

# Transesterification Kinetics of Soyabean Oil

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**Abstract**—The present study reports the results of the kinetic study of base catalyzed transesterification of soybean oil carried out at an optimum temperature of 338k, methanol to oil ratio of 6:1 and catalyst concentration 1% (w/w) for KOH. The yield of methyl ester (FAME) has been used to study the effect of different parameters which resulted in a maximum yield of 87.9%. The kinetic model of the transesterification reaction was analyzed using zero order, first order and second order kinetic models. The kinetic data informed to second order kinetic model. Activation energy obtained from this study was  $-10076.568\text{KJ/kmol}$  and a pre-exponential factor of  $1.1195 \times 10^{-5} \text{min}^{-1}$ .

**Keywords**— Methyl ester, Fatty acid Methyl ester, Soybean oil, Kinetics, Transesterification.

## I. INTRODUCTION

Globally, the demand for energy is increasing and the world will have to meet this demand with alternative energy sources because fossil fuel reserves are limited and are one of the main causes of pollution and global warming [1]. The depletion of the world's petroleum deposit and the attendant pollution caused by these non renewable energy sources has necessitated the need for an alternative source of energy [2]. Biodiesel is one of such renewable, alternative fuel derived from triglycerides by transesterification of vegetable oils and animal fat [3, 4]. Biodiesel has been gaining worldwide acceptance as an alternative energy source because it has many attractive features such as it is domestically produced offering the possibility of reducing petroleum imports. It has lower emission pollutants, higher cetane number, no aromatics, no sulphur and contains 10–11% oxygen by weight [5]. In addition it has higher biodegradability, high flash point and contributes a minimal amount of net green house gases, such as  $\text{CO}_x$  and  $\text{NO}_x$  emission and sulphur to the atmosphere [6]. Cetane number, energy content, viscosity and phase changes of biodiesel are similar to those of petroleum – based change diesel [1, 7].

Biodiesel can be produced by three major processes such as pyrolysis micro-emulsification and transesterification of which the most common method is transesterification reaction [8, 9].

Transesterification reaction can be alkali catalyzed, acid catalyzed and enzyme catalyzed. It is a reaction of a lipid with an alcohol in the presence of catalyst to form esters and a by-product, glycerol. The reaction is reversible, and thus an excess of alcohol is usually used to force the equilibrium towards the production of fatty acid esters and glycerol [10].

Transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, palm, cotton seed, canola, coconut seed, olive, peanut oil etc. [11, 9, 12, 13, and 14].

Biodiesel production from soybean oil is very popular. It has five fatty acids: approximately equal amount of palmitic acid, oleic acid and linolenic acid (about 13% each). Linoleic acid (approximately 55%) and stearic acid (approximately 4%).

A useful industrial application of soybean oil is in biodiesel blends. Soybean oil derived biodiesel possess enhanced biodegradation, increased flash point, reduced toxicity, lower emissions and increased lubricity [15]

Numerous studies have been carried out on the kinetics of transesterification of esters with alcohol [16], only a few researchers are concerned with transesterification of vegetable oils [17, 7, and 18].

In this work, the primary objective is to determine the optimum conditions required to produce biodiesel by transesterification of soybean oil with methanol using potassium hydroxide as catalyst. The main thrust of this work is to evaluate the kinetic mechanism and to determine the reaction constants and activation energy.

## II. MATERIALS AND METHODS

### 2.1 MATERIALS

Refined Soya cooking oil was bought from a shop in Ogbete main market. The chemicals and reagents were ordered and obtained from Pymotech Research Laboratory Abakpa Nike, Enugu. The chemical and reagents used include methanol ( $\text{CH}_3\text{OH}$ ), potassium hydroxide (KOH), Phenolphthalein and distilled water. Other materials used include double ring 102 fitter paper and aluminum foil.

The fatty acid compositions of SBO from standard are shown in Table 1. The fuel properties of refined SBO

were determined as per standard methods and are repeated in Table 2.

The molecular weight of the oil from standard is 920g/mol and the acid value from characterization gave 0.1 mgKOH/g from which the saponification value was determined using standard titration methods [19] and the procedure described by Gryglewicz [20].

$$M = \frac{56.1 \times 1000 \times 3}{SV - AV} \quad (1)$$

Where SV and AV are the saponification and acid values (mgKOH/goil), respectively.

