



# The Effect of Reaction Temperature on the Yield of Biodiesel Produced Using Two Types of Clay as Catalyst

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**Abstract-** This study was based on the effect of the reaction temperature on the yield of biodiesel using the oil from *Elaeisguineensis dura* as the feedstock. Humans need for fossil energy increase every year. Biodiesel is the main way to resolve this world problem. The transesterification of non-edible oils for biodiesel production is one of the promising process for biodiesel production to overcome this future crises of energy. Two types of clay samples were used as catalysts (Ukpo and Nsu) and it was discovered that Ukpo gave a better yield in biodiesel production due to the less presence of Aluminum oxide. Statistical analysis, which includes ANOVA and Surface Response model were used to optimize the process using Matlab toolbox and it was discovered that optimum yield occurred at calcination temperature of 960.89 °C, reaction temperature of 65 °C, Potassium hydroxide concentration of 0.45M and a reaction time of 65.33 minutes. The yield can be improved by increasing reaction temperature. Another experiment was conducted at the optimal conditions by increasing the reaction temperature to 72oC which increased the yield to 91.22%. Other optimal values are global except for reaction temperature.

**Keywords-** Biodiesel, Clay, Temperature, Optimization, Transesterification

## I. INTRODUCTION

Declining of world's crude oil reserve and increasing of green fuel needs, led to the developing of renewable fuel production [1]. The movement of world economy requires development of technology as well as energy section. Green diesel demand predicted to reach 900 million tons in 2020 [2]. Green fuel demand was not balanced by the supply, managing the fossil fuel for being the main fuel sources.

Greater amount of green fuel production will maintain the situation and replaced the fossil fuel production. Green fuel as well as green diesel and bio diesel produced mostly from plant oil which needs time to grow and grant the oil ready. The major restricting factor in the development of biodiesel is the feedstock for its formation. According to previous researcher [3,4], the most common commercial process for biodiesel production is homogeneous alkali-catalyzed transesterification

in the presence of methanol using refined edible or non-edible oils as raw materials. In Malaysia, palm oil is effectively used as a feedstock for the production of biodiesel due to abundant cultivation of palm trees. However, this type of edible oil has considerable amount of free fatty acids (FFAs) which required a proper choice of catalyst for transesterification during biodiesel formation process. The use of heterogeneous catalyst in fatty acid methyl esters (FAME) production was introduced to solve the problems encountered in applying homogeneous catalysts. Some of such problems include: soap formation, difficulty in separation of the final products leading to generation of large waste water, poor recoverability of products etc. among others.

The selection of catalyst for such process is an art due to requirement of its high effectiveness for biodiesel yield as well as separation from main product. Most of homogeneous catalysts are active for biodiesel formation reactions but sensitive to water and FFAs present in feedstock which can form unwanted soap as a by-product. This by-product makes the final product separation difficult and also reduces the activity of the catalyst. A massive environmental unfriendly water washing process is required for separation of such type of soap by-product as well as removal of homogeneous catalyst from final product. Heterogeneous catalyst can overcome these problems as compared to homogeneous one for both commercial and environmental point of view. So far, a variety of different heterogeneous catalysts for biodiesel production have been investigated, including zeolite [5,6], alkaline earth oxides, ion-exchange resin [7], hydrotalcites, inorganic-oxide solid acid, supported alkaline or alkaline earth metals and supported noble-metal oxide [8, 9]. Most of these catalysts are commonly found hydrophilic and their activity decreases due to the presence of water which produces during FFA esterification. Moreover, they have high cost, bad structure stability and low density of effective acid sites. Therefore, such drawbacks have limited these catalysts for their practical use in biodiesel production

