = activation energy (J·mol⁻¹); R = gas constant (8.314J·mol⁻¹·K⁻¹); and T = temperature (K).

Product Analysis

The analysis of methyl esters of *Balanites aegyptiaca* was accomplished using GC-MS (AGILENT, 6890N series) machine. One microliter of the methyl ester sample was introduced into the gas chromatograph at injector temperature of 250°C. The column temperature was programmed from 120°C to 250°C at a linear flow rate of 5°C/min, hold 5 min at 260°C. The chromatographs obtained were scanned and the biodiesel components were identified based on software matching with mass spectra.

RESULTS AND DISCUSSION

A concentration (%) versus time (mins) curve for the transesterification of Balanites oil at 35°C is

presented in Figure 3.2. The figure reveals an undulating curve consisting two peaks and one trough which implies a two stage production and decomposition of Methyl Oleate (m-oleate); or a reversible trans-esterification process. Very similar curves were produced at 40°C, 45°C, 50°C and 55°C as shown in Figures 3.2, 3.3, and 3.4. This is contrary to a typical concentration versus time plot for production process which would normally be a smoothly rising curve that will approach a plateau as the production ceases.

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It is obvious, that the usual approach of testing the Concentration-Time data for order-reaction (first, second or third) will not apply for first order kinetics for the data obtained at 35°C. However, careful inspection of the undulated Concentration versus Time plots suggests a latent trend in the production of m-oleate. It then became imperative to carry out a mathematical trend analysis on the Concentration versus Time plot. Moreover, due to the challenges of integrating the GCMS peak data,
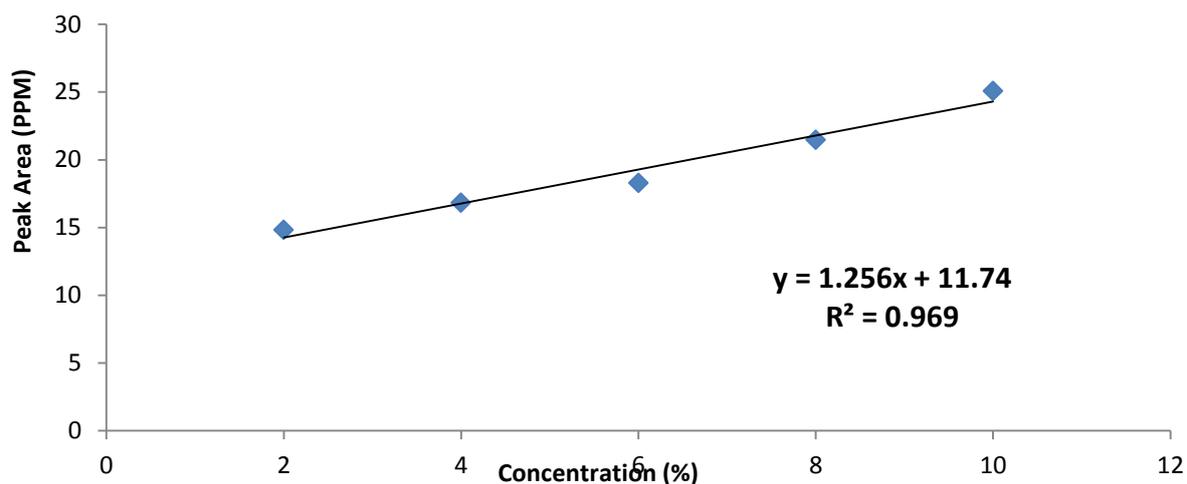

