

Reaction Kinetics of Biodiesel Production from Refined Cottonseed Oil Using Calcium Oxide

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Abstract—Power law approximation was used in this study to evaluate the reaction orders of calcium oxide, CaO catalyzed transesterification of refined cottonseed oil and methanol. The kinetics study was carried out at temperatures of 45, 55 and 65 °C. The kinetic parameters such as reaction order 2.02 and rate constant $2.8 \text{ hr}^{-1}\text{g}^{-1}\text{cat}$, obtained at the temperature of 65 °C best fitted the kinetic model. The activation energy, E_a obtained was 127.744 KJ/mol. The results indicate that the transesterification reaction of the refined cottonseed oil using calcium oxide catalyst is approximately second order reaction.

Keywords—Refined cottonseed oil, transesterification, CaO, heterogeneous catalysts, kinetic model.

I. INTRODUCTION

DEPLETION of world petroleum reserves and increasing environmental concerns has necessitated the search for renewable fuels in recent years. Biodiesel is the most promising renewable fuel which has attracted attention worldwide [1]. This is because of its outstanding benefits over the conventional petro diesel. It is renewable, biodegradable, non-toxic, with high flash point and good reduction in greenhouse emissions [2]-[5].

Biodiesel also known as fatty acid methyl ester (FAME) is renewable and environmentally friendly fuel which can be obtained by transesterification of vegetable oils or animal fats with alcohol in the presence of both homogeneous and heterogeneous catalysts [6]. The transesterification of vegetable oils is usually performed by using sodium hydroxide (NaOH) and potassium hydroxide (KOH) as alkaline catalysts or sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) as acid catalysts in a homogeneous manner [7]–[9]. The homogeneous catalytic systems have some drawbacks. A large amount of waste water is produced during the process of separating and cleaning the catalyst and the products. Therefore, it is considerably more costly to separate the catalyst from the produced solution [10]. The replacement of homogeneous catalysts with heterogeneous catalysts eliminates the drawbacks of homogeneous catalyst.

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Heterogeneous base catalysts have received much attention in biodiesel production because of many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. Meanwhile, they are much more easily separated from the liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [11]–[13]. Thus the biodiesel production process becomes more economic and environment friendly [14], [15]. The reusability is the main problem in biodiesel production with heterogeneous catalysts. The leaching of support or active sites causes catalyst loss and thus decreases the FAME yield. After solving this problem, the cleaner biodiesel production will become more competitive with petroleum diesel [16].

Every vegetable oil has a peculiar fatty acid composition. The fuel characteristics of biodiesel depend on the fatty acid composition of the oil used. Cottonseed oil is rich in linoleic acid, which contains 18 carbon atoms and one double (unsaturated) bond. Therefore, this property results in superior cold flow property for canola based biodiesel. Also, cottonseed is used as a feedstock in biodiesel production because of its high oil content [1].

Many compounds have been used as heterogeneous catalyst for the biodiesel synthesis. Yuan et al. [17] employed Na_2CO_3 as a heterogeneous base catalyst in synthesis of biodiesel using castor oil under microwave radiation and obtaining yield of 90%. Alkaline earth oxides, in particular magnesium oxide (MgO) [16], [18]–[20] and calcium oxide (CaO) [21], [22] are potential heterogeneous catalysts for use in biodiesel production research and have attracted attention in recent years. CaO has attracted many interests as a heterogeneous catalyst because it can be synthesized from cheap sources like calcium carbonate, calcium acetate and calcium nitrate. It can be used as a simple, safe and non-toxic catalyst for the biodiesel production reaction. It also possesses basicity as high as alkali metal oxides while it showed less leaching of active sites into the product stream. CaO was employed as a heterogeneous catalyst in this study.

The transesterification reaction kinetics is indispensable for the production process development and the reactor design operation and scale-up. The understanding of the transesterification reaction kinetics is also necessary for development of mathematical models describing the reaction rate and the product yield [22].