## II. LITERATURE REVIEW

Biodiesel can be simply defined as a fuel produced from the transesterification of varied range of vegetable oils (edible

and non-edible), animal fats, used frying oil and waste cooking oil to form fatty acid methyl esters in the presence of catalyst (Akhiero,2010). Biodiesel production from fats and oils is feasible due to the content of fat and oils which is a glycerol molecule that is attached to three fatty acids, the compound that emerged from this arrangement is called a triglyceride and this is the major component of oil. Classification of feedstock into three categories gives vegetable oils (edible or non-edible), animal fats and waste cooking oils. Biodiesel has many advantages over the conventional fuel; these advantages include high flash point, high cetane number, high lubricity, lower carbon monoxide emission profile and biodegradable. Thus it is viewed as green fuel from the environmental viewpoint (Dorado et al, 2003). Transesterification is process involving a reaction of the hydroxyl group of alcohol and carboxylic group of triglycerides to form ester. One good thing about Biodiesel is its biodegradability that is why it cannot pose any threat environmentally. Biofuel study is not just a matter of finding the right type of biomass and converting it to fuel, but it must also find environmentally and economically sound uses for the by-products of biofuel production (Dragone et al, 2010). The biodegradable nature of biodiesel is shown when it was observed that 90-98% of biodiesel is mineralized in 21-28 days under aerobic and anaerobic conditions (Akhiero et al, 2010). Co- metabolism is a process by which biodiesel increases the biodegradable nature of crude oil, rendering it less harmful to the environment. Biodiesel can burn in the internal combustion engines diesel vehicles without modification. The main advantage of biodiesel over conventional diesel is the carbon neutrality of biodiesel since the whole carbon emitted was recently captured during the growing phase of the plant from which the biofuel was made (Das, 2008).

Biodiesel use also reduces emission of carbon monoxide and other pollutants such as Sulphur IV Oxide and unburned Hydrocarbon by 20 to 40%. Research on the conversion of biodiesel into electricity utilizing fuel cells is equally in top gear. Vegetable oils are known to be renewable, relatively cheap and readily available source of energy having energetic content equal to diesel fuel. It is a known fact that Rudolf Diesel himself started research on vegetable oil use as fuel for diesel engines. Last two decades witnessed a more organized and strategic research method that evolved into what we know now as biofuel, direct use of vegetable oils in fuel engines is not advised because of their viscosity which is too high, they also have low volatility. Another pitfall is that their combustion is incomplete and consequently forms deposits in the fuel injector of most diesel engines. Acrolein, a toxic substance, is produced through thermal decomposition of glycerol, which is another shortcoming. The feedstock used in the producing of biodiesel varies. The most common feedstocks are vegetable oils (soybean, palm, peanut, rapeseed, sunflower, coconut) and animal fats (tallow) as well as waste cooking oil (WCO). Vegetable oils includes edible and non-edible oil source.

The use of animal fats, waste greases and waste vegetable oils give more attractive prices but edible oil like vegetable oils still dominant in biodiesel production till date. The objective of this paper was to determine the major impact which the reaction temperature has on the biodiesel yield.

### III. METHODOLOGY

Analytical grade methanol from Keimel and percentage purity of 99.5% was used. Also, an highly corrosive sulfuric acid of molecular weight 98.08 g / ml was used in acid esterification as a catalyst to quicken the reaction. As a dehydrating agent, it forces the equilibrium towards the right which gives greater yield of ester. Analytical grade sulfuric acid sourced from keimel and percentage purity of 97.99%. Clays can be located in several location in Nigeria, they include Mbayion clay, Benue; Mayo-Belwa in Adamawa; kachia,kafanchan, Wusasa in Kaduna (Manukajiet al,2013); Sheda, Abaji and karimu in Abuja (Manukaji et al, 2013); Abakiliki in Ebonyi, clay deposits in ekiti, south-west Nigeria and Ugbegun clay deposit in Edo central Nigeria amongst others. In Anambara state of Nigeria, clay deposits abound in large number of spots importantly around Ukpo; Ihiala Local government Area. Olokoro, Otamiri and Nsu in South- east Nigeria. The two selected clays for this study, Ukpo and Nsu have the following physical properties as stated in table below. From their physical and chemical properties, their major application is in the ceramics and refractive industry. Refractory materials contain more than 25% Al<sub>2</sub>O<sub>3</sub> and not more than 70% SiO<sub>2</sub> and have the following properties (plasticity, shrinkage porosity, bulk density, cold crushing strength and thermal conductivity) while clay used for making ceramics are majorly composed of kaolinite

