

14. Molenbroek J. F. N., Ramnekers K., Snijders C. J. (2003) 'Revision on the Standard work task in Industries' *Ergonomics*. 46 (7), 681-694
15. Qutubuddin S.M, Hebbal S.S. and Kumar A.C. (2013). 'Ergonomic Risk Assessment using Postural Analysis Tools in a Bus Body Building Unit' *Industry Engineering Letters*, 3 (8)
16. Raimi O.A. (2014). 'Effect of Motor Vehicle Assembly and Fabricated Metal product on the Manufacturing Capacity Utilization of Nigeria Economy (1985-2010)' *European Journal of Statistics and Probability*, 2(3), 34-42.
17. Sluiter J. K. and Frings-Dresen M. H. (2007). What do we know about ageing at work? Evidence based fitness for duty and health in fire fighters. *Ergonomics*. 50 (11), 1897–1913.
18. Snook SH (1978). The design of manual handling tasks. *Ergonomics*. 21 (12), 963–985.
19. Uhumwangho O. M., Njinaka I, Edema O. T., Dawodu O. A. and Omoti A. E. (2010). Occupational eye injury among sawmill workers in Nigeria. *Asian Journal of Medical Sciences*. 2(5), 233–236.

## Kinetics and Thermodynamics Studies of Oil Transesterified From Castor Seeds

Babatunde, K. A., \*Ogunleye, O.O. Osuolale, F.N. & Agbede, O.O.

Chemical Engineering Department  
Ladoke Akintola University of Technology  
Ogbomoso, Nigeria

\*Corresponding author: oogunleye@lautech.edu.ng

### ABSTRACT

Transesterification process of oil was performed using methanol and calcined catalyst refluxed at 50 °C for 1 hr as the catalyst activation step. The optimum methanol concentration was 250 g, and the highest oil yield was obtained at 65 °C temperatures, agitation rate of 1000 rpm and the reaction time of 3hr. The transesterification process was observed with regard to the percent oil yield versus time, and the reaction order was found to be 1<sup>st</sup>-order reaction kinetics by the differential method. The activation energy for the oil transesterification kinetics of castor seeds was found to be  $E_a = 9.84$  J/mol at the Arrhenius constant of 0.14 s<sup>-1</sup>. The other thermodynamic parameters  $\Delta H$  and  $\Delta S$  were calculated to be 0.06 J/mol, and -197.50 J/mol K respectively, which were used to deduce  $\Delta G$  at different temperatures.

**Keywords:** Castor oil, Biodiesel, Transesterification, Kinetics and Thermodynamics.

### Aims Research Journal Reference Format:

Ajayeoba A. O., \*Onawumi, A.S., Adebisi K. A., Olagunju T. O. and Oyediran D. D. (2016): Kinetics and Thermodynamics Studies of Oil Transesterified from Castor Seeds. *Advances in Multidisciplinary Research Journal*. Vol. 2. No. 2 Issue 1, Pp127-135

### 1. INTRODUCTION

World today depends heavily on fossil fuel for transportation, industrial use and agricultural machineries due to growth in both human and industrial populations. The fact is that a few nations that produce the bulk of petroleum being used are now experiencing decline in oil reserves and this had led to price fluctuation and uncertainty in supply for the consuming nations. Apart from these, the degradation of environment and its associated health problems, global climatic changes and threat to the commercial energy requirements of industries had been a menace to the life and properties of the world. This in turn has led to the search for alternative energy sources most especially renewable energy sources. Among the alternatives being considered are methanol, ethanol, biogas and vegetable oil (Munack, Schroder, Krahl, and Bunger, 2001; Raja *et al.*, 2011).

Biodiesel is renewable fuel that can be manufactured from vegetable oils, animal fats, or recycled restaurant greases. Emission benefits include less particulate matter, reduced levels of carbon monoxide and total hydrocarbons, and an improved odour. It is significantly safer than petroleum-derived diesel; it has a lower flashpoint, and so does not ignite easily; it does not produce explosive vapours and even has a low degree of toxicity to humans and animals if ingested. In contrast to conventional diesel, it is also essentially free of aromatic compounds and sulphur, both of which are toxic and subject to legislation (Broder and Barrier, 1990; Rao and Gopalakrishnan, 1991).