Although homogeneously catalyzed kinetics of transesterification has been investigated in several papers [23]–[29], the kinetics of heterogeneously catalyzed reaction has been rarely studied. Biodiesel production reaction with homogeneous catalyst such as NaOH or KOH proceeds via

formation of methoxide anions from the reaction of the catalyst and methanol. A heterogeneous catalytic reaction process involves adsorption of reactants onto the catalyst surface, reaction on the catalyst surface and desorption of products [22]. According to Filippes et al. [30] in the presence of solid base catalysts the active species for transesterification reactions are methoxide ions formed upon adsorption of methanol on the catalyst surface. Hattori et al. [31], proposed a five step mechanism for the transesterification of ethyl acetate with different rate determining steps according to the catalyst basicity. The first order kinetic model with respect to triglyceride [32] or methanol [33] was presented for the reaction kinetics of metal oxide catalyzed transesterification of soybean oil and methanol at high temperatures. Kouzu et al. [34] reported that the reaction kinetics varied from the zero order to the first order with respect to triglyceride. Ilgen [22] evaluated power law approximation and the reaction orders of dolomite catalyzed transesterification of canola oil and methanol.

In this study, the kinetics parameters and thermodynamics properties of the transesterification reaction between the refined cottonseed oil and methanol using CaO were investigated.

II. MATERIAL AND METHODS

A. Materials

The commercial refined, edible grade cottonseed oil was purchased from Shoprite Enugu, Nigeria. The methanol and CaO were purchased from De-Cliff Integrated Services Ltd Enugu, Nigeria and they were of analytical grade.

B. Preparation of Catalyst

The catalyst (CaO) was calcined in a muffle furnace at temperature of 550°C for 5h to remove any absorbed water. They were stored in a desiccator in the presence of silica and KOH pellets in order to avoid water and CO₂ contact with the catalysts.

C. Transesterification Reaction

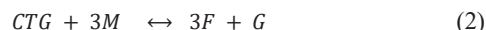
The transesterification was carried out in a batch reactor. A 200ml round-bottom flask was equipped with a reflux condenser. The reaction temperature was controlled by a hotplate with temperature sensor and magnetic stirring rate of 500rpm was adjusted. The refined cottonseed oil was precisely quantitatively transferred into the reactor. Then specific amount of catalyst, CaO (by weight of refined cottonseed oil) dissolved in the required amount of methanol was added. The reaction flask was kept on a hot magnetic stirrer at a particular temperature with defined agitation throughout the reaction. At the defined time, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e. the glycerol in the lower layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of layer biodiesel with the weight of refined cottonseed oil used.

Biodiesel yield,

$$Y_b (\%) = \frac{\text{weight of fatty acid methylester}}{\text{weight of oil used}} \times 100\% \quad (1)$$

D. Kinetic Model and Determination of Reaction Kinetics

The overall transesterification reaction of refined cottonseed oil with methanol is presented as (2):



where CTG is the cottonseed triglyceride, M is methanol, F is FAME and G is glycerin.

$$-r_{CTG} = -\frac{d[CTG]}{dt} = k[CTG]^\alpha[M]^\beta \quad (3)$$

The reaction is considered irreversible because of the excessive presence of M in the reaction. In this study, the overall reaction equation following nth order is adopted to determine the best rate order with rate equation between pseudo first order and pseudo second order models for the transesterification reaction.

$$-r_{CTG} = -\frac{d[CTG]}{dt} = k[CTG]^\alpha \quad (4)$$

where k is the rate constant, α is reaction order of CTG, β is the reaction order of M, [CTG] and [M] are concentration of the reactants CTG and M respectively. Therefore, from (3) and (4), the rate equation for the heterogeneous catalyzed transesterification can be expressed as:

$$-r_{CTG} = \frac{N_{CTG_0}}{W} \frac{dX_{CTG}}{dt} = kC_{CTG}^\alpha \quad (5)$$

$$C_{CTG} = C_{CTG_0}(1 - X_{CTG}) \quad (6)$$

where N_{CTG_0} is initial number of moles of cottonseed triglyceride, C_{CTG} and C_{CTG_0} are the final and initial concentrations of cottonseed triglyceride, X_{CTG} is the conversion and W is the catalyst weight.

$$\frac{N_{CTG_0}}{W} \frac{dX_{CTG}}{dt} = kC_{CTG_0}^\alpha (1 - X_{CTG})^\alpha \quad (7)$$

