

Investigation of Kinetics of Transesterification for Methyl Ester Production using *Jatropha Curcas* Seedoil

Yunus, M.M.

Department of Chemistry, Yobe State University KM 7, Gujba Road, P.M.B.1144 Damaturu, Nigeria

Abstract:- In this work, transesterification of *Jatropha curcas* seedoil using homogeneous catalyst (NaOH) was conducted in a reactor with methanol. The transesterification reaction at 6:1methanol to oil ratio with 1wt% catalyst was studied at 35°C, 40°C, 45°C, 50°C and 55°C. The study attempted to determine the rate of transesterification of *Jatropha curcas* seed oil (JSO) by measuring the rate of formation of methyl oleate using GC-MS technique. The concentration of the product (methyl-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. The data generated was used to test for first, second and third order kinetics. The process reveals that, the first order kinetics model doesn't apply for the first three working temperatures of 35°C to 45°C showing negative rate constant (k) values of -0.146, -0.141 and -0.131 mol/second, while for the transesterification process at 50°C and 55°C, rate constant values are 0.132 and 0.115 respectively. 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: *Jatropha* seedoil, GC-MS technique, Kinetic model, JSOME's and Conc-Time Data

I. INTRODUCTION

There is a growing realization that, the world reserve of the fossil fuels is finite and its depletion is eminent sooner than latter given the fact that consumption of fossil fuels far outstrips the discovery of new reserves. The world would be confronted with energy crisis not only due to fossil fuel depletion but environmental degradation as well (Fazal *et al.*, 2011). Increase in population globally and rapid industrialization to meet human demands has led to enormous energy utilization. It is a fact that the demand for petroleum is on the increase daily, possibly due to increasing world population and the quest for better living standard (Demirbas, 2010; Tomomatsu and Swallow, 2007). More so, most of the needed services that enhances our standard of living are energy dependant, thus their optimal delivery can only be achieved through sufficient energy supply. On the other hand, fossil fuels are implicated as the dominant global source of carbon dioxide (CO₂) emissions which is posing strong threat to clean environment. Furthermore, the current weather vagaries which are manifesting in the form of rising sea

levels, floods, desertification, erosion, sand storms etc. are being traced to human activities associated with the utilization of fossil fuels (Faraq *et al.*, 2013; Bunce *et al.*, 2011 and Ahickpor and Kuwornoo, (2010). Modern civilization is under threat from all angles. Therefore, it is not surprising that all global media outlets are dominated by the call for search and development of alternative fuels (Carraretto *et al.*, 2008). With growing human population, land is needed to grow food for human survival, which poses a challenge to biofuel production. However, *Jatropha* is a plant which gives high yield of oil that is not suitable for human consumption and could make a best feedstock for biodiesel production (Solomon *et al.*, 2010 and Vyas *et al.*, 2010). *Jatropha curcas* seed oil (JSO) is known to content high amount of free fatty acids which is a potential challenge compared to other oil seeds like soybean, rapeseed, sunflower and palm oils. Some properties of *Jatropha Curcas* oil are reported in Table 1.

Table 1. Properties of JSO

Property	<i>Jatropha Curcas</i> oil
Yield (%)	47.76 ± 0.65
Density (g/cm ³) 20°C	0.92 ± 0.01
Viscosity at 40°C (cSt)	31.05 ± 0.28
Moisture content (%)	0.54 ± 0.07
FFA contents (%)	14.40 ± 0.35
Flash point °C	245.0 ± 1.55
Pour point °C	-2.20 ± 0.95
Iodine value (gI ₂ /100g)	105.0 ± 8.80

For the conversion of high free fatty acids *Jatropha* seed oil to alkyl esters, two-step processes of esterification/transesterification methods are employed. It involved an acid catalysed pre-treatment step to reduce the FFA's using con. H₂SO₄ as acid catalyst (esterification) which is followed by transesterification of the pre-treated oil to convert it to alkyl esters using an alkali catalyst (Achten *et al.*, 2009, and Houfang *et al.*, 2009). The aim of this study is to investigate the kinetics of conversion of *Jatropha Curcas* seedoil into biodiesel at different temperature range of 35°C to 55°C to decide an optimal value for maximum alkyl ester yield. Another objective of the study is to determine the reaction rate

constants at the described temperatures and estimate the transesterification route as first or second order rate-law compliant.