There are a number of kinetic studies in the literature on the transesterification of esters with alcohol. However, only a limited of these researches deal with vegetable oil and fatty esters. Some works on the transesterification kinetics for non-fatty esters include: the reaction rate constants determination, and the estimation of activation energy for the acid- catalyzed reaction of butanol with ethyl acetate according to

Farkas, Schachter and Vronen, 1994. The transesterification kinetics for vegetable oils and fatty esters has been conveyed in a few studies. Freedman *et. al.* (1986) explored both acid- and alkaline-catalyzed transesterification of soybean oil in the presence butanol and methanol. They concluded the reaction rate constants as reaction parameters such as temperature, molar ratio of alcohol to soybean oil, and catalyst type while varying concentration. Mostly, a second- order reaction for all the three reversible reactions gave a satisfactory mechanism. At a molar ratio of methanol to soybean oil of 6:1, a second-order mechanism with a fourth-order shunt mechanism best described the kinetics.

Another factor of specific significance in the transesterification process is the degree of mixing between the alcohol and triglyceride (TG) phases. Triglyceride and alcohol phases are not miscible they form two liquid layers upon their initial introduction into the reactor. In order to increase the contact between the reactants introduction of mechanical mixing is normally applied which resulting in an increase in mass transfer rate. Therefore, differences in mixing strength are likely to alter the kinetics of the transesterification reaction (Noureddini and Zhu, 1997).

The investigation of the kinetics of transesterification of soybean oil with methanol was also explored by Noureddini and Zhu (1997). In their research, three stepwise and reversible reactions are understood to happen. The result of variations in mixing strength (Reynolds number = 3,100 to 12,400) and temperature (30 to 70°C) on the rate of reaction were considered while the molar ratio of alcohol to triglycerol (6:1) and the concentration of catalyst (0.20 wt %) were held constant. It was revealed that the variations in mixing strength appear to effect the reaction parallel to the variations in temperature. A reaction mechanism involving of an initial mass transfer-controlled region was then suggested. The experimental data for the latter area appear to be a good fit into a second-order kinetic mechanism. The reaction rate constants and the activation energies were estimated for all the forward and reverse reactions. A research on kinetics of palm oil transesterification was also carried out by Darnoko and Cheryan (2000). In their study, methyl esters were produced by transesterification of palm oil with methanol in the presence of KOH catalyst. The of transesterification rate in a batch reactor increased with temperature up to 60°C. The conversion of triglycerides (TG), diglycerides (DG) and monoglycerides (MG) appeared to be second order up to 30 minutes of reaction time.  $0.018 - 0.191 \text{ (wt\%.min)}^{-1}$  reaction rate constants was obtained for TG, DG and MG on hydrolysis reactions, and which were found to be higher at higher temperatures and higher for the MG reaction than for the TG hydrolysis. Activation energies of 14.7, 14.2 and 6.4kcal/mol were obtained for the TG, DG and MG hydrolysis reactions respectively and at 1% KOH optimal catalyst concentration.

## 2. MATERIALS AND METHODS

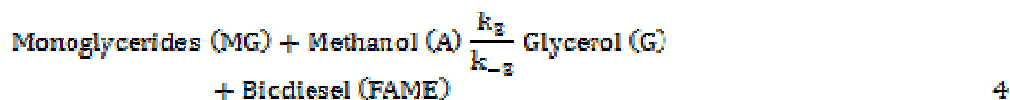
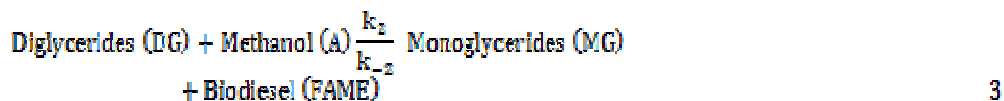
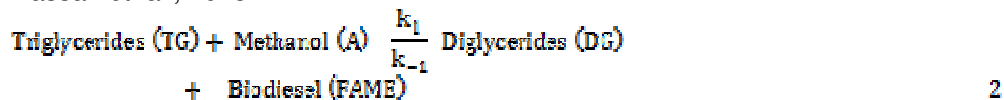
### Batch process of Biodiesel Production