The conversion of CTG (X_{CTG}) and FAME yield, Y_b were assumed to be of each other by using (5)-(7).

$$Y_b = \frac{C_F}{3C_{CTG_0}} \quad (8)$$

$$C_{CTG} = C_{CTG_0} - C_F \quad (9)$$

By substituting (8) into (9), (6) can be transferred to give (10):

$$C_{CTG} = C_{CTG_0}(1 - Y_b) \quad (10)$$

According to (6) and (10), the X_{CTG} is equal to Y_b . In order to determine the reaction order, α , the Y_b was determined in (1).

$$\frac{dX_{CTG}}{dt} = \frac{W}{N_{CTG_0}} k C_{CTG_0}^{\alpha} (1 - X_{CTG})^{\alpha} \quad (11)$$

$$\frac{dX_{CTG}}{dt} = K' (1 - X_{CTG})^{\alpha} \quad (12)$$

$$K' = \frac{W}{N_{CTG_0}} k C_{CTG_0}^{\alpha} \quad (13)$$

Taking natural logarithm of both sides, (12) becomes

$$\ln\left(\frac{dX_{CTG}}{dt}\right) = \ln K' + \alpha \ln(1 - X_{CTG}) \quad (14)$$

A plot of $\ln\left(\frac{dX_{CTG}}{dt}\right)$ against $\ln(1 - X_{CTG})$, gives a slope of α and intercept of $\ln K'$.

$\frac{dX_{CTG}}{dt}$ was calculated using finite difference formula on yield of biodiesel and time.

Activation energy of the reaction was determined applying Arrhenius equation.

$$K = K_0 \exp \frac{-E}{RT} \quad (15)$$

$$\ln K = \left(\frac{-E}{RT}\right) + K_0 \quad (16)$$

where K_0 = Pre-exponential factor, E = Activation energy J/mol, R = Gas constant 8.314 J/mol, T = Absolute temperature.

From a plot of $\ln K$ against $\frac{1}{T}$ gives a slope of $\frac{-E}{R}$. Then,

$$-E = \text{Slope} \times R \quad (17)$$

$$\ln K_0 = \text{intercept} \quad (18)$$

$$K_0 = e^{\text{intercept}} \quad (19)$$

III. RESULT AND DISCUSSION

The heterogeneous-catalyzed transesterification of cottonseed oil at three temperatures were studied. The molar ratio of methanol to cottonseed oil was constant at 6:1, reaction time of 3 hours and calcium oxide, CaO amounted to 6% based on the mass of the cottonseed oil.

Under the optimum conditions FAME yields of 80% were obtained with calcium oxide.

A. Kinetic Model and Determination of Reaction Kinetics

Figs. 1-3 are the plots of $\ln\left(\frac{dX_{CTG}}{dt}\right)$ against $\ln(1 - X_{CTG})$, at various temperatures of 45, 55 and 65 °C. It could be observed that the rate constant increased as temperature increased. This could be because the rate constant increased with increase in the temperature of the reaction. Fig. 4 was used to determine activation energy for the reaction kinetics. From the figure, Activation energy, $E_a = 127.744 \frac{\text{KJ}}{\text{mol}}$. The high value of coefficient of determination R^2 showed that the data conformed to Arrhenius equation. The rate equation obtained for the reaction are, $-r_{CTG} = 0.183 C_{CTG}^{0.893}$ for 45°C, $-r_{CTG} = 1.39 C_{CTG}^{1.93}$ for 55°C and $-r_{CTG} = 2.8 C_{CTG}^{2.02}$ for 65°C.

Table I gives the coefficient of determination, R^2 values of the reaction orders of the temperatures studied. From the table,

it was shown that the coefficient of determination increased as the temperature increased and reaction at 65 °C has highest coefficient of determination. This showed that reaction order and reaction rate better matched experimental data at 65 °C. Table I indicates that the most appropriate reaction order is 2.02 with respect to CTG.