Table 2. Fuel properties of JSOME's

Property	JSOME's	Standard Biodiesel
Yield (%)	89.0 ± 6.54	96.0
Density (g/cm ³) 20°C	0.85 ± 0.00	0.88
Viscosity at 40°C (cSt)	4.80 ± 0.10	1.9 to 7.0
Cloud point (°C)	3.30±0.42	-3 to 12
Sulphur (%)	0.02±0.01	0.05
Flash point oC	167 ± 1.42	100 to 170
Diesel index	37.6 ± 0.00	45 to 55
Calorific value (MJ/Kg)	36.8 ± 1.80	37 to 41

II. MATERIALS AND METHODS

Materials

Methanol, Hydrochloric and Ethyl acetate (BDH Poole), NaOH (Fisons, UK), pure Oleic acid (Qualikems), distilled water and *Jatropha Curcas* seed oil. Chemicals used in this work were analytical reagent (AR) grade.

Equipment

A 50cm³ 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 (10cm³, spodex) 5cm³ and 1µL syringes, ice-bath and refrigerator.

Reaction Conditions

Pure refined *Jatropha curcas* seedoil was pretreated by 2M H₂SO₄ for six hours (esterification), then followed by transesterification process. The latter was carried out under the following conditions: 6:1 M methanol/oil, 400 rpm stirring, 0.33g NaOH per 27.6.0g of oil, and 35°C to 55°C reaction temperature range.

Experimental Procedure

Method reported by Leevijit *et al.*, 2004 and Wu *et al.*, 2014) was adapted with slight modification in this test. To obtain 6:1 M ratio of methanol to JSO, 7.6cm³ of methanol was reacted with 30cm³ oil. The reactor (50cm³ volumetric flask) was charged with oil (30cm³), stoppered with cork fitted with a stirrer and placed in circulation water bath at 35°C. CH₃OH and NaOH were mixed and heated separately to 35°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, 2cm³ of reaction sample was collected at intervals of 10 minutes for a period 60 minutes

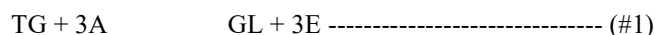
using a 5cm³ pre-cooled syringe. The sample aliquot was placed immediately in a pre-cooled test-tube and few drops of 0.5MHCl were added to the solution, closed and placed in ice-bath kept below 0°C to quench the reaction. Mixture was washed severally with distilled water, shaken vigorously and kept until the aqueous and organic phases separated. Upon washing; glycerol, CH₃OH and the remaining NaOH or HCl solutions were transferred to the water phase which was discarded. The organic phase containing the ester was centrifuged to ensure thorough separation and then transferred to a vial which was closed, labelled and refrigerated below 0°C for subsequent GC-MS analysis. This process was repeated for each reaction sample collected at interval of 10 minutes; thus six methyl ester samples were collected over 60 min. period with the reactor temperature kept at 35°C. Each of the six methyl ester samples was analyzed using GC-MS to generate time versus concentration data at 35°C. For the same oil, above procedure was repeated at 40, 45, 50 and 55°C. Table 2 and 3 depicted the fuel properties of *Jatropha* seedoil methyl esters (JSOME's) and their fatty acid composition.

Background Theory

The mechanism proposed for Transesterification of *Jatropha Curcas* seedoil is composed of a series of reversible decompositions of triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol. Each step consuming 1mole of alcohol and producing 1 mole of ester as in the following equations (Ahickpor and Kuwornoo, 2010 and Mendow *et al.*, 2011).



The overall reaction is given as:



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 the trans-esterification reaction could be determined by either measuring the disappearance of the triglyceride or the formation of the glycerol or methyl ester. In this work, an attempt is made to determine the rate of the transesterification of *Jatropha* seed oil by measuring the rate of formation of methyl-oleate using the GC-MS technique. In particular, the concentration of methyl-oleate will be monitored by measuring the peak area of the GC-MS chromatogram as explained below. Generally, quantitative analysis in chromatography is based on measurement of the Peak Area of the chromatographic peak which is proportional to the quantity of a 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 the unknown component is calculated using the following equation (Harris, 2003).

$$X = \frac{S.A_x}{F.A_s} \text{-----} \#2, \quad \text{where; } A_x \text{ is the peak area of the analyte sample}$$

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, 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 as shown in figure 2.1. The peak areas obtained in the GC analysis of the esters produced during the transesterification of *Jatropha* seed oil will be used to interpolate their corresponding concentrations (in percentage) on the methyl oleate standard curve. The concentration data will then be used for kinetic analysis to obtain kinetic parameters for the transesterification of the oils.

