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# Transesterification of Palm-olein using a Synthesized Heterogeneous Catalyst (CaO-Calciumoxide Nanoparticle)

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**Abstract** Calcium oxide nanoparticle was produced by chemical co-precipitation method and was used for catalysis in the production of a liquid fuel (biodiesel). Different runs (20) set with different processing conditions for the production. The biodiesel yields for the 20 runs are; 59%, 61%, 62%, 72%, 73%, 65%, 61%, 76%, 76%, 67%,65%, 68%, 76%, 76%, 80%, 58%, 59%, 60%, 69% and 76% respectively. The statistical analysis of variance (ANOVA) was carried out using the software (Design-Expert 12 software – the latest version (Stat-Ease Inc., USA) so as to evaluate the precision of the model, the fitness and the significance of the model, the effects of the individual parameters and interaction effects on the responses.

**Keywords** Palm-olein, Heterogeneous Catalyst, CaO-Calciumoxide, Nanoparticle

## Introduction

Transesterification reactions can be without a catalyst, alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. Alkali-catalyzed transesterification is much faster and most often used commercially. Alkali-catalyzed transesterification is the most economical process requiring low temperatures and pressures to achieve a 98% conversion yield [1]. However, one limitation to the alkali-catalyzed process is its sensitivity to the purity of reactants. It is very sensitive to both water and free fatty acids content [1-2]. The information on biodiesel production using Nigerian crude palm oil by means of one-step and two-step transesterification processes is hard to find. The present studied both one-step and two-step transesterification processes and then optimized the yield of biodiesel via two-step transesterification process [3].

## Biodiesel Fuel

Biodiesel is a biodegradable, sustainable and clean energy source that can be derived from a variety of biomass feedstocks oils such as waste vegetable oil, yellow grease, animal fats, and virgin vegetable oils [3]. It has proven itself as a technically sufficient alternative diesel fuel in the fuel market since the beginning of the 1990s. Biodiesel is defined as a fuel made up of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of national fuel specification, American Society for Testing and Materials (ASTM D6751), European norm (EN-14214), or its equivalent [4-6].

Biodiesel blends are biodiesel fuel meeting the ASTM D6751 specification blended with petroleum-based diesel fuel designated BXX, where XX is the volume percent of biodiesel (e.g., B20) [7]. Biodiesel production is performed through several chemical engineering processes but the most commonly employed is the process of transesterification, in which animal fat or vegetable oil is combined with a low molecular weight alcohol such methanol and ethanol and a catalyst to produce an alkyl ester (biodiesel, B100) and glycerol [1,4]. It has a reducing characteristic for greenhouse gas emissions, help on reducing a country's dependence on crude oil importations, its aids agricultural activities by providing a new market for domestic crop-plants, it has high

lubricating properties that eradicates the need of any lubricating additives and it has broad acceptance by vehicle manufacturers [3].

Energy from renewable sources, that use indigenous resources have the potential to offer energy services with zero or almost zero emissions of both greenhouse gases and air pollutants. Renewable energy technologies create marketable energy by converting natural materials into useful forms of energy currently, energy from renewable sources supply 14% of the total world energy demand Large-scale hydropower supplies 20% of global electricity. Energy from renewable sources are derived from those natural, mechanical, thermal, and growth processes that repeat themselves within our lifetime and may be relied upon to produce predictable quantities of energy when required. Renewable technologies like hydro and wind power probably would not have provided the same fast increase in industrial productivity as of fossil fuels [3]. Thus the share of Energy from renewable sources is expected to increase very significantly (30 to 80% in 2100). Biomass, wind, and geothermal energy are commercially competitive and are making relatively fast progress.

**History of Biodiesel**

Biodiesel was first utilized by German scientist, Rudolph Diesel, the inventor of compression ignition (CI) diesel engine in 1900. Because of the availability of crude oil in large reserves and its easy refining process and use on diesel engines, the direst use of peanut oil as a fuel to run the diesel engine was not broadly put in to practice. Hence, both animal fats and vegetable oils were neglected as sources of fuel. But, recently, because of the realization that crude oil is no more abundantly available, and poses threat to the well being of mankind due to emissions of carbon-dioxide gases, vegetable oil especially has been used for its efficiency as fuel in CI diesel engines [8]. On the other hand, because of low volatility and high viscosity, its long-term use posed diverse difficulties such as ring sticking, deposition, and injector choking in engine. For this reason, augmentation in the vegetable oil was seen to improve the fuel quality. Thus, to reduce the viscosity of vegetable oils and animal fats; thermal and chemical processes were tried to make fats and oils compatible with CI diesel engines [9].