The following Apparatus and equipment used for this study Beakers, Conical Flask, measuring Cylinder, Digital weighing balance, Crucibles Retort stand, Pipette, Burette, Separating Funnel, water bath, Soxhlet extractor, muffle furnace, centrifuge, PH meter, Magnetic stirrer, NDJ-55 Digital viscometer, Pycnometer bottle, Oven.

### IV. EXPERIMENTAL PROCEDURES

#### A. Clay Preparation (Catalyst):

After beneficiation, the clay samples obtained were sun-dried for three days, the dried samples were ground to a powdery form and sieved with 0.75mm mesh size. The sieved samples were then calcined (heated to drive away volatile components and to open the pores) in a muffle furnace at a calcination temperatures of 700°C, 800°C, 900°C and 1000°C. The clay was size reduced using a mesh size of 0.5mm so as to increase the surface area. Appropriate calculation took place to ascertain the quantity of clay needed.

#### B. Palm Oil Extraction:

The fruit here is *Elaeisguineensis* Dura (Ojukwu) and the process of local extraction was followed. 20kg of the ripe oil palm fruits was boiled in a large pan for 1hour. Separation of fiber from the kernel took place by pounding. The fiber which contained the palm oil was introduced into a bowl and the oil was first extracted without water, after which water was added and the oil was boiled for another 15minutes to evaporate the water contained in it. Hot water served as a solvent to extract the remaining oil from the fiber and kernel, the whole mass was immersed in the hot water, stirred and the oil which rose to

the surface was skimmed off into another pot. The fibers were removed from the water manually and finally, the nuts were collected and separated from the remaining fibers. The oil thus obtained was boiled in a vessel where any fiber still present sinks. The oil was again skimmed to further remove traces of water and sieved to remove any impurity contained in it.

**C. Bleaching Of Palm Oil:**

The oil was thermally bleached at 170°C for 2hrs. The reason for bleaching is to eliminate the color pigments ( $\beta$ -carotene) from the oil. It also helps to remove trace metals phosphatides and sulfur compounds Hydro peroxides, the initial products of oxidation are broken down during the bleaching process and some of the final oxidation products, the Carbonyl compounds are removed (Gerpens et al, 2004).

**D. Acid esterification and Pre-treatment:**

640ml of the oil was poured into a conical flask which serves as a reaction flask and heated for 15minutes. Magnetic stirrer is used to ensure uniform Temperature of 60°C. 45% v/v methanol to oil volume was introduced into the heated oil, stirred and allowed to stay for some time. 1.2% v/v of concentrated H<sub>2</sub>SO<sub>4</sub> was added and heating and stirring continued for another 60 minutes at atmospheric pressure. Then the mixture was poured into a separating funnel and allowed to settle for 2hrs in order to separate the excess methanol, impurities and sulfuric acid. They formed the top layer and were discarded. The lower layer is separated for further processing of the transesterified into methyl ester. This process reduces the acid value of refined oil to less than 1% of FFA.

**E. Transesterification Process:**

This took place in a conical flask; hot plate with magnetic stirrer arrangement was used as a heating and stirring device respectively. The magnetic stirrer was set at a constant speed of 300 rpm throughout the period to ensure uniform agitation.