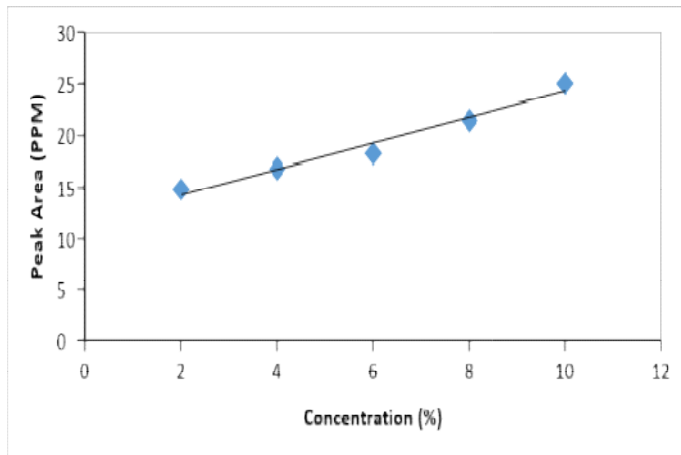


Fig. 2.1: Standard Calibration Plot for Methyl Oleate

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

$$\text{Rate of production of Methyl Oleate} = \frac{1}{3} \frac{dc}{dt} = KC^n, \quad \text{Where } C = \text{concentration of the methyl ester,}$$

K = rate constant, n = reaction order

$$\text{On separation of variables and integration we get: } \int_{c_1}^{c_2} \frac{dc}{c^n} = 3k \int_{t_1}^{t_2} dt \text{-----} \#3$$

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

$$\text{Ln}C_2 - \text{Ln}C_1 = 3k(t_2 - t_1) \text{-----} \#4, \text{ the rate constant } (k_1) \text{ for First Order is given by}$$

$$k_1 = \frac{(\text{Ln}C_2 - \text{Ln}C_1)}{3(t_2 - t_1)} \text{-----} \#5$$

For Second Order ($n=2$), integration of equation #3 gives: $\frac{1}{c_1} - \frac{1}{c_2} = 3k_2(t_2 - t_1) \text{-----} \#6$

$$\text{Thus, rate constant } (k_2) \text{ for Second Order is given by } k_2 = \frac{c_2 - c_1}{3c_1c_2(t_2 - t_1)} \text{-----} \#7$$

For Third Order ($n=3$), Integration of equation #3 gives: $\frac{1}{2c_1^2} - \frac{1}{2c_2^2} = 3k_3(t_2 - t_1) \text{-----} \#8$

$$\text{So that the rate constant } (k_3) \text{ for Third Order is given by } k_3 = \frac{c_2^2 - c_1^2}{6c_1^2c_2^2(t_2 - t_1)} \text{-----} \#9$$

Equations 5, 7 and 9 will be used separately to compute the rate constants for trans-esterification of *Jatropha* 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:

$$k = Ae^{-E/RT} \text{-----} \#10, \quad \text{normally recast into the logarithmic form as follows:}$$

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

Where k = rate constant (the unit depends on the reaction order);

A = pre-exponential factor (same unit as that of k); E = activation energy ($\text{J} \cdot \text{mol}^{-1}$);

R = gas constant ($8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); and T = temperature (K).

Product Analysis

The analysis of methyl esters of *Jatropha curcas* seedoil 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 $5^\circ\text{C}/\text{min}$, hold 5 min at 260°C . The chromatographs obtained were scanned and the biodiesel components were identified based on software matching with mass spectra.

III. RESULTS AND DISCUSSION

A concentration (%) versus time (mins) curve for the transesterification of *Jatropha* oil at 35°C is also presented in Figure 3.10. The figure shows an undulating curve consisting two large peaks and two troughs which implies a two stage production and decomposition of Methyl Oleate and regrouping of reactants; or a reversible trans-esterification process. Very similar curves were produced at 45°C , 50°C and 55°C as presented in Figures 3.20, and 3.30, respectively. This is unusual for a typical concentration (C) versus time (t) plot

for production process which would normally be a smoothly rising curve that approaches a plateau as the production ceases as mentioned earlier. This is indicative that the approach of testing the Concentration-Time data for order-reaction will not apply as shown in Figures 3.50, 3.60 and 3.70 for first order kinetics for the data obtained at 35°C, 40°C and 45°C working temperatures. Careful inspection of the undulating curves suggests a latent trend in the formation of the product. This makes it necessary to carry out a mathematical trend analysis on these concentrations versus time plots alongside smoothening the curves using polynomial equations to obtain plots shown in Figures 3.10 to 3.40.