Transesterification method employed by Endalew, Yohannes and Rolando (2011) was adopted here for biodiesel production, using a three – necked round bottom flask glass reactor system as a batch reactor on a magnetic stirrer. The condenser was fixed at the center of the reactor; the agitator was placed inside the flask and the thermometer at the left hand side. For a particular run, 100 g of methanol and 10 g of calcined catalyst were first mixed and refluxed at 50 °C for 1 hr as the catalyst activation step. Then, 250 g of refined castor oil was added to transesterify for a stated experimental duration stipulated by design matrix as shown on Table 3.1. The reactor was heated to 65 °C temperatures, and then magnetic stirrer was switched on at 1000 rpm on after the 65 °C temperatures was attained and the reaction was allowed to take place for 3hr in order to obtain a clear phase separation. The mixture was then filtered to remove catalyst particles; the clear solution obtained was then separated using separating funnel and the yield of biodiesel produced was calculated based on the principle of equation 1

$$Y(\%) = \frac{W_2}{W_1} \times 100 \quad 1$$

## 2.1 Kinetics Studies Of the Transesterification Process.

The overall trans-esterification reaction process for biodiesel synthesis is a sequence of three consecutive reversible reactions according to Levenspiel, (2003), Topallar and Gecgel, (2000) and Hassan *et. al.*, 2013



The overall transesterification reaction can then be seen as the formation of three molecules of Fatty Acid Methyl Ester (FAME) which is the biodiesel as shown on equation 5:



Based on previous researches, the transesterification has been assumed to follow first order kinetics as a function of the concentration of FAME formed during reaction (Steinfeld, Francisco and Hase, 1989; Kafuku and Mbarawa, 2010; Jain, Sharma and Rajvanshi, 2011; Shah, Jigisha and Kalpana, 2013; Nautiyal, Subramanian and Dastidar, 2014). The rate constant of the particular reaction is dependent on the increase in the amount of product at a particular time interval (Jain and Sharma, 2010). Hence the rate equation for the formation of FAME is as given in equation 5:

$$\text{Rate} = -\frac{d(\text{FAME})}{dt} \quad 5$$

The rate equation for the reaction can also be expressed as equation 6:

$$-\text{Rate} = k(\text{FAME}) \quad 7$$

Where  $k$  is the rate constant ( $\text{min}^{-1}$ ). Equations 6 and 7 can be combined to form equation 8:

$$\frac{d(\text{FAME})}{dt} = k(\text{FAME}) \quad 8$$

Assuming that the initial concentration of biodiesel as  $\text{FAME}_0$  at time  $t = 0$  and concentration after time  $t$  as  $\text{FAME}_t$ , on integration of equation 8, equation 9 is obtained:

$$\int_{\text{FAME}_0}^{\text{FAME}_t} \frac{d(\text{FAME})}{\text{FAME}} = k \int_0^t dt \quad 9$$

$$\ln\left(\frac{\text{FAME}_t}{\text{FAME}_0}\right) = kt \quad \text{or} \quad k = \frac{\ln(\text{FAME}_t) - \ln(\text{FAME}_0)}{t} \quad 10$$

Using equation 9, the value of  $k$  was calculated for various temperatures and a differential plot of  $\ln d(FAME)/dt$  and  $\ln(FAME)$  which is a straight line based on equation 8 it was used to verify the assumption of the first order reaction.

## 2.2 Activation Energy Determination

The rate constant is a function of activation energy and temperature of a reaction as given by the Arrhenius equation as shown in equation 11:

$$k = Ae^{-\frac{E_a}{RT}} \quad 11$$

where  $A$  and  $E_a$  are the Arrhenius parameters which stand for frequency factor or pre-exponential coefficient ( $\text{min}^{-1}$ ) and activation energy ( $\text{J/mol.}$ ), respectively.  $R$  is the molar universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature ( $\text{K}$ ). By taking the natural logarithm equation 11 can be expressed as equation 12:

$$\ln k = \ln A - \frac{E_a}{RT} \quad 12$$

The activation energy and frequency factor of reaction were determined from the plot of  $\ln k$  and  $1/T$  which is a straight line.