Table 1: Fatty acid composition of soybean oil

Fatty acid	Formula	% Composition
Palmitic acid (p)	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	7 – 12
Palmitoleic	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	0 – 0.4
Stearic acid (s)	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	2 – 5
Oleic acid (o)	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	19 – 30
Linoleic acid (L)	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	48 – 58
Linolenic acid	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	5 – 9
Arachidic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	0 – 0.9

Source: www.welch.holme-clark.com

Table 2 Fuel Properties of Soybean Oil

S/NO	PROPERTIES	SOYBEAN OIL
1	FFA contents (%)	0.05
2	Flash point (°C)	130
3	Density (kg/m <sup>3</sup> @150°C)	920
4	Kinematic viscosity (cst@30°C)	4.3
5	Acid value (mgKOH/g)	0.1

## 2.2 Characterization of Oil

The Kinematic viscosity, density, flash point, acid value and FFA content were analyzed by American Society for Testing and Materials (ASTM) standard methods.

## III. EXPERIMENTAL PROCEDURE

The reactor was initially charged with 100ml of filtered soyabean oil, placed in the constant temperature water bath and thermostated to the desired temperature of 50°C (323K). The 100ml filtered SBO was transferred into a 250ml conical flask containing a measured amount of methanol and (KOH) catalyst solution. The reaction was timed as soon as mechanical stirrer was turned on.

### 3.1 Reaction Conditions

The 6:1 molar ratio of methanol to soybean oil was used in all experiments from literature 1% w/v of catalyst (KOH) to oil is usually used per 100ml of oil. This was dissolved into methanol before use. The experiments were carried out at 318K, 328k and 338K and at atmospheric pressure. The impeller speed of 250rpm was applied to produce a uniform dispersion of methanol into the oil [20].

### 3.2 Transesterification

The methods used by [18, 21 and22] were applied. Batch transesterification of the soybean oil were carried out, 328K and 338K in a batch reactor. A batch reactor of (250ml) was charged with 100ml of oil and heated to the desired temperature in a water bath. The catalyst in pellet form was weighed and mixed with alcohol. The mixture was then shaken for about 1hr until all the catalyst dissolved. The mechanical stirrer was started, and reaction was timed when the solution (mixture) was added. The samples (5ml) were removed from the reaction mixture during the progress of the reaction; immediately quenched by adding aqueous sulphric acid solution to neutralize the catalyst. The product of reaction was exposed to open air to evaporate excess methanol for 30mins. The product was then allowed to settle overnight. Two distinct liquid phases: Crude ester phase at the top and glycerol phase at the bottom. The biodiesel produced was then purified by washing with distilled water to remove all the residual by-products like excess alcohol, excess catalysts, soap and glycerine. The volume of distilled water added was approximately 30% of the biodiesel volume.

$$\% \text{ conversion} = \frac{\text{Volume of methylester converted}}{\text{Total volume collected}} \times 100 \quad (2)$$

To examine the temperature dependency of the reaction rate constants at 318k, 328K and 338k, a fraction of the sample were taken at reaction times from (60 – 300) minutes to study the kinetics of transesterification.

## IV. RESULT AND DISCUSSION

Fig. 1 shows that during transesterification, 87.9% yield of ME was obtained at 328K using 1% KOH (w/w). As the value of the reaction parameters increases beyond this value FAME yield decreases due to reversible nature of reaction [23]. Fig. 2, it can be observed that the slope of the graph is negative and thus it can be deduced from the graph that the reaction did not follow zero order kinetic model. The correlation coefficients obtained are 0.876, 0.869 and 0.845 at temperatures of 318K, 328K and 338K respectively.

It is seen from the Fig. 3 that the transesterification reaction did not follow first order kinetic model as the correlation coefficient of 0.879, 0.865, and 0.846 were obtained at 318K, 328K, and 338K respectively. This is in agreement with the transesterification reaction of palm oil to methylester at the molar ratio 6:1 (methanol to oil) [25].

The high values of correlation coefficient as shown in Fig. 4, indicates that the transesterification reaction conformed to second order kinetic model. The values of the reaction rate constants K were obtained as 0.863, 0.865, and 0.879 at 318K, 328K and 338K respectively. The result shows that rate constant increased with increase in temperature, hence the reason for higher yield of FAME of higher temperature.