Figure 3.1: Standard Calibration Plot for Methyl Oleate

It was necessary to smoothen the Concentration-Time plots using appropriate polynomial equations and juxtaposed plots shown in Figures 3.2 to 3.4. The smoothed curves were used to generate a refined Concentration data at 10, 20,30,40,50 and 60 minutes for the five temperatures as shown in Appendix IA. The datum were then used to test for First, Second and Third Order Kinetics (Appendix IB). The plots obtained for the transesterification process are shown in figures 3.5 to 3.8. It is obvious that the First Order Kinetic model applies with rate constants (k) of 0.141, 0.128, 0.032, 0.138 and -0.139 mol/sec. for the transesterification process at 35°C, 40°C, 45°C, 50°C and 55°C respectively as shown in Appendix IC. There is a general decrease in the reaction rate with increase in temperature and a surprising inversion of the reaction at 55°C which is difficult to interpret.
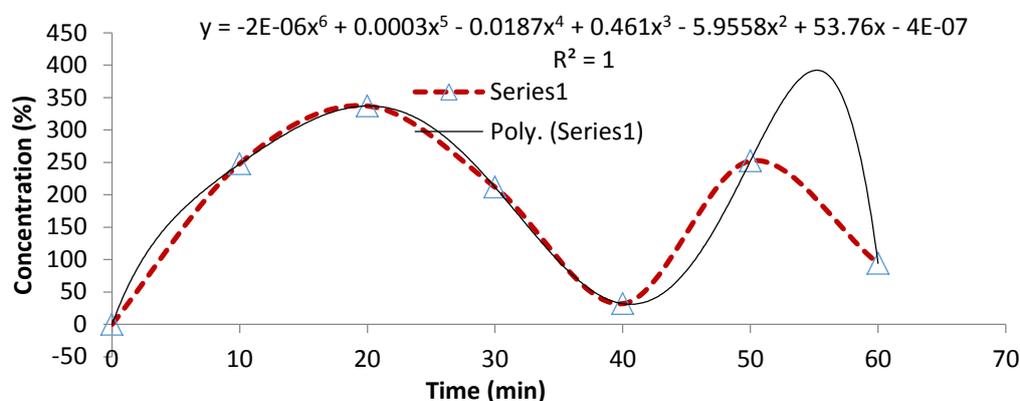
$y = 3E\text{-}06x^6 - 0.000x^5 + 0.039x^4 - 1.249x^3 + 17.10x^2 - 61.50x - 1E\text{-}07$

$R^2 = 1$
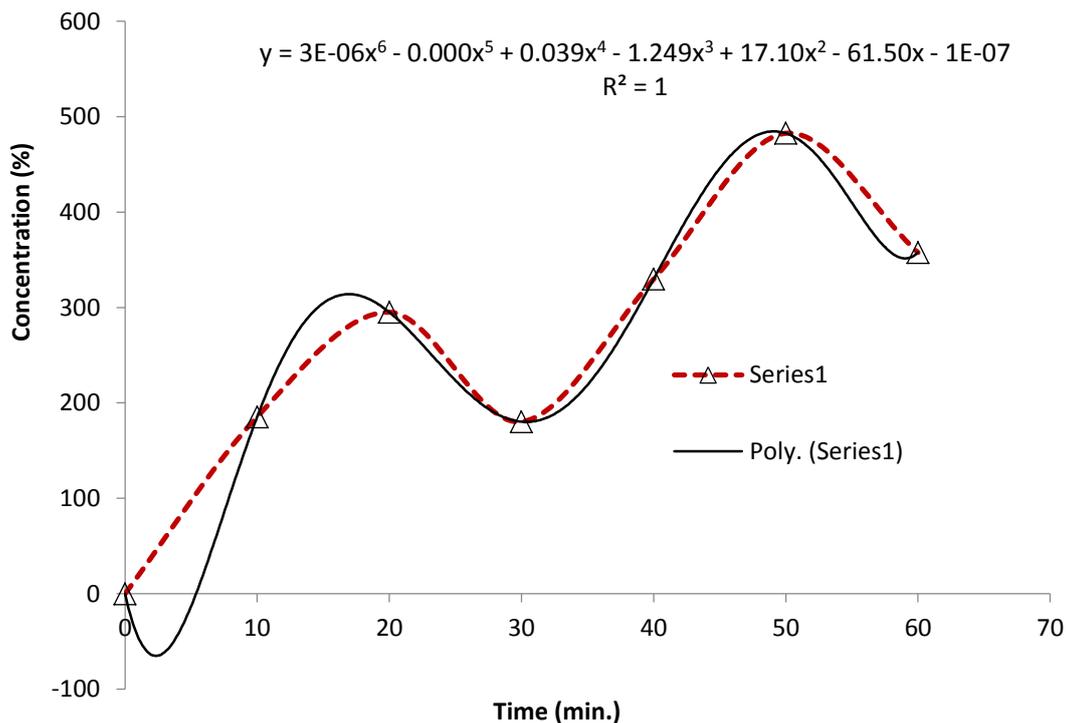
Figure 3.2: Concentration vs Reaction Time for m-oleate obtained for *Balanites* at 35°C

$y = -4E\text{-}06x^6 + 0.000x^5 - 0.063x^4 + 2.265x^3 - 37.71x^2 + 238.5x - 6E\text{-}08$

