Influence of Temperature on Chemical Kinetics of Rubber Seed Oil Acid Esterification

Sabarish CS, Jilse Sebastian, C Muraleedharan

Abstract— Rubber seed oil is a potential source for biodiesel production due to its abundance. Since rubber seed oil have high acid value, direct conversion of oil to biodiesel is not possible and acid esterification has to be carried before base transesterification.The current work focusses on the kinetic study of this process, studying the temperature dependence of the process by fitting the same to an Arrhenius equation. The kinetics of the esterification of free fatty acids in rubber seed oil with methanol in the presence of sulphuric acid (5% v/v of oil concentration) as catalyst and methanol/fatty acid mole ratio 4:1 was studied for a temperature range of 30 ^{0}C - 60 ^{0}C.The reaction rate constants, the activation energy and pre- exponential factor were found out experimentally. The experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order one for the reverse reaction.

Index Terms—Acid Esterification, Acid Value, Activation Energy, Chemical Kinetics, Rubber Seed Oil

—————————— ◆ ——————————

1 INTRODUCTION

Biodiesel is technically a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, commonly designated as B100. Energy demand, economic and environmental concerns in the present scenario gave rise to the use of bio-fuels on a large scale. Usually, biodiesel is produced through the reaction of an oil or animal fat with methanol in the presence of a suitable catalyst with the yield of glycerol. Thus, biodiesel is chemically called as Fatty Acid Methyl Esters (FAME). Biodiesel is produced through a variety of techniques. Chemical transesterification is the most established method among them. Rubber seed oil has been identified as a potential source for biodiesel production in the recent past since it is nonedible and easily available. Table 1 compares properties of biodiesel obtained from various sources.

TABLE 1.
PROPERTIES OF BIODIESEL OBTAINED FROM VARIOUS SOURCES

Biodiesel source	Acid value(mgKOH/g of oil)	Kinematic Viscosity(mm2/s)	Specific Gravity	Reference
Coconut oil	0.5	5.1	0.868	[1]
Palm oil	0.4	4.61	0.87	[2]
Rubber seed oil	0.42	3.89	0.885	[3],[4]
Jatropha oil	0.49	4.35	0.8768	[5]
Pongamia pinnata oil	0.62	4.8	0.876	[6],[7]

Satyanarayana and Muraleedharan

[8] compared the properties of biodiesel obtained from various sources like rubber seed oil, coconut, and palm kernel oil. Though rubber seed is easily available, it is normally regarded as waste (other than cultivation purpose) and hence at present rubber seed is highly underutilized. It was noted that rubber seed oil has high free fatty acid (FFA) content compared to other oils. In order to facilitate transesterification process, the FFA content should be reduced. Freedman et al. [9], Liu [10], Mittelbach et al. [11] and Ramadhas et al. [12] claim that oils with acid value (numerically twice FFA content) below 2 mg KOH/g of oil can only be used for production of biodiesel. If the acid value is above this level saponification reaction predominates and hinders transesterification reaction. Ramadhas et al. [12] also suggested a 2 step pre-treatment for high FFA contained rubber seed oil. Berrios et al. [13], Farag et al. [14], Egle et al. and Thiruvengadaravi et al. [15] experimentally found out reaction rate constants for acid esterification by assuming pseudo-homogeneous reaction on sunflower oil, used vegetable oil and Pongamia pinnata oil. In addition, they made detailed study on chemical kinetics of esterification process and calculated the activation energy and pre- exponential factors for the reactions.

2 MATERIALS AND METHODS

2.1 Acid Esterification
The oil used for esterification test was rubber seed oil. The acid value of the samples ranged from 50 to 60 mg KOH/g oil, which is much higher than the acid value levels of other edible as well as non-edible oils. The acid value was determined by standard AOCS titration procedure. As mentioned the acid value of the oil was very high, a two-step acid esterification process was conducted prior to the base transesterification process. The esterification catalyst used was sulphuric acid. Free fatty acids were esterified with analytical grade methanol, using a methanol/oleic acid mole ratio of 4:1 and a catalyst concentration of 5%v/v of oil. The experimental procedure was