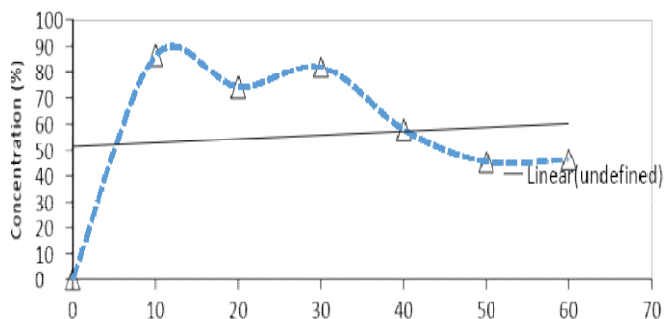


Fig. 3.10: Concentration versus Reaction Time for Methyl Oleate obtained for *Jatropha* at 35°C

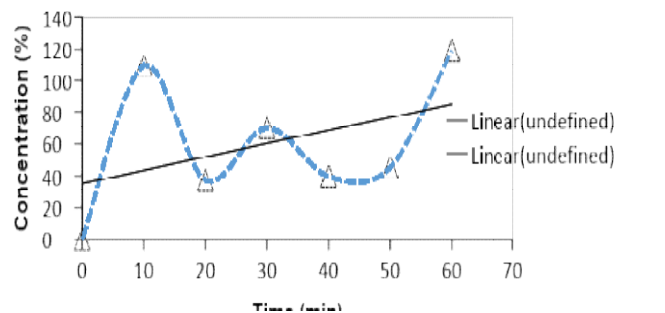


Fig. 3.20: Concentration versus Reaction Time for Methyl Oleate obtained for *Jatropha* at 45°C

The smoothened plots were used to generate a refined concentration data at 10, 20, 30, 40, 50 and 60 minutes for the five temperatures used in studying the reactions.

Table 3. Fatty acid (FA) composition (%) of JSOME's

FA	JSOME's
C16:0	14.45
C18:0	7.84
C18:1	30.62
C18:2	41.34
C20:0	0.46
C21:1	0.22
SFA	22.75
MUFA	30.84
PUFA	41.34

SFA=Saturated fatty acids; MUFA=Mono unsaturated fatty acids; PUFA=Poly unsaturated fatty acids

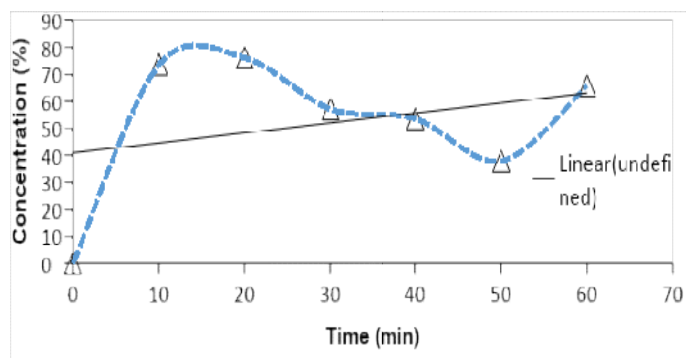


Fig. 3.30: Concentration versus Reaction Time for Methyl Oleate obtained for *Jatropha* at 50°C

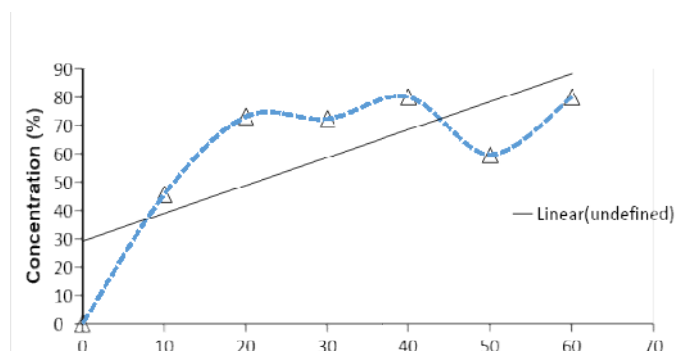


Fig. 3.40: Concentration versus Reaction Time for Methyl Oleate obtained for *Jatropha* at 55°C

The data obtained was used to test for first, second and third Order Kinetics. The plots derived for the transesterification are given in Figures 3.50 to 3.80. The process reveals that, the first order kinetics model does not apply for the first three working temperatures of 35°C, 40°C and 45°C showing negative rate constant (k) values of -0.146, -0.141 and -0.131 mol/second; while for the transesterification process at 50°C and 55°C, rate constant values are 0.132 and 0.115 respectively.