$R^2 = 1$
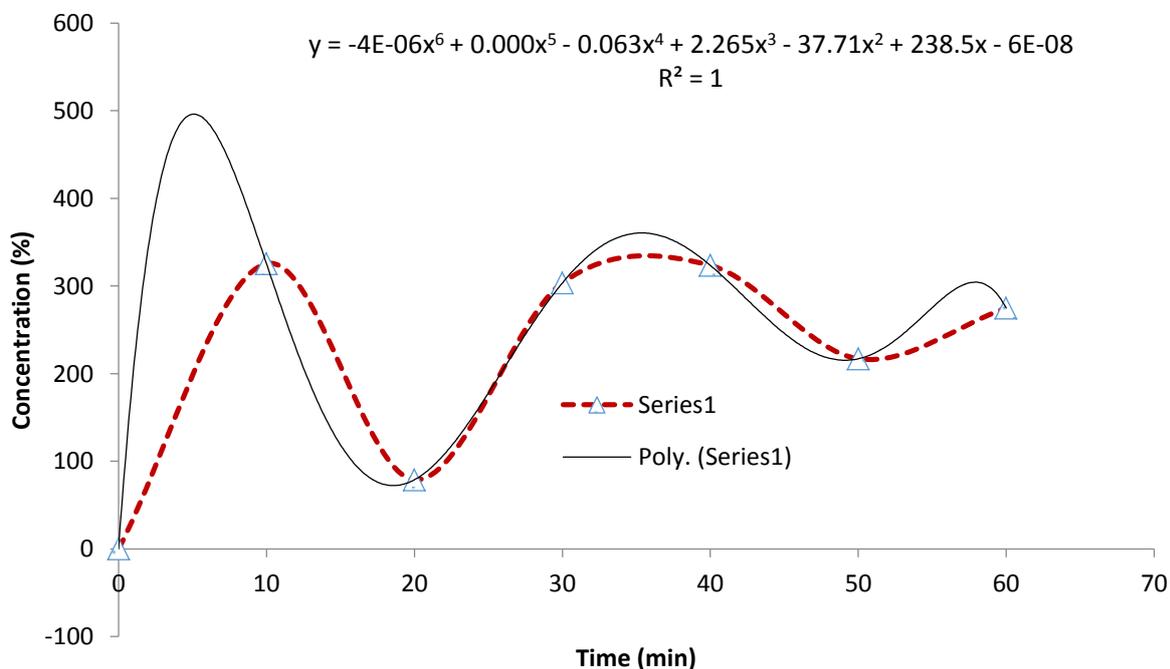
Figure 3.3: Concentration vs Reaction Time for m-oleate obtained for *Balanites* at 40°C

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The Arrhenius plot for the trans-esterification process at 35°C, 40°C, 45°C and 50°C is shown in Figure 3.8 It is obvious that the trans-esterification process did not proceed in accordance with the Arrhenius equation. This means, although the kinetic model and rates of trans-esterification process were determined, the activation energy (E) and frequency factor (A) could not be determined for the process.
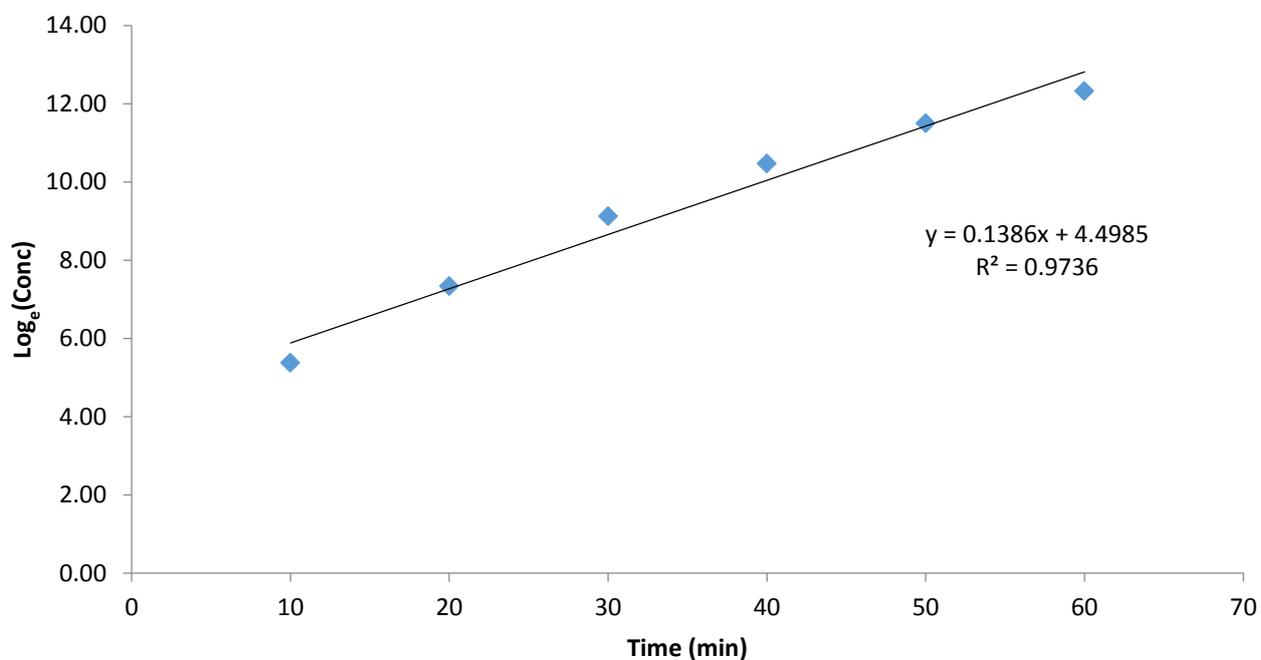