Sabarish CS is currently pursuing Masters Degree program in Thermal Sciences, NIT Calicut, PH-9567041958.E-mail: sabarish.gectcr@gmail.com
Co-Author 1: Jilse Sebastian is currently pursuing PhD in Mechanical engineering department in NIT Calicut, India, PH-9447568494. E-mail: jilsesebastian@gmail.com
Co-Author 2: Dr. C Muraleedharan is currently Professor in Mechanical engineering department in NIT Calicut, India, PH-9446668655. E-mail: murali@nitc.ac.in

as follows: 300 ml of oil was taken in the reaction vessel, preheated it to 100 ^{0}C to remove moisture and volatile impurities, and then set to a temperature of 55 ^{0}C. Methanol (analytical grade) was added to the oil at a fixed oil to methanol mole ratio of 4:1 and the reactants were continuously stirred using a magnetic stirrer with hot plate, for a few minutes. 5% v/v of oil H_2SO_4 was added to the reactant mixture maintaining the temperature at 60 ^{0}C. Samples were taken at a regular interval of time such as 10, 20, 30, 40, 50 and 60 minutes and kept for separation in conical flasks. After separation acid value of each sample was tested. The experiment was repeated by changing the reaction temperatures as 30, 40 and 50 ^{0}C.

2.2 Kinetic Study

The kinetic model used by Berrios et al. [13], Thiruvengadaravi [15], was selected for the present work. The kinetic model relied on certain assumptions:

- The esterification reaction was a reversible heterogeneous process.
- Non-catalyzed reactions were not occurring.
- The chemical reaction occurred in the oil phase.

Under these conditions, the reaction was assumed to be first-order in the forward direction (free fatty acid to ester conversion) and second-order in the reverse direction (ester to free fatty acid conversion).
The general chemical reaction is represented as:

$$\text{R1-COOH} + \text{R2-OH} \xrightarrow{\text{Acid}} \text{R1-COO-R2} + H_2O$$

Free fatty acid   methanol   ester   water
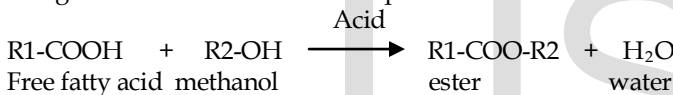
Based on the assumptions the kinetic law is written as,

$$\frac{-d[A]}{dt} = K_1.[A] - K_2.[C][D] \tag{1}$$

Where,
[A] is the concentration of FFA in mg KOH/g oil
[C] and [D] are concentrations of FAME and water, respectively
K1 and K2 are kinetic constants for forward and reverse reactions, respectively.

$$\frac{dE}{dt} = K_1.\left(A_0 - E\right) - K_2.E^2 \tag{2}$$

E is the acidity removed.
A_0 is the initial concentration of FFA.
Upon Integration of Eqn. (2),

$$2.K_2.\alpha.t = \ln \frac{\left[A_0 + E.(\beta - 0.5)\right]}{\left[A_0 - E.(\beta + 0.5)\right]} \tag{3}$$

where, $\alpha = \sqrt{\left(\frac{K^2}{4}\right) + K.A_0}$; $\beta = \frac{\alpha}{K}$ & $K = \frac{K_1}{K_2}$

K_1 and K_2 were found out by trial and error method. Regression lines were plotted based on Eqn. (3). RHS of Eqn. (3) was plotted against t based on the experimental results for various molar ratios as shown in Figs. 2, 3, 4 and 5. β values were adjusted such that the ordinate intercept was negligible enough.

The slope of the regression line gave $2.K_2.\alpha$. By back substitution values of K_1 and K_2 were found.

Arrhenius equation was used in determining the rate of chemical reactions and for calculation of the activation energy. The Arrhenius equation is of the form:

$$K = A\exp[-Ea/RT] \tag{4}$$

K- rate constant
A-Pre-exponential factor
R-Universal gas constant (8.314 kJ/kgmolK)
Taking natural logarithm,

$$\ln K = \ln A - (Ea/RT) \tag{5}$$

The experimentally obtained values of reaction rates for various temperatures were plotted and the goodness of fit of the same ascertains the exponential dependence of rate constants with temperature. The slope and intercept values of plots of lnK vs T were noted. By back substitution the activation energy and pre-exponential factors for both forward and backward reactions were found out.