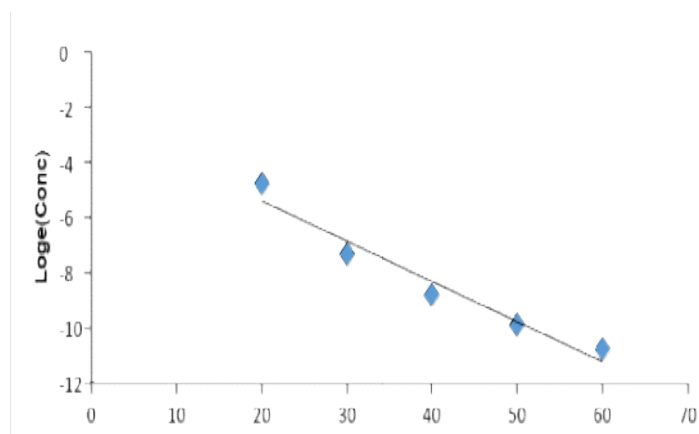


Fig. 3.50: First Order Plot for Methyl Oleate obtained from *Jatropha* at 35°C

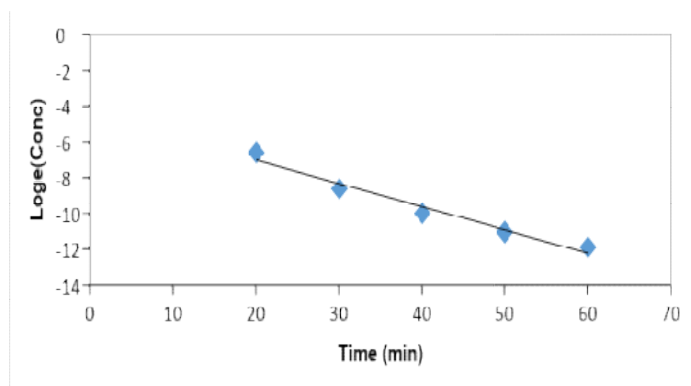


Fig. 3.60: First Order Plot for Methyl Oleate obtained from *Jatropha* at 45°C

A sudden decrease in rate of reaction with increase in temperatures from 35°C to 45°C accompanied by a surprising inversion of the reaction rate at the above mentioned temperatures. Suddenly, there was a turnover in production process when the transesterification was carried at 50°C and 55°C. Surprisingly, a general increase in rate with increasing temperature was observed. It is difficult to interpret this behaviour considering the small data one has at hand. The Arrhenius plot for the transesterification process of *Jatropha* seed oil at 35°C, 40°C and 45°C can't be established due to the inversion of these reaction rates. Hence, the production process did not proceed in accordance with the Arrhenius equation. The Arrhenius plot for the transesterification process of *Jatropha* seed oil at 35°C, 40°C and 45°C can't be established due to the inversion of these reaction rates.