$$y = -2E{-}06x^6 + 0.0003x^5 - 0.0187x^4 + 0.461x^3 - 5.9558x^2 + 53.76x - 4E{-}07$$
$$R^2 = 1$$

Figure 3.4: Concentration vs Reaction Time for m-oleate obtained for *Balanites* at 55°C
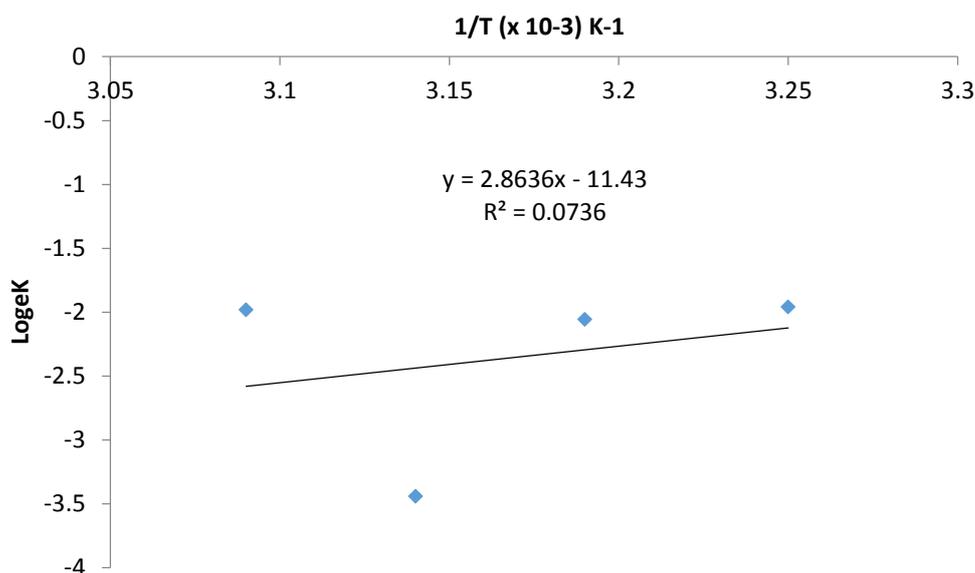