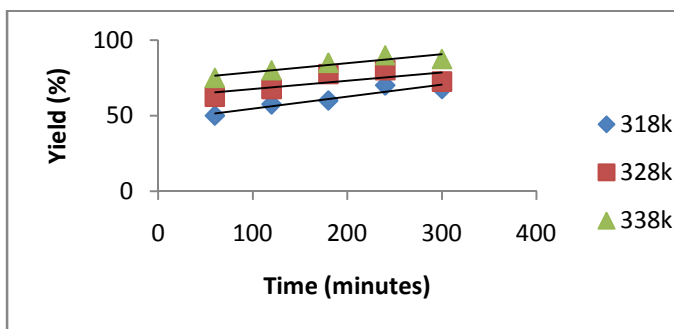


Fig. 1: ME yield (%) against time.

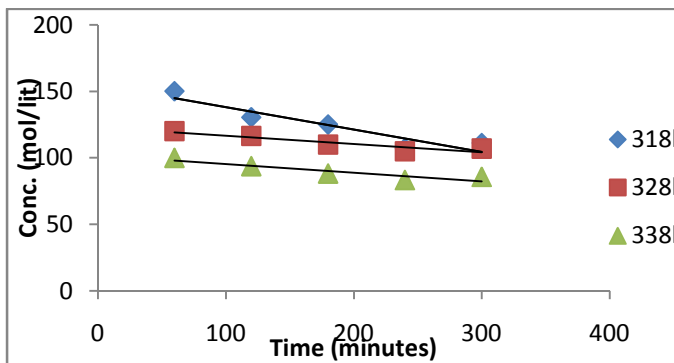


Fig. 2: Zero Order Plot  $C_A$  vs.  $t$

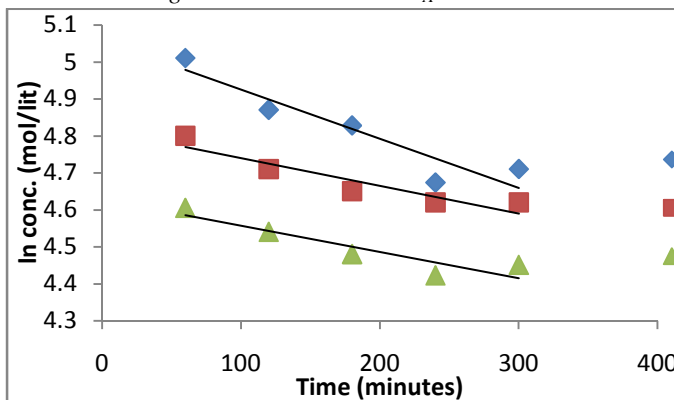


Fig. 3: First Order Plot  $\ln C_A$  vs.  $t$

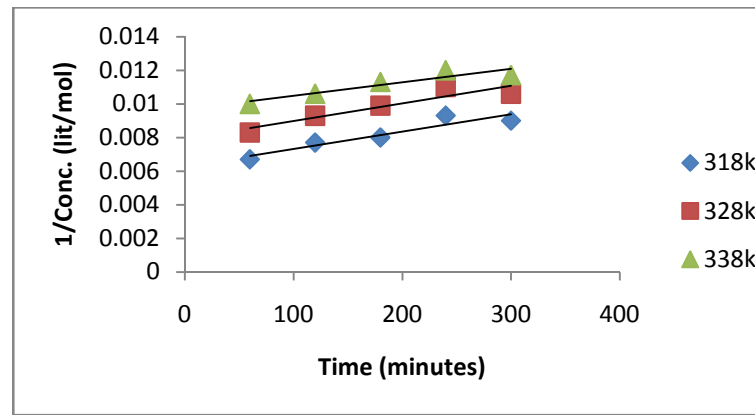
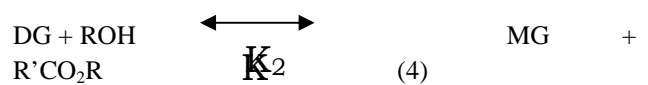
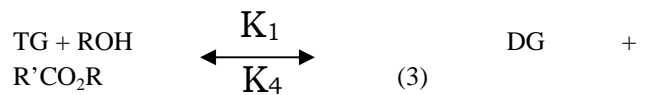


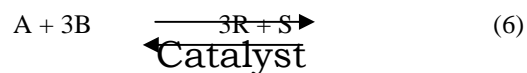
Fig. 4: Second Order Plot  $1/C_A$  vs.  $t$

#### 4.1 Kinetics of transesterification of soybean oil

Transesterification reaction of triglycerides (TG) proceeds in three step in which the triglycerides reacts with an alcohol (methanol) to produce diglycerides (DG), which further reacts with methanol to yield monoglycerides (MG) that finally reacts with methanol to produce methylester and glycerol and as can be seen in equations below [25].