TABLE I
THE VALUES OF R^2 FOR THE ORDER OF REACTION CONSIDERED

Order of reaction	K (hr ⁻¹)	α reaction order	R^2
45°C	0.183	0.893	0.936
55°C	1.39	1.93	0.950
65°C	2.8	2.02	0.97

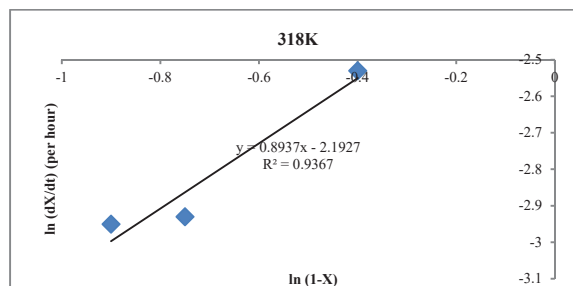


Fig. 1 Kinetics plot for cottonseed oil transesterification at 45 °C

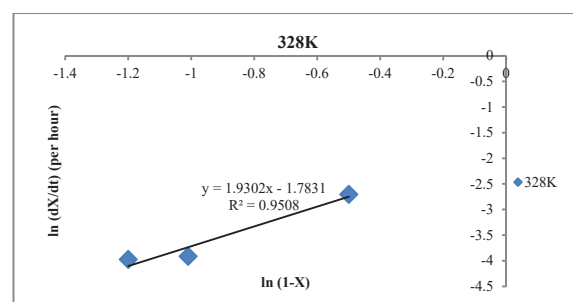


Fig. 2 Kinetics plot for cottonseed oil transesterification at 55 °C

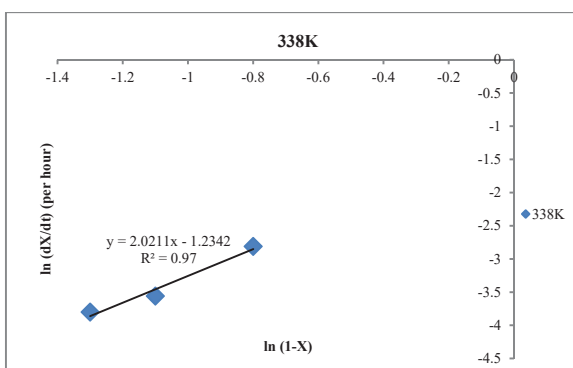


Fig. 3 Kinetics plot for cottonseed oil transesterification at 65 °C

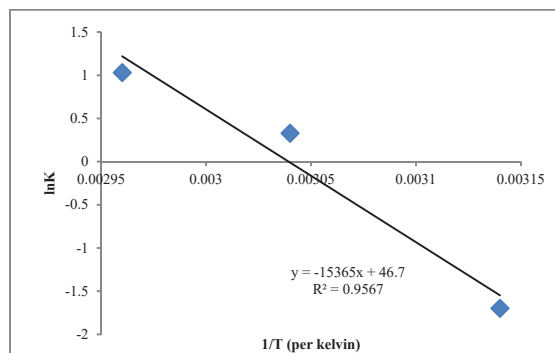


Fig. 4 Activation energy plot for cottonseed oil transesterification

IV. CONCLUSION

The reaction kinetics of heterogeneous catalyzed transesterification of refined cottonseed oil and methanol was studied to calculate the rate constants and reaction orders. The kinetic equation developed by Singh and Fernando [35] was used after modification. The reaction orders for triglyceride at temperatures of 45, 55, and 65 °C were determined as 0.893, 1.93 and 2.02 with rate constants of $0.183 \text{ hr}^{-1} \text{ g}^{-1} \text{ cat}$, $1.39 \text{ hr}^{-1} \text{ g}^{-1} \text{ cat}$, $2.8 \text{ hr}^{-1} \text{ g}^{-1} \text{ cat}$ respectively. Good correlations were obtained for reaction orders and rate constants for the different temperatures with 65 °C having the highest coefficient of determination. The reaction orders and rate constants at 65 °C was accepted as the best values for the kinetic model of the heterogeneous transesterification reaction. Activation energy E_a , was evaluated as 127.744 KJ/mol. The high value of coefficient of determination R^2 showed that the data conformed to Arrhenius equation.

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