$$y = 0.1419x + 4.5968$$
$$R^2 = 0.9719$$
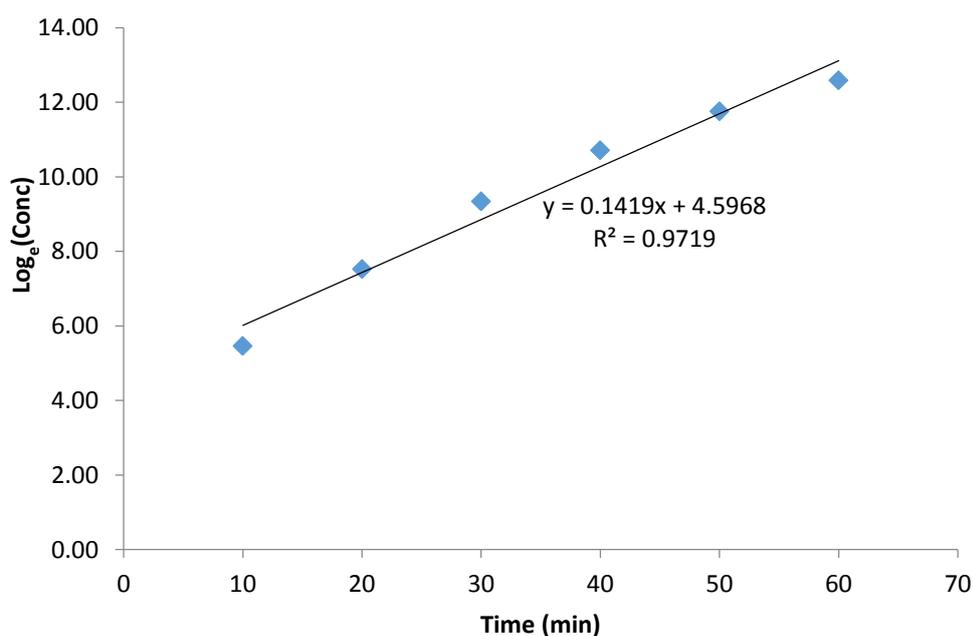
Figure 3.5*: First Order Plot for m-oleate of *Balanites* at 35°C using smoothed Conc-Time Data.

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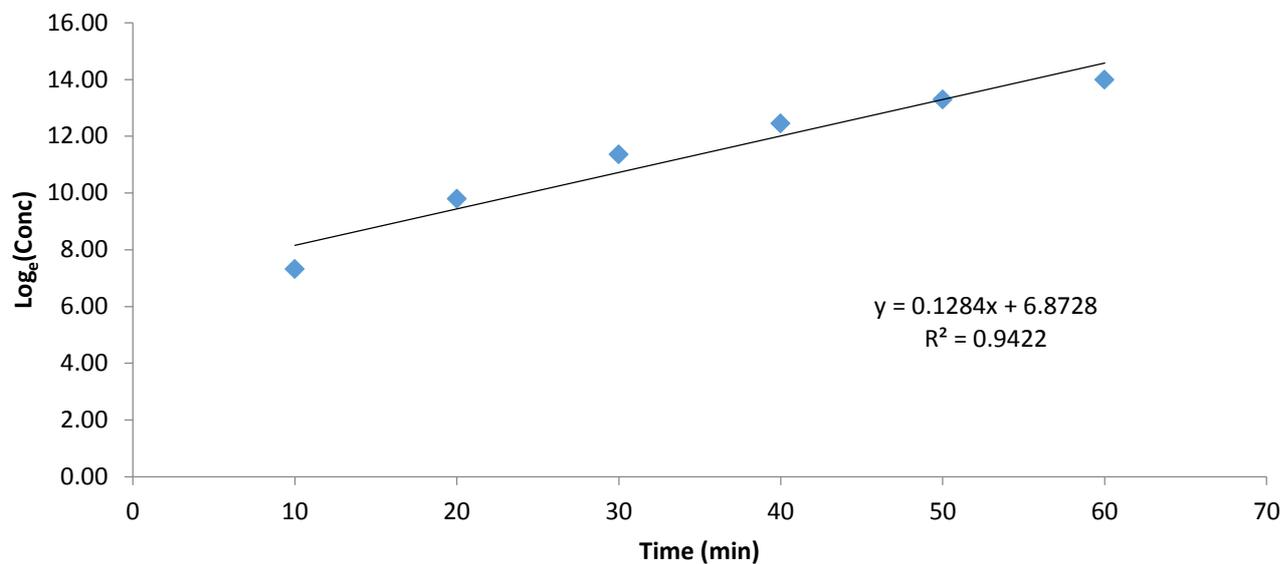
Figure 3.6: First Order Plot for m-oleate obtained from *Balanites* at 40°C

Figure 3.7: First Order Plot for m-oleate obtained from *Balanites* at 50°C.

Figure 3.8: Arrhenius Plot for m-oleate production from *Balanites aegyptiaca* oil

CONCLUSION

Adaptation of GC-MS technique for quantitative determination of sample was introduced and applied. Kinetic study for the transesterification process of *Balanites* oil suggest that, First Order Kinetic model applies with decreasing rate constant (k) values as the temperature increases. The processes did not proceed in accordance with Arrhenius equation. It suggests the kinetic modelling is not sufficient to predict transesterification completely, since the activation energy of the process couldn't be determined. This reaction need further studying with parameters like; catalyst size, mixing intensity and reactants ratio.