**Renewable Energy Use and interest**

The bio-energy commercialization has offered an efficient way to decrease the difficulty of petroleum shortage and the influence on environment. In this circumstance, substantial quantities of researches were performed over the past three decades**,** to increase this new sustainable and renewable energy resource that might function as an alternate for petroleum. In comparison to diesel, biodiesel is said to be carbon neutral, as biodiesel yielding plants take in more carbon-dioxide than that added to the atmosphere when used as fuel [7, 10]. Further, biodiesel is exceedingly biodegradable in soil as well as in fresh water. In addition, under aerobic or anaerobic conditions, the best part of biodiesel (90–98%) is mineralized in 21–28 days [11-12]. As for a local production, biofuel manufacturing plants can make use of hundreds or thousands of workers, thus, creating new jobs especially in country sides. The production of biofuel will also increase the demand for appropriate biofuel crops, providing economic stimulation to the agriculture industry [13]. Transesterification is converting an alkyl group of an ester to another alkyl group as shown in Figure 1.

Transesterification is the reversible reaction of a fat or oil with an alcohol (methanol or ethanol) to form fatty acid alkyl esters and glycerol. It can be alkali-, acid-, or enzyme-catalyzed; however, currently the majority of the commercialized technology resides in transesterification using alkali-catalyzed reaction. The common catalyst employed during alkaline transesterification at industrial level application includes the homogeneous catalysts sodium hydroxide, potassium hydroxide, etc [10, 15-16].

Transesterification reaction is an equilibrium reaction. In this reaction, however, a larger amount of methanol is used to shift reaction equilibrium to right side and produce more methyl esters as proposed product. Ethanol is a preferred alcohol in transesterification reaction compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment; however, methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol) [3]. Generally, the reaction temperature near the boiling point of the alcohol is recommended. Nevertheless, the reaction may be carried out at room temperature. The reactions take place at low temperatures (~338 K) and at modest pressures (2 atm, (1 atm= 101.325 kPa)). Biodiesel is further purified by washing and evaporation to

remove any remaining methanol. The oil (87%), alcohol (9%), and catalyst (1%) are generally the inputs in the production [2].

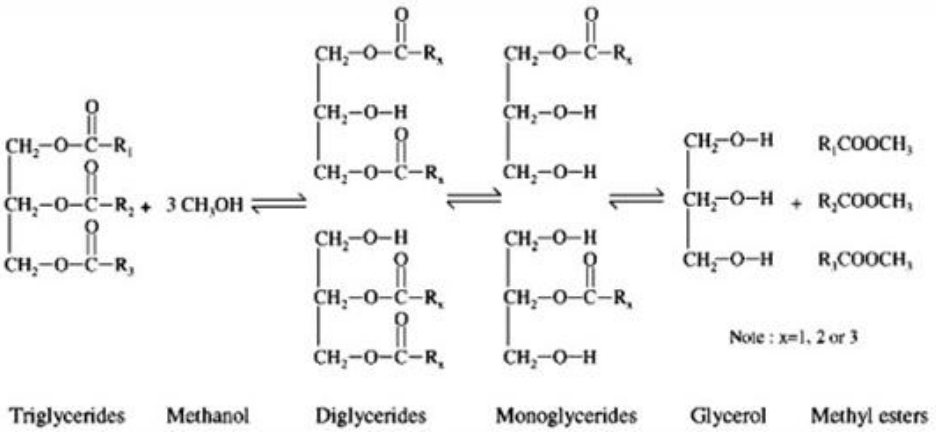



*Figure 1: Reactions in the transesterification of a triglyceride [3]*

**Materials and methods**

Crude palm-oil, sodium sulphate, transesterification reactor, water bath, beakers, separating funnel, evaporation apparatus, thermometer and conical flasks were used in order to achieve the aims and objectives of the research.

**Method**

**Synthesis of CaO nanoparticles**

In a typical procedure, 0.5 M $Ca(NO_3)_2$ $4H_2O$ and 0.7 M of NaOH were separately dissolved in 50 ml de-ionized water and mixed to form 100 ml mixture (solutions). The mixture was stirred for 10 minutes at room temperature and it turned into white gels. After 10 minutes stirring at room temperature, the mixture turned into white gels. These were then irradiated by microwave energy using domestic microwave oven having frequency 2.45GHz (maximum power 800 W) in ambient atmosphere for 10 minutes. After microwave processing, the solution was allowed to cool to reach room temperature, naturally. The resulting precipitate was collected by vacuum filtration and washed with de- ionized water and absolute ethanol, and dried in a vacuum at 80 °C for 1h.