## 2.3 Thermodynamic Studies of the Transesterification Process

The Eyring-Polanyi equation was used to calculate the Gibbs free energy ( $\Delta G$ ) according to Nautiyal, Subramanian and Dastidar (2014) as shown on equation 13:

$$k = \frac{k_b T}{h} \exp\left(-\frac{\Delta G}{RT}\right) \quad 13$$

$$\Delta G = \Delta H - T\Delta S \quad 14$$

Taking natural logarithm of equation 12 and substituting equation 13 gives equation 14:

$$\ln\left(\frac{k}{T}\right) = -\left(\frac{\Delta H}{RT}\right) + \left[\ln \kappa + \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R}\right] \quad 15$$

where  $\Delta H$  is the enthalpy,  $\Delta S$  is entropy of reaction,  $k$  is the rate constant ( $\text{min}^{-1}$ ),  $T$  is the absolute temperature ( $\text{K}$ ),  $R$ ,  $k_b$  and  $h$  are the universal gas ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), Boltzmann ( $1.38 \times 10^{-23} \text{ J/K}$ ) and Plancks ( $6.63 \times 10^{-34} \text{ J s}$ ) constants respectively.

The transmission coefficient  $\kappa$ , is often taken as unity. From the plot of  $\ln(k/T)$  and  $1/T$ , using equation 15, the values of slope and intercept were used to calculate  $\Delta H$  and  $\Delta S$  and then at various temperatures using equation 14,  $\Delta G$  was calculated.

### 3. RESULTS AND DISCUSSION

#### 3.1 Kinetics of the Transesterification Process

First order reaction was assumed for the transesterification reaction from equation 2 to 8. In order to establish the correctness of this assumption and then estimate the value of the reaction constant  $k$  at various temperatures, plots of  $\ln(dY/dt)$  versus  $\ln Y$  at temperatures 45, 50, 55, 60 and 65 °C were made as shown of Figure 1 while the values of  $k$  are as shown on Table 1 using the KOH (1:5) impregnated bentonite clay. The resulting plots in Figure 1 were all straight line confirming the first order assumption while all  $R^2$  values of the plot ranged between 0.8646 and 0.9939. This relatively high  $R^2$  of the estimate values are indications of accuracy.

**Table 1: Reaction constants at various temperatures**

| T (°C) | $k \cdot 10^{-3}(\text{min}^{-1})$ |
|--------|------------------------------------|
| 45     | 3.47                               |
| 50     | 3.71                               |
| 55     | 3.84                               |
| 60     | 4.75                               |
| 65     | 4.82                               |

#### 3.2 Determination of Activation Energy and Arrhenius Constant

In order to estimate the activation energy and the Arrhenius constant, the plot of  $\ln(k)$  against  $1/T$  was made as shown on Figure 2 using the values on Table 2. The calculated values for activation energy and the Arrhenius constant were 9.84 J/mol. and 0.14 s<sup>-1</sup>, respectively. The activation energy of the particular reaction is subject to reaction parameters involved, i.e. temperature, catalyst concentration, nature of reactants, and also the slower the reaction, the higher will be the activation energy due to the presence of unsaturation.

Arrhenius constant of 0.14 s<sup>-1</sup> obtained is a measure of collision between reactants (higher value of frequency factor means higher probability of successful collision that cause chemical change) and favours the forward reaction. This is similar to Ong, Kurniawan, Suwandi, Lin, Zhao, and Ismadji (2013) who affirmed the higher frequency factor that led to the formation of methanol ester during transesterification process and higher activation energy of transesterification that caused slower formation of methyl ester, which is due to intra and inter-molecular van der Waal repulsion that retarded nucleophilic attack on the carbocation of triglyceride by methoxide radicals. Another factor that caused the increase of activation energy is the structural conformation of the transition state involving the changes of both lengths and angles (complex molecular structure).

**Table 2: Showing  $k$ ,  $\ln k$  and  $1/T$  at various Temperatures**

| Temp. (°C) | $k \cdot 10^{-3}(\text{min}^{-1})$ | $\ln k$ | $1/T \cdot 10^{-3} (\text{K}^{-1})$ |
|------------|------------------------------------|---------|-------------------------------------|
| 45         | 3.47                               | -5.66   | 3.14                                |
| 50         | 3.71                               | -5.59   | 3.10                                |
| 55         | 3.84                               | -5.56   | 3.05                                |
| 60         | 4.75                               | -5.34   | 3.00                                |
| 65         | 4.82                               | -5.57   | 2.96                                |