From the above three process steps of transesterification reaction, six rate constants of  $K_1 - K_6$  are reported in the literature for the whole reaction from triglyceride (TG) to methyl ester (ME) biodiesel as shown in equation 6 below.



Where A is TG, B is methanol, R is FAME and S is a glycerol.

According to the above equation, whole transesterification results ultimately in the production of FAME and therefore, all the intermediate reaction products (e.g. DG and MG) can be ignored and simple mathematical model expressing the whole conversion as one step has been developed.

The reaction mechanism of the transesterification of soybean at different temperatures was analyzed using zero, first and second order kinetic models.

**ZERO ORDER:**

Zero order kinetic model was used to treat the kinetic data as shown below:

$$\text{Rate} = -\frac{dC_A}{dt} = KC_A^n \quad (7)$$

Where n is the order of the reaction.

$$-\frac{dC_A}{dt} = KC_A^{(0)}$$

$$-\frac{dC_A}{dt} = K(1) = K$$

$$-\frac{dC_A}{dt} = K$$

Separating the variables

$$dC_A = Kdt \quad (8)$$

Integrating above equation

$$\int -dC_A = \int dt$$

$$C_A = Kt$$

The Zero Order model can be obtained by plotting  $C_A$  against t to give a rate constant K which is the slope of the graph.

**First Order**

The First Order model proposed by Freedman et al (1986) was adopted. Second Order Kinetic model according to Nouredini and Zhu (1997) was used to treat the kinetic data.

The First Order rate constant of the reaction can be expressed below.

$$\text{Rate} = -\frac{dC_A}{dt} = KC_A \quad (10)$$

Rate equation of first order may also be written as

$$\text{Rate} = -\frac{dC_A}{dt} = KC_A$$

Where (-) represents the % TG yield.

Since the TG concentration is related to the conversion degree of TG,  $X_A$ , as follows:

$$C_A = C_{A0}(1 - X_A)$$

Where  $C_A$  and  $C_{A0}$  are the actual and initial TG concentrations.

$$-\frac{dC_A}{dt} = \frac{dX_A}{dt} = K(1 - X_A) \quad (11)$$

$$\frac{dX_A}{dt} = K(1 - X_A)$$

$$-\frac{dX_A}{dt} = K(1 - X_A)$$

Separating variables

$$-\frac{dX_A}{1 - X_A} = Kdt$$

Integrating the above equation

$$\int_0^{X_A} \frac{1}{1 - X_A} = K \int_0^t dt \quad (12)$$

$$-\ln(1 - X_A) = Kt + C$$

Where C is the constant of integration and  $C_A = (1 - X_A)$

$$\ln C_A = -Kt$$

The First Order model can be obtained by plotting the values of  $\ln C_A$  against time to obtain a rate constant K which is the slope of the graph.

**Second Order**

Second Order Kinetic model according to Nouredini and Zhu (1997) was used to treat the kinetic data

$$(-r_A) = -\frac{dC_A}{dt} = \frac{KC_A^2}{C_{A0}(1 - X_A)^2} \quad \text{where } C_A^2 = C_{A0}^2(1 - X_A)^2$$

$$-\frac{dC_A}{dt} = \frac{dX_A}{dt} = \frac{KC_{A0}(1 - X_A)^2}{dt}$$

where K is the reaction rate constant for the irreversible pseudo-second order reaction. Separating the variables we obtain

$$-\frac{dX_A}{(1 - X_A)^2} = KC_{A0}dt$$

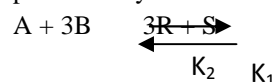
Integrating the above equation yields

$$\int \frac{1}{(1 - X_A)^2} dX_A = KC_{A0} \int_0^t dt$$

$$\frac{1}{1 - X_A} = KC_{A0}t + C_1$$

Where  $C_1$  is the constant of integration and  $C_A = (1 - X_A)$  The reaction rate and integration constants can be estimated from the slope and intercept of the linear graph dependence of  $1/C_A$  versus time, respectively.

The overall vegetable oil methanolysis reaction can be presented by the following stoichiometric equation.