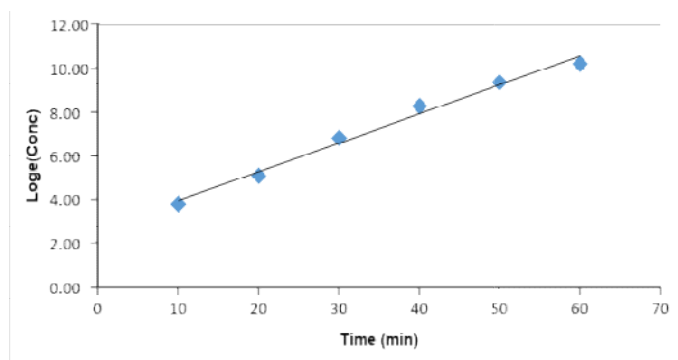


Fig. 3.70: First Order Plot for Methyl Oleate obtained from *Jatropha* at 50°C

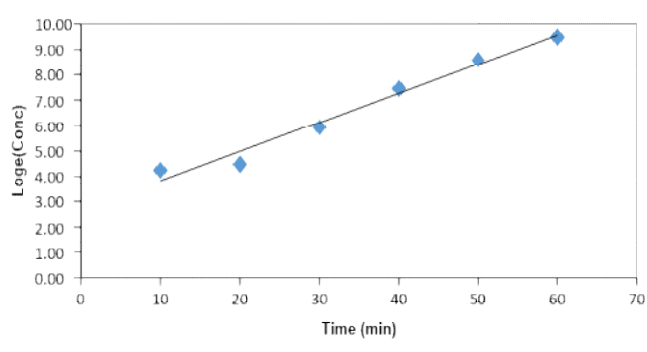


Fig. 3.80: First Order Plot for Methyl Oleate obtained from *Jatropha* at 55°C

IV. CONCLUSION

Based on the study carried out, the following conclusions were drawn; Kinetic study for the transesterification process of *Jatropha* seed oil reveals that, First Order Kinetic model applies with decreasing rate constant (k) values as the temperature increases. The Arrhenius plot for the transesterification process of *Jatropha* oil at 35°C, 40°C and 45°C can't be established due to the inversion of these reaction rates. The process did not proceed in accordance with Arrhenius equation.

REFERENCES

- [1] Achten, W. M. J., Verchot, L., Franken, Y. J., Mathijs, E., Singh, V. P., Aerts, R. and Muys, B. (2009). *Jatropha* Biodiesel Production and Use (a Review). *Biomass & Bioenergy* (32):1063–84.
- [2] Ahickpor, J. C. and Kuwornoo, D. K., (2010). Kinetics of palm kernel oil and ethanol transesterification. *Energy and Environment*, 1 (20): 1097–1108
- [3] Bunce, M., Synder, D., Adi, G., Koehler, J., Kumar, S., Garimella, P., Santon, D. and Shaver, G. (2011). Optimization of soya-biodiesel combustion in a modern diesel engine. *Fuel*, 90: 2560–70.
- [4] Carraretto, C., Mirandola, A. M., Stoppato, A. and Tonon, S. (2008). Biodiesel as Alternative Fuel: Experimental analysis and energetic evaluations. *Energy* (29): 2195–211.
- [5] Demirbas, A. (2010). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy conversion and Management*. 49:125–30.
- [6] Farag, H. A., El-Maghraby, A. and Taha, N. (2013). Kinetic study of used vegetable oil for esterification and Transesterification process of biodiesel production. *Int. Journal of Chemical and Biochemical Sciences* (3)1–8
- [7] Fazal, M. A., Haseeb, A. S., Masjuki, H. H. *Renew. Sust. Energ. Rev.* 15 (2011) 1314-1324.
- [8] Harris, D. C. (2003). *Quantitative Chemical Analysis*, 6th Edition, W. H. Freeman and Company, New York, p590.
- [9] Houfang, Lu., L. Yingying, Z. Hui, Y. Yang, M. and Liang, B. (2009). Production of biodiesel from *Jatropha curcas* L. oil. *Comp. Chem. Eng.* 33: 1091–96.
- [10] Leevijit, T., Wisutmethangoon, W., Prateepchaikul, G. and Allen, M. A. (2004). Second Order Kinetics of Palm Oil Transesterification, *Sustain. Ener. and Environ.* 8: 254.
- [11] Mendow, G. Veizaqa, N. S. and Querini, C. A. (2011). Ethyl ester production by homogeneous alkaline transesterification: influence of catalyst, *Bioresour Technol*, 102: 6385–6391
- [12] Solomon, G., Luqman, C. A. and Nor, M. A. (2010). Investigating “Egusi” (*Citrulluscolocynthis* L.) seed oil as potential feedstock. *Energies*, (3): 607–618.
- [13] Tomomatsu, Y. and Swallow, B. (2007). *Jatropha Curcas* Biodiesel Production in Kenya: Economics and potential value chain development for smallholder farmers, working paper, World Agro Forestry Centre, p 33
- [14] Wu, H. Zhang, J. Liu, Y. and Zheng J. (2014). Biodiesel production from *Jatropha* oil using mesoporous molecular sieves supporting K_2SiO_3 as catalysts for transesterification. *Fuel process Technol*, 119: 114–120
- [15] Vyas, A. P. Verma, J. L. and Subrahmanyam, N. (2010). A review on FAME production processes, *fuel*, 89: 1-9