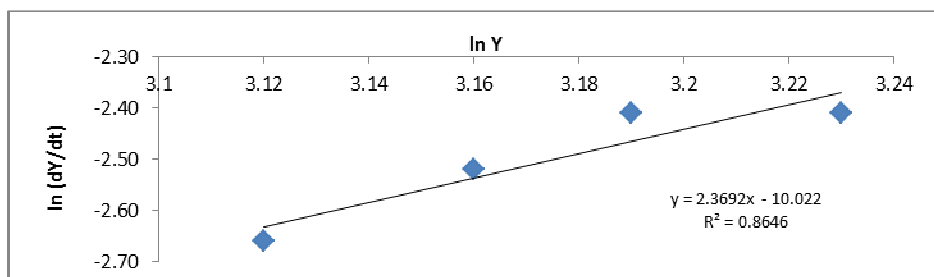
#### 3.3 Transesterification Process Thermodynamics

Considerations of thermodynamics of the transesterification process are necessary in order to conclude whether the process is spontaneous or not. The spontaneity of chemical reaction was determined by the change in Gibb's free energy ( $\Delta G$ ).

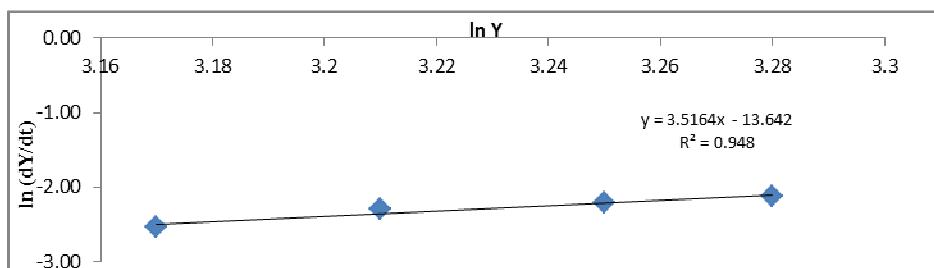
### 3.4 Determination of Thermodynamic Parameters

Thermodynamics analysis was addressed by evaluating activation enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibb's free energy ( $\Delta G$ ), these are important parameters that were used to interpret the behavior of transesterification reactions. Activation complex theory which was developed by Eyring in 1935 was used along with temperature dependent rate constant to evaluate thermodynamic parameters above, having determined Arrhenius constant and activation energy. A plot of  $\ln(K/T)$  against  $1/T$  (Equation 11) gives a straight line whose slope ( $-\Delta H/R$ ) was found to be  $-0.0067$  and the intercept was  $0.0038$  for Castor seed oil transesterification process (Figure 3).

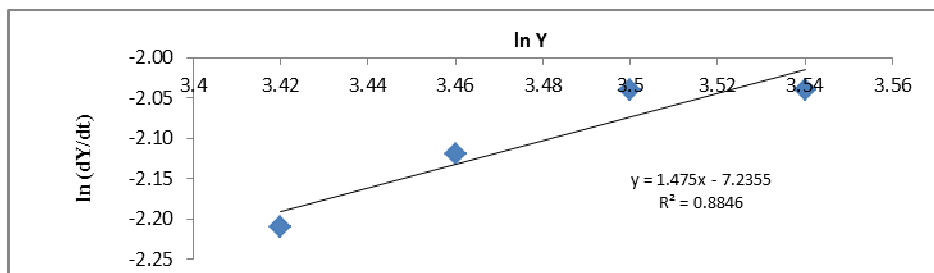
The values of  $K$ ,  $\Delta S$  and  $\Delta G$  for transesterification of castor oil using methanol under impregnated bentonite heterogeneous catalyst were calculated using equations 15 which is Van't Hoff relation. The reaction system initially consists of the castor seed oil, catalyst and methanol, whereas the oil molecules are transesterified from the Castor seed oil during the transesterification process, and therefore, the values of  $\Delta H$  and  $\Delta S$  were calculated to be  $0.06$  J/mol,  $-197.50$  J/mol K respectively, these values were used to deduce  $\Delta G$  at different temperatures (table 3).