44.9g of palm oil was poured into separate conical flask (used as a reactor) and heated to 45°C to improve the oil mixability with methanol. The catalyst used was calcined clay at previously specified temperatures. The catalyst was prepared in concentration of 1.2% w/w and to achieve the first concentration level 0.56g and 0.54g of catalyst (calcined clay) was dissolved in 32ml of methanol for the palm oil reactions. The mixture was stirred for 20mins to form methoxide. The methoxide was introduced gently in to the heated oil in the reactor and the entire content was heated to 65°C at the rate of 5°C/mins and held at this temperature for an hour (60min). The reaction product mixture was allowed to separate into phases by standing for 8hrs in a separating funnel so that the reaction can be driven to completion and for the mixture to separate into methyl ester and glycerol phase. The methyl ester moved to the top of the separating funnel and the glycerol phase, together with the impurities settle in the bottom and are withdrawn. To further remove impurities, the methyl ester was washed in deionized water. Finally, the washed methyl ester was dried in

the oven for 2hrs. This experiment was repeated severally, varying the calcination temperature from 700 to 1000°C, reaction time from 20 to 80mins, reaction temperature between 35 to 65°C and impregnation with KOH concentration from 0.2M to 1M. Catalyst quantity or concentration level was calculated using;

$$b = \frac{\text{Weight of clay}}{\text{weight of oil}} \times \frac{100}{1} \tag{1}$$

Yield fraction (g) was obtained using;

$$g = \frac{\text{Weight of product (biodiesel)}}{\text{Weight of reactant (oil)}} \tag{2}$$

and percentage yield =  $g \times 100$

**V. RESULTS AND DISCUSSION**

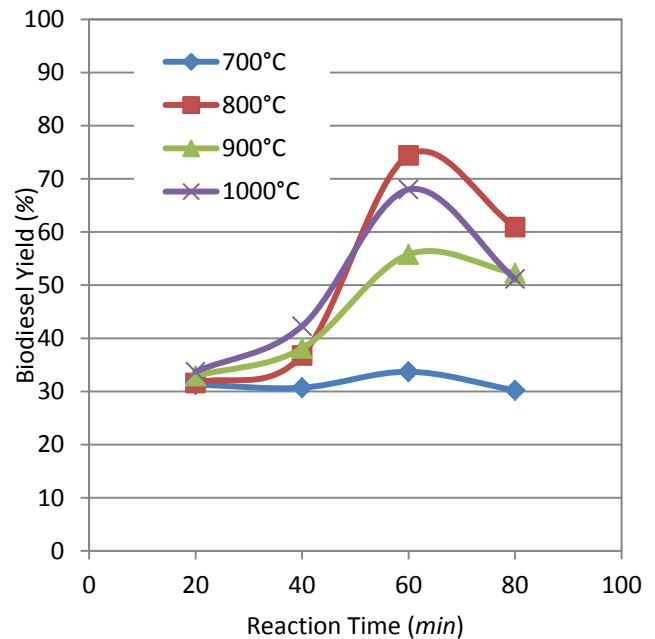


Figure 1. Effect of calcined clay temperature and time on the yield of biodiesel at constant reaction temperature (65°C) and KOH(0.2M) for Ukpor clay

Figure 1 shows the relationship between the calcination temperature, the reaction temperature, the reaction time and KOH concentration. It depicts that there is a maximum yield in biodiesel production at the reaction time of 60min. Also, it states the fact that the maximum calcination temperature lies between the minimum values of 900°C to a maximum value of 1000°C. It lays emphasis on the fact the reaction temperature leading to a greater yield is definitely above 65°C. It is also observed that the concentration corresponding to the maximum yield in biodiesel is 0.2M.