3. RESULTS AND DISCUSSION

3.1 Acid Esterification

Acid value variation with respect to temperature is shown in Fig. 1. Methanol/oil ratio of 4:1 was selected and the influence of temperature was examined. Obviously, the rise in temperature increased the rate of reduction of acid value. The highest rate was at a temperature of 60 ^{0}C, which is near the boiling point of methanol at atmospheric pressure. The trend shows that as the temperature is further increased the esterification reaction rate should increase. However, it requires the reaction pressure to be raised which is currently out of scope of the work.

3.2 Kinetic Study

RHS of Eqn. (3) was plotted against time t and the regression lines were drawn. By back-substitution, we get the values of K_1 and K_2. K_1 and K_2 values were found out for various reaction temperatures. At 30 ^{0}C, K_1 value obtained was 0.0065 min^{-1} and K_2 value 2.22857 x 10^{-6} g/mg-min. The low value of K_2 shows the low probability of the backward hydrolysis reaction (conversion of ester to free fatty acid). K_1 and K_2 values obtained for various temperatures are given in Table. 2. Using these values ln K was plotted against 1/T and a regression line was fitted through the same (shown in Fig. 6). R^2 value for ln K_1 of 0.9905 confirms the goodness of fit of the experimental values with Arrhenius plot. However for the backward reaction, the R^2 value is less. By back substitution, values of energy of activation and pre-exponential factor were found out for the reaction. Table 3 shows the value of energy of activation and preexponential factors obtained for forward and backward
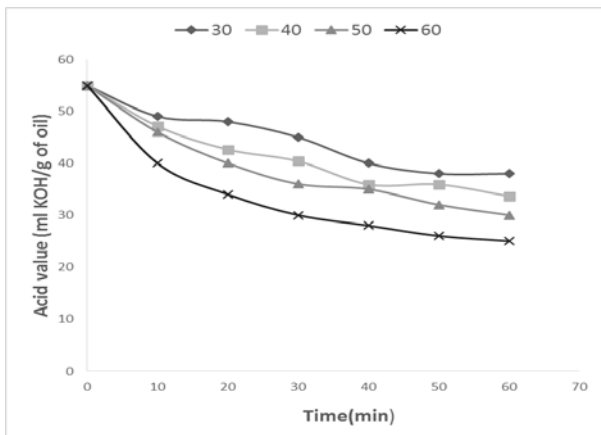
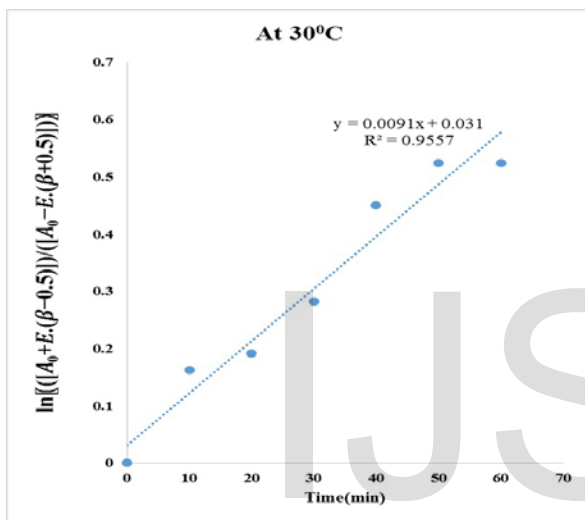Fig. 1. Variation of acid value with temperature

more compared to the forward reaction. For reactants to transform into products, they must first acquire a minimum amount of energy which is called the activation energy E_a. The lower value of activation energy for forward reaction and the higher value of reverse reaction show the ease with which forward reaction occurs with respect to the backward reaction.
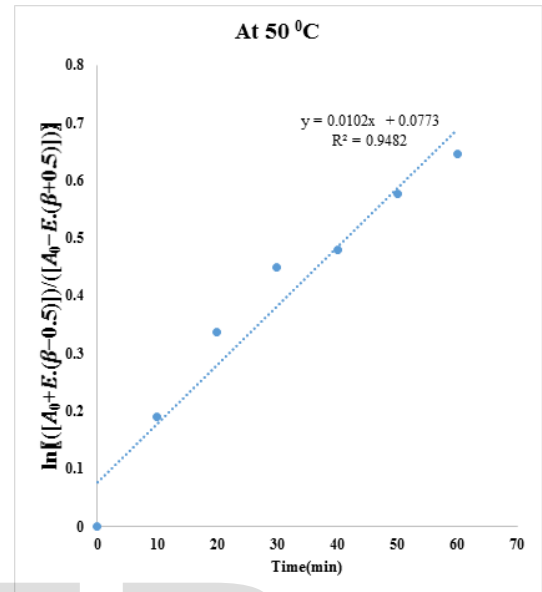