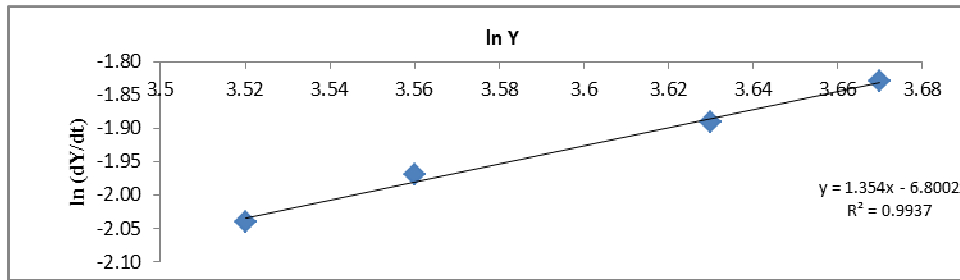
(a)



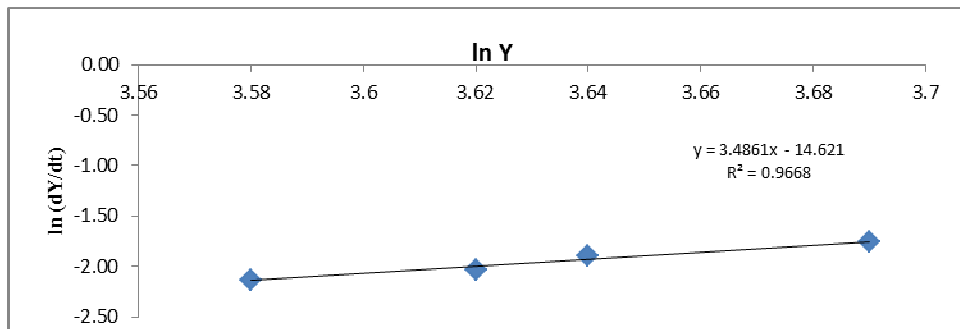
(b)



(c)



(d)



(e)

Figure 1: Plot of  $\ln(dY/dt)$  against  $\ln(Y)$  at (a)45°C (b) 50°C (c)55°C(d)60°C (e)65°C

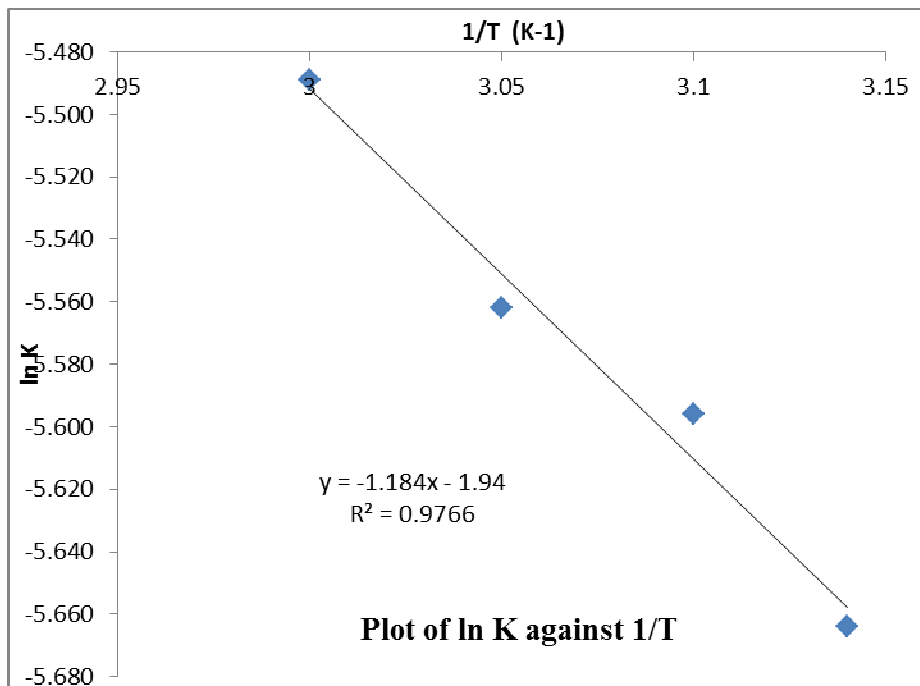


Figure 2: Arrhenius plot for transesterification of biodiesel.