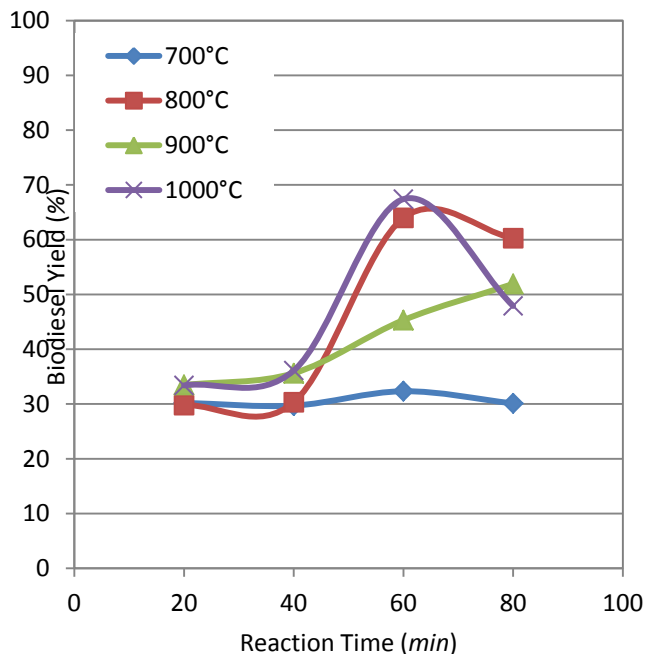


Figure 2. Effect of calcined clay temperature and time on the yield of biodiesel at constant reaction temperature (65°C) and KOH(0.2M) for Nsu clay

From figure 2, it is noticed that Nsu clay did not give a better yield than that of Ukpok clay due to a high presence of Aluminium oxide in it, forming a thin passivation of about 4nm of clay surfaces which slows down reaction (Campbell et al, 1999). In general, majority of recent research in heterogeneous catalysts from wastes and natural resources (clay) for biodiesel production uses interplay of these variables to produce cost effective and reusable catalysts.

From the surface plot in figure 3, for Ukpok which basically has been proven to be better than Nsu clay, yield increases quadratically with increase in Calcination temperature but almost linearly with increase in Reaction temperature. A global optimal was not bracketed. This indicates that the reaction can still go on if the present conditions are extended

Taking Ukpok into consideration as it gives a better yield, Statistical analysis which includes ANOVA and response surface model is used to optimize the process and the model is said to be a PUREQUADRATIC model. The coefficient for a variable is significant if the magnitude of the t-stat value is  $\geq 2$  or its pval is  $\leq 0.05$ .

Rxn Time<sup>2</sup>, KOH Conc<sup>2</sup>, Rxn Time are Significant. KOH Conc and Constant term are only significant at 90% confidence interval. The P-val of the F-statistics shows that the model is ADEQUATE for the study, since it is less than 0.05.

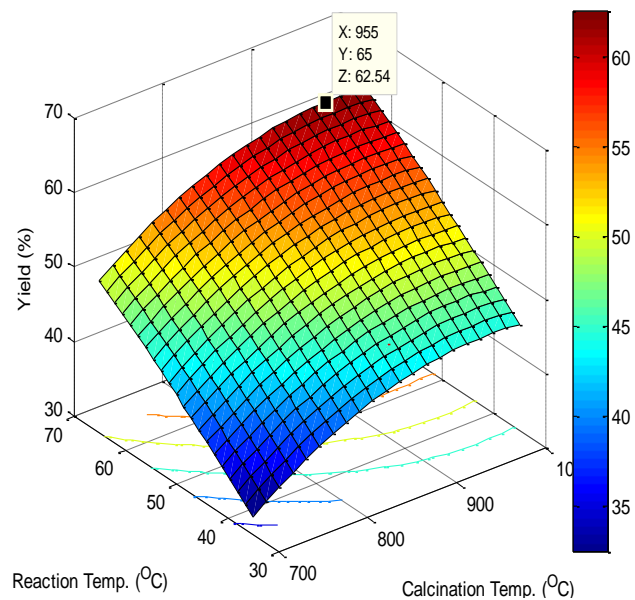


Figure 3. Surface Plot of Calcination Temp. and Reaction Temp. Interact Ukpok clay

From the above surface plot, the yield increases quadratically with increase in Calcination temperature but almost linearly with increase in Reaction temperature. A global optimal was not bracketed.