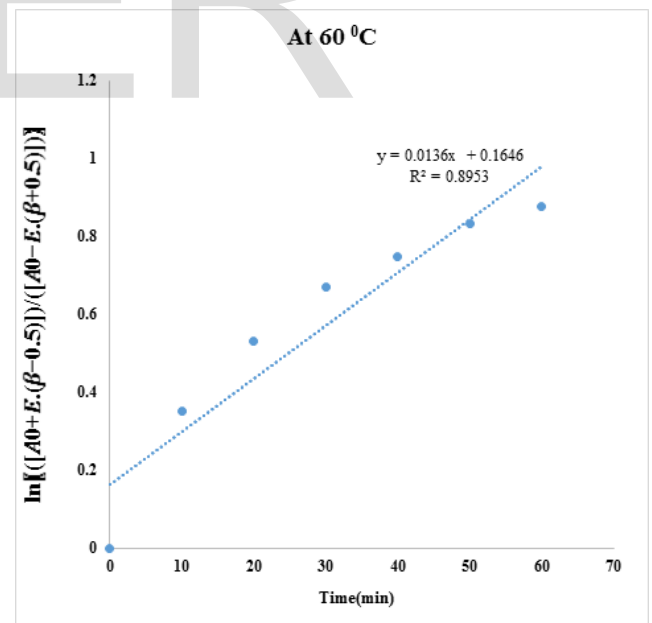Fig. 2. Determination of rate constants using Eqn. 3 at 30 ^{0}C

Fig. 4. Determination of rate constants using Eqn. 3 at 50 ^{0}C

Fig. 4. Determination of rate constants using Eqn. 3 at 40 ^{0}C

Fig. 5. Determination of rate constants using Eqn. 3 at 60 ^{0}C

reactions. The activation energy for the backward reaction is

TABLE 2.
VALUES OF K$_1$ AND K$_2$ FOR VARIOUS TEMPERATURES

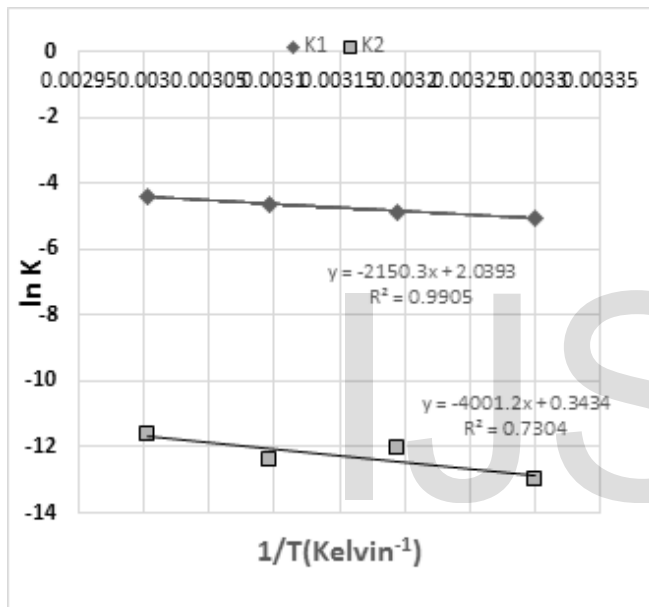| Temperature (K)	K$_1$	K$_2$
303	0.0065	2.22857×10^{-06}
313	0.007818182	5.86364×10^{-06}
323	0.009622642	4.24771×10^{-06}
333	0.012363636	9.27273×10^{-06}

Fig. 6. Determination of rate constants using eqn. 3 at 50 ^{0}C

TABLE 3.
VALUES OF ACTIVATION ENERGY AND PRE-EXPONENTIAL FACTOR

Reaction	Activation energy(J/mol)	Pre exponential factor
K$_1$	17877.5942	0.128087
K$_2$	33265.9768	0.023496

4. CONCLUSIONS

The rate of reduction in acid value depends on the temperature of the reaction. As the temperature increases, acidity removal rate increases. However the temperature of the reaction was limited to 60^{0}C above which the methanol boils off. The trend is in close agreement with the observations of Berrios et al. [13]. The energy of activation and pre-exponential factors for forward reaction found out by Mittelbach et al. [11] was 13.3 kJ/mol and 1.27, respectively. The high energy of activation for the reverse reaction shows the least possibility of the same to occur in the reaction conditions.