REFERENCES

1. Oliveira, L.E. and Da Silva, M.L. Comparative study of calorific value of rapeseed, soybean, jatropha curcas and crambe biodiesel. *Renew Ener and Power Quality Jnl*. 11 (2013) 77.

2. Walker, D.A. Biofuels for better for worse? *Ann App Biol*, 156 (2015) 319.

3. Sreedhar, I. and Yandapalli, KK. Process standardization and kinetics of ethanol driven biodiesel production by transesterification of ricebran oil. *Int. J. Ind. Chem*. 7 (2016) 121.

4. Atadashi,I. Aroua, M. Abdul, AA. and Suleiman, N. The effects of water on biodiesel production and refining technologies: a review, *Renew Sust. Energ. Rev,* 16 (2012), 3456.

5. Demirbas, A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats, *Energy Convers Manage*, 49 (2008) 125.

6. Jain, S. and Sharma, M.P. Effects of metal contents on oxidation stability of biodiesel/diesel blends *Fuel*, 116 (2014) 14.

7. Meher, L.C. Vidya, S.D. and Naik, S.N. Technical aspects of biodiesel production by transesterification-a review. *Renew. Sust. Energ. Rev.,* 10 (2006) 248.

8. Viswanathan, B. and Ramaswamy, A. Selection of Solid Heterogeneous Catalysts for Transesterification Rxtn. National Centre for Catalysis Research, Indian Inst. of Technol. Madras, 2008.

9. Kim, M.J. Park, M. Chang, D. and Seo, G. Transesterification of triacetin, tributyrin and soybean oil with methanol over hydrotalcites with different water contents, *Fuel Proc. Technol* 91(2010), 618.

10. Vyas, A. Verma, J. and Subrahman, N. A review on FAME production processes,*Fuel,* 89 (2010)1.

11. Mendow, G. Veizaga, N.S. and Quirini, C.A. Ethyl ester production by homogeneous alkaline transesterification: influence of catalyst, *Biores Technol* 102 (2011), 6385.

12. Acosta, A. Filice, M. Fernandez-Lorente, G. and Guisan,J.M. kinetically controlled synthesis of monoglycerol esters from chiral and parochial acids methyl esters catalysed by immobilized *Rhizomucor miehei lipase*, *Biores. Technol*, 102 (2011), 507.

13. Alam, J. Shawon, Z.A. Sultan, M. Rahman, W. and Khan, R.M. Kinetic Study of Biodiesel Production from Soybean Oil, *Power and Ener. Syst.* 15 (2014), 425.

14. Chapagain, B. P. Yehoshua, Y. and Wiesman, Z. Desert date as an arid lands sustainable bioresource for biodiesel, *Biores. Techno*, 100 (2009), 1221.

15. Hall, J.B. Walker, D.H. *Balanites aegyptiaca* Del.-A Monograph, School of Agricultural and Forest Science, University of Wales, Banger, 1991.

16. Yehoshua, y.. *Balanites aegyptiaca* as a phyto-diesel production model in arid lands. M.Sc. Thesis, submitted to Ben Gurion University of the Negev, 2008.

17. Mohammed, A.M. Wolf, W. and Spies, W.E. Physical, morphological and chemical characteristics, oil recovery and fatty acid composition of Balanites aegyptiaca Kernels, Plant Foods Hum. Nutr. 57 (2006) 179.

18. Shahid, M.D. and Bundy, C. Kinetics of Rapeseed Oil Methanolysis in presence of KOH Catalyst—Studied with Gas Chromatography, Int. Jnl. of Sci. and Techn. 2 (2012) 762.

19. Leevijit, T.,Wisutmethangoon, W., Prateepchaikul, G. and Allen, M.. A second Order Kinetics of Palm Oil Transesterification, Sustain. Ener. and Environ. 8 (2004) 254.

20. Ahickpor, J. C. and Kuwornoo, D.K.,Kinetics of palm kernel oil and ethanol transesterification, *Ener* and *Environ.* 20 (2010) 1097.

21. Harris, D. C., Quantitative Chemical Analysis, 6[th]Ed., p. 590, W. H. Freeman Ltd, New York, 2003.

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