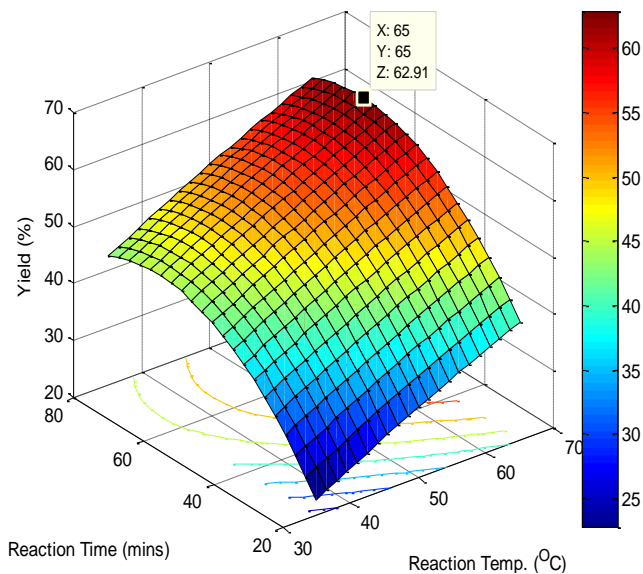


Figure 4. Surface Plot of Reaction Time and Reaction Temp. Interaction for Ukpok clay

From the surface plot above, the yield increases quadratically with increase in Reaction Time but almost linearly with increase in Reaction temperature. A global optimal was not bracketed.

## VI. OPTIMIZATION USING RESPONSE SURFACE MODEL WITH MATLAB

The appendix sections of this work contain a detailed study of the optimization using response surface methodology, see the summary below:

Optimization terminated: magnitude of directional derivative in search

direction less than 2\*options.TolFun and maximum constraint violation

is less than options.TolCon.

Active inequalities (to within options.TolCon = 1e-006):

lower upper

2

x = 960.8925 65.0000 0.4476 65.3278.

OPTIMUM YIELD OCCURS AT:

CALCINATION TEMPERATURE = 960.8925 OC

REACTION TEMPERATURE = 65 OC

KOH CONCENTRATION = 0.4476 M

REACTION TIME = 65.3278 mins

The yield can be improved by increasing reaction temperature. Other optimal values are global except for reaction temperature.

The optimal conditions are Calcination Temperature 960.8925°C, Reaction Temperature 65°C, Potassium Hydroxide 0.4476M and Reaction Time of 65.3278mins. And Biodiesel yield at these conditions is 65.8014%. But since the reaction temperature is not global at the above conditions, a validation experiment is conducted at the above optimal conditions by increasing the reaction temperature up to 72°C, the yield Obtained is 91.22%.

TABLE I. RESULTS OBTAINED BY PERFORMING THE REACTIONS AT OPTIMAL CONDITION

Calcination Temp.	Reaction Temp.	Reaction Time	KOH Conc.	Yield
960.89°C	72°C	65.32	0.45M	91.22%

## VII. CONCLUSIONS

Best variation reaction is shown in 65oC reaction condition with a 65.8014% yield despite performing them at various temperatures and variable condition but a validation experiment at 72oC reaction condition yielded 91.2, making a perfect fit since it is not optimally global at 65oC. The effect of

Calcination temperature of clay, reaction temperature, KOH concentration and reaction time on the yield of biodiesel using palm oil from *Elaeisguineensis dura* was studied. Two clay samples (Ukpo and Nsu) were used and it was discovered that Ukpo Clay gave a better yield in biodiesel production. Factorial design analysis, ANOVA and surface response model were used to optimize the process using Matlab toolbox and it was discovered that optimum yield occurred at calcination temperature of 960.8925°C, KOH concentration of 0.4476 M and a reaction time of 65.3278 minutes. The yield can be improved by increasing reaction temperature. Other optimal values are global except for reaction temperature as mentioned earlier. GC analysis result showed that the biodiesel contain about 99% saturated fatty acid which makes it a good alternative to diesel as cetane number increases with degree of saturation. Calcination has an effect on the evolution of catalytic properties such as acid site density and strength, it also has effect on the surface area and pore volume. High temperature treatment is known to eliminate the loosely bonded water, CO<sub>2</sub> and O<sub>2</sub> molecules by exposing the catalytic sites. High temperature also rearranges the surface of the catalyst. The essence of this research is to determine the effect of calcining clay at different temperatures.

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