REFERENCES

[1] M.S Zanuttini, M.L Pisarello, C.A Querini, "Butia Yatay coconut oil: Process development for biodiesel production and kinetics of esterification with ethanol," Energy Conversion and Management, 85, pp. 407–16, 2014.

[2] M Habibullah, H.H Masjuki, M.A Kalam, F. Rizwanul, A.M Ashraful, H.M Mobarak, "Biodiesel production and performance evaluation of coconut, palm and their combined blend with diesel in a single-cylinder diesel engine," Energy Conversion and Management, vol. 87, pp. 250–57, 2014.

[3] A Junaid, Y Suzana, B Awais, N Ruzaimah, "Study of fuel properties of rubber seed oil based biodiesel," Energy Conversion and Management; vol. 78, pp. 266–275, 2014.

[4] A.S Ramadhas, S Jayaraj, C Muraleedharan, "Characterization and effect of using rubber seed oil as fuel in the compression ignition engines," Renew Energy, vol. 30, pp. 795–803, 2005.

[5] S.A Eugenio, M Gerardo, D Jose, R Lozada, R Luis, Hernandez, R.B Erick, B Horacio, "Biodiesel production and de-oiled seed cake nutritional values of a Mexican edible Jatropha curcas," Renewable Energy, vol. 76, pp. 143-147, 2015.

[6] S.K Karmee, A Chadha, "Preparation of biodiesel from crude oil of Pongamia pinnata", Bioresource Technology, vol. 96, pp. 1425–1429, 2005.

[7] M Habibullah, H.H Masjuki, M.A Kalam, F Rizwanul, A.M Ashraful, H.M Mobarak, "Production and comparison of fuel properties, engine performance,and. emission characteristics of biodiesel from various non-edible vegetable oils: A review", Energy Conversion and Management, vol. 80, pp. 202–228, 2014.

[8] M Satyanarayana, C Muraleedharan, "Biodiesel Production from Vegetable Oils; A Comparitive Optimization Study", Journal of Biobased Materials and Bioenergy, vol. 4, pp. 335-41, 2009.

[9] B Freedman, E.H Pryde, TL Mounts, "Variables affecting the yields of fatty esters from transesterified vegetable oils", JAOCS, vol. 61, pp. 1638–43, 1984.

[10] K Liu, "Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials", JAOCS, vol. 71(11), pp. 1179–87, 1994.

[11] M Mittelbach, B Pokits, A Silberholz, "Diesel fuel derived from vegetable oils, IV: production and fuel properties of fatty acid methyl esters from used frying oil", Liquid fuels from renewable resources, Proceedings of the alternative energy conference, Michigan (USA): American Society of Agricultural Engineers, pp. 74, 1994.

[12] A.S Ramadhas, S Jayaraj, C Muraleedharan, "Biodiesel production from high FFA rubber seed oil", Fuel, vol. 84, pp. 335–40, 2005.

[13] M. Berrios, J Siles, M.A Martin, A Marttin, "A kinetic study of the esterification of free fatty acids in sunflower oil", Fuel, vol. 86, pp. 2383-88, 2007.

[14] H.A Farag, A El-Maghraby, N.A Tasha, "Kinetic study of used vegetable oil for esterification and trans-esterification process of biodiesel production", IJCBS, vol. 3, pp. 1-8, 2013.

[15] E Sendzikiene, V Makareviciene, P Janulis, S Kitrys, "Kinetics of free fatty acids esterification with methanol in the production of biodiesel fuel", Eur J Lipid Sci Technol, vol. 106, pp. 831–6, 2004.

[16] K.V Thiruvengadaravi, J Nandagopal, S Sathya, K Dinesh, P Vijaya-lakshmi, and S Sivanesan, "Kinetic study of the esterification of free fatty acids in non-edible Pongamia pinnata oil using acid catalyst", Indian Journal of Science and Technology, vol.2, pp. 20-24, 2009.