Where A is vegetable oil (Triglyceride), B is the alcohol (methanol), R is biodiesel (FAME) and S is glycerol.

$$(-r_A) = \frac{dC_A}{dt} = K_1 \frac{N_A}{V} \frac{N_B}{V} - K_2 \frac{N_R}{V} \frac{N_S}{V}$$

Where  $K_1$  and  $K_2$  are the reactant rate constants for the forward and reverse reactions, respectively. And  $C_B$ ,  $C_R$  and  $C_S$  are the actual concentrations of methanol, FAME and glycerol respectively. The initial concentrations of biodiesel (FAME) and glycerol are zero and the initial concentration of methanol is  $C_{BO}$ .

$$\text{Where } \frac{N_A}{V} = C_A, \frac{N_B}{V} = C_B, \frac{N_R}{V} = C_R, \frac{N_S}{V} = C_S$$

$$(-r_A) = -\frac{dC_A}{dt} = K_1 C_A C_B - K_2 C_R C_S$$

Since  $C_A = (1 - X_A)$ ,  $C_B = C_{BO} - 3C_{AO}X_A$ ,  $C_R = 3C_{AO}X_A$  and  $C_S = C_{AO}X_A$ , it follows that

$$\frac{-dC_A}{dt} = \frac{dX_A}{dt} = K_1(1 - X_A)(C_{BO} - 3C_{AO}X_A) - 3K_2C_{AO}X_A^2$$

Where  $K = \frac{K_2}{K_1}$  is the reciprocal value of the equilibrium constant for the overall methanolysis reaction, and  $M = \frac{C_{AO}}{C_{BO}}$  is the initial molar ratio of TG to methanol.

The equilibrium constant can be calculated from the equilibrium degree of TG conversion,  $X_{Ae}$ , which can be experimentally determined, since it is

$$\frac{dX_A}{dt} = K_1 C_{BO} [C_1 - X_{Ae}(1 - 3MX_{Ae}) - 3KM X_{Ae}^2] = 0$$

$$K = \frac{3MX_{Ae}^2 - (1+3M)X_{Ae} + 1}{3MX_{Ae}^2}$$

#### 4.1.1 Arrhenius Parameters

The collision theory shows that for a reaction to occur the reactants should collide with the proper orientation and sufficient energy; Arrhenius believed that for molecules to react upon collision they must become "activated" and the parameter  $E_a$  has become known as the activation energy.

The Arrhenius equation [26] was used to determine the activation energy.

Where  $K$  is reaction rate constant,  $A$  is pre-exponential factor ( $\text{min}^{-1}$ ),  $E_a$  the activation energy KJ/mol,  $T$  is the absolute temperature (K) and  $R$  is the universal gas constant. Since the activation energy is dependent on temperature and therefore, the rate constants at any temperature within the validity of the Arrhenius equation (Activation energy wikipedia, 2008) can be computed using equation below

$$\ln K = \ln A - (E_a/RT)$$

Experimentally from a plot of  $\ln K$  against  $1/T$  (where  $T$  = absolute temperature) for temperatures of 318K, 328K, and 338K gives  $E_a/R$ .

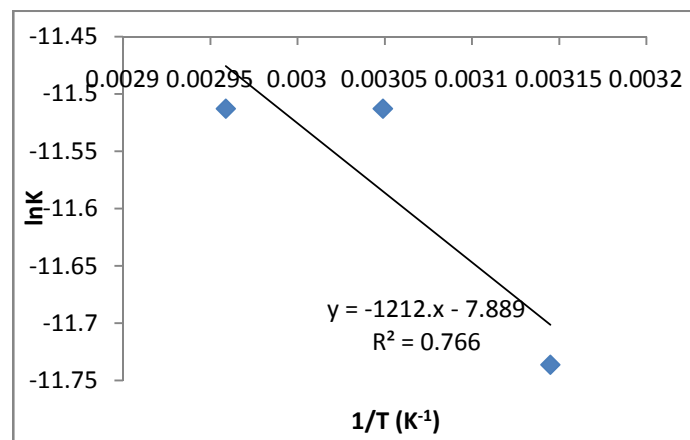


Fig. 5: Plot of  $\ln K$  vs.  $1/T$

## V. CONCLUSION

The present study deals with the kinetics of soybean oil. The optimum reaction for the methanolysis of soybean oil was achieved at methanol to oil ratio 6:1, reaction temperature of 338K, rate of mixing 250rpm-350rpm and a reaction time of 240min.

The rate parameters showed that the kinetic transesterification of soybean oil data conformed to second order kinetic model with respect to ester formation. The rate constant of the second order reaction are  $8 \times 10^{-6} \text{min}^{-1}$ ,  $1 \times 10^{-5} \text{min}^{-1}$ , and  $1 \times 10^{-5} \text{min}^{-1}$  at 318K, 328K and 338K respectively. This also represents that the energy required for the transesterification to occur which is calculated as 10076.568KJ/kmol. The lower activation energy indicating that methanol biodiesel has better combustion properties.

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