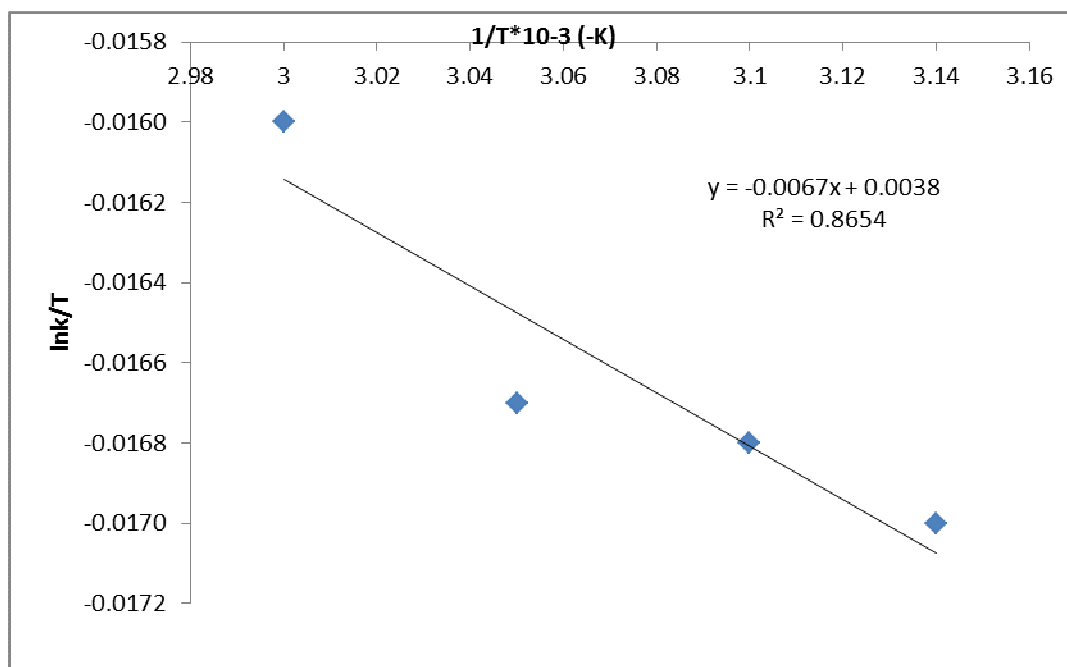


Figure 3: A plot of  $\ln k/T$  against  $1/T$  for the transesterification of biodiesel

Table 3: The thermodynamic parameters ( $\Delta G$  and  $\Delta S$ ) for oil yield at various temperatures

| T (K) | $\Delta H$ (J/mol.) | $\Delta S$ (J/mol. K) | $\Delta G$ (J/mol.) |
|-------|---------------------|-----------------------|---------------------|
| 313   | 0.06                | -197.50               | 62808.06            |
| 323   |                     |                       | 63792.56            |
| 328   |                     |                       | 64780.06            |
| 333   |                     |                       | 65767.56            |

A positive value of  $\Delta H$  shows physicochemical nature of the oil transesterification process and that heat contribution is mandatory to bring the reactants to form the products. A negative value of  $\Delta S$  specifies that the degree of systematic geometry is better as compared to reactants in the transition state and that the process is reversible (Liau *et al*, 2008 Topallar and Geçgel, 2000 and Khraisha, 2000) while at temperatures less than 333 K the reaction is irreversible. Positive values of  $\Delta G$  indicate that the reaction was unspontaneous and endergonic in nature. The degree of spontaneity of the transesterification reaction increase with increase in temperature as  $\Delta G$  become more positive, this is to confirm that transesterification using heterogeneous catalyst become more favourable at higher temperature.

#### 4. CONCLUSION

It was established from the positive value of  $\Delta H$  that heat contribution is mandatory to bring the reactants to form the products. While the negative effect of  $\Delta S$  stipulates the degree of systematic geometry is better as compared to reactants in the transition state and that the process is reversible. Transesterification process using heterogeneous catalyst become more favourable at higher temperature with positive range of value of  $\Delta G$  and thereby increase the degree of spontaneity.

## REFERENCES

1. Broder, J.D. and Barrier, J.W. (1990) "Producing Fuels and Chemicals from Cellulosic Crops" In Janick, J. and Simon, J. E. (eds), *Advances in New Crops*, Timber Press, Portland.
2. Darnoko, D., and Cheryan, M., (2000). Kinetics of Palm Oil Transesterification in a Batch Reactor. *Journal of American Oil Chemical Society*, 77: 12163–1267.
3. Endalew, A.K, Yohannes K. and Rolando Z. (2011). Heterogeneous catalyst for Biodiesel Production from *Jatropha Curcas* Oil. *Journal of Energy*, 02: 1-8.
4. Farkas, L., O. Schachter and Vronen, B. H. (1949). On the Rate of Acid-Catalyzed Transesterification of Butyl Alcohol and Ethyl Acetate, *Journal of American Oil Chemical Society*, 71(6):1991-1994.
5. Freedman B. H., Butterfield R., O. and Pryde E., H. (1986) Transesterification Kinetics of Soybean Oil. *Journal of American Oil Chemical Society*, 63: 1375-1380.
6. Hassan, S. Z., Chopade, S. A. and Vinjamur, M. (2013). Study of Parametric Effects and Kinetic Modeling of Trans- esterification Reaction for Biodiesel Synthesis. *Research Journal of Recent Sciences*, 2: 67-75.
7. Jain, S., Sharma, M. P. and Rajvanshi, S. (2011). Acid Base Catalyzed Transesterification Kinetics of Waste Cooking Oil. *Fuel Process Technology*, 92(1):32–38.
8. Kafuku G, and Mbarawa M. (2010). Biodiesel Production from *Croton Megalocarpus* Oil and its Process Optimization. *Fuel*, 89(9):2556–2560.
9. Khraisha, Y.H. (2000). Reporting of Oil Shale Followed by Solvent Extraction of Spent Shale: Experiment and Kinetic Analysis. *Journal of Energy Sources*, 22:374–355
10. Liauw, M.Y., Natan, F.A., Widiyanti, P., Ikasari, D., Indraswati, N., and Soctaredjo, F.E. (2008). Extraction of Neem oil (*Azadirachta indica* A. Juss) Using n-hexane and Ethanol: Studies on Oil Quality, Kinetic and Thermodynamic. *Journal of Engineering and Applied Sciences*, 3(3): 48-54.
11. Levenspiel, O. (2003) *Chemical Reaction Engineering*. Third edition, John Wiley and Sons Inc., New York. 376-426.
12. Munack, A., Schroder O, Krahl J. and Bungler J. (2001). Comparison of Relevant Exhaust Gas Emissions from Biodiesel and Fossil Diesel Fuel. *Agricultural Engineering International: the CIGR Journal of Science Researches and Development*, 3:1- 12).
13. Nautiyal, P., Subramanian, K. A. and Dastidar, M. G. (2014). Kinetic and Thermodynamic Studies on Biodiesel Production from *Spiulina platenis* algae Biomass using Single Stage Extraction- Transesterification Process. *Fuel*, 135:228-234.
14. Nouredini, H and Zhu. D. (1997). Kinetics of Transesterification. *Biocatalysis*, 74 (11):1457.
15. Ong. L. K., Kurniawan, A., Suwandi, A. C. Lin, C. X., Zhao, X. S. and Ismadji, S. (2013) Transesterification of Leather Tanning Waste to Biodiesel at Supercritical Condition: Kinetics and Thermodynamics Studies. *Journal of Supercritical Fluids*, 5:11-20.
16. Topallar, H., and Gecgel, U. (2000), Kinetics and Thermodynamics of Oil Extraction from Sunflower Seeds in the Presence of Aqueous Acidic Hexane Solutions. *Turkish Journal of Chemistry*, 24: 247-253.
17. Raja D. S., Anthony, S., Robinson S. and Lindon R. L. (2011). Biodiesel Production from *Jatropha* Oil and its Characterization. *Research Journal of Chemical Science*, 1(1):81-87.
18. Rao, P. S., and Gopalakrishnan, K. V. (1991). Vegetable Oils and their Methyl Esters as Fuels for Diesel Engines. *Indian Journal of Technology*, 29:292-297.
19. Shah, K. A., Jigisha, K. P. and Kalpana, C. M. (2014). Optimization Studies and Chemical Kinetics of Silica Sulfuric Acid-Catalyzed Biodiesel Synthesis from Waste Cooking Oil. *Bio-Energy Resources*, 7:206–216.
20. Sneha C., Vinayaka P., and Seemab B. (2014). Utilization of Vegetable and Fruit Waste for Bio-Energy Generation. *Journal of Automation and Control Engineering* 2, (2): 143-145.
21. Steinfeld, J. I., Francisco, J. S. and Hase, W. L. (1989). *Chemical Kinetics and Dynamics*. New York: Prentice Hall. p. 6.