**Two-Step Alkali-catalyzed Transesterification Reaction**

In the acid-catalyzed esterification process, the following conditions were adopted; oil to alcohol molar ratio, 10:1, time of reaction, 90min., temperature, 60$^{o}$C, and 3% of $H_2SO_4$. The reaction mixture was then poured into a separating funnel to remove excess alcohol, sulfuric acid and impurities. The sample produced having free fatty acid of 0.20% was used for the alkali-catalyzed transesterification reaction. The crude palm oil has an initial free fatty acid value of 3.00%.The experimental set-up for alkali-catalyzed transesterification was the same as the one used for acid-catalyzed pretreatment process. It is worthy to mention that the experimental conditions presented in Table 1 were adopted for the two-step experimental process. The table also gives the product (yield %) of all the variables. In the variables, there is variation in catalyst concentration (factor A), variation in molar ratio i.e. alcohol to oil (methanol to palm oil), variation in temperature for the reaction but the time for the reaction is kept constant till the completion of the reaction. Time for the reaction is 70 min.

**Results and Discussion**

**Analysis of Biodiesel**

The yields of biodiesel samples (table 1) were analyzed by a HP 6890 Gas Chromatogram (GC) equipped with a Flame Ionization Detector (FID) and capillary column DB23 (60-m×0.25-m×0.15-µm) according to a methodology proposed by Agilent. Normal hexane solutions of the biodiesel samples with a concentration of 100 mg/ml were injected by an auto injector at an oven temperature of 50 °C, which was then heated up to 230 °C. The injector temperature and the detector temperature were 250°C and 280 °C, respectively; helium was

used as the carrier gas. Besides, other physical properties such as density, viscosity, cetane number, pour Point, moisture water content, cloud Point and flash point were determined using ASTM D6751 and EN 14214.

**Table 1:** Process parameters and the Yields of Biodiesel (transesterification)

| | Factor 1. | Factor 2. | Factor 3. | R.1. |
|---|---|---|---|---|
| **Run** | **A:Cat.con.** | **B:M.R** | **C:Temp.** | **Yield.** |
| | **w/w%** | | **$^{o}$C** | **%** |
| 1 | 3 | 10 | 50 | 59 |
| 2 | 1.75 | 6 | 55 | 61 |
| 3 | 3 | 6 | 60 | 62 |
| 4 | 1.75 | 8 | 55 | 76 |
| 5 | 1.75 | 8 | 50 | 73 |
| 6 | 1.75 | 10 | 55 | 65 |
| 7 | 3 | 10 | 60 | 61 |
| 8 | 1.75 | 8 | 55 | 76 |
| 9 | 1.75 | 8 | 55 | 76 |
| 10 | 0.5 | 8 | 55 | 67 |
| 11 | 0.5 | 6 | 50 | 65 |
| 12 | 0.5 | 10 | 50 | 68 |
| 13 | 1.75 | 8 | 55 | 76 |
| 14 | 1.75 | 8 | 55 | 76 |
| 15 | 1.75 | 8 | 60 | 80 |
| 16 | 3 | 8 | 55 | 58 |
| 17 | 0.5 | 6 | 60 | 59 |
| 18 | 3 | 6 | 50 | 60 |
| 19 | 0.5 | 10 | 60 | 69 |
| 20 | 1.75 | 8 | 55 | 76 |

**Data Analysis**

The statistical analysis of variance (ANOVA) was carried out using the software (Design-Expert 12 software – the latest version (Stat-Ease Inc., USA) so as to evaluate the precision of the model, the fitness and the significance of the model, the effects of the individual parameters and interaction effects on the response. In accordance with the results obtained using the ANOVA Table 1. the model was significant with a p-value less than 0.0001. Additionally, the Model F-value of 9.01 implies that the model is significant. In addition, Catalyst concentration A, Ethanol to Oil molar ratio B and the reaction temperature C, reaction temperature – catalyst concentration interaction, CA, and the interaction term of molar ratio – catalyst concentration, BA, were significant model terms with The lack of fit is regarded as the weighted sum of squared deviations between the mean response at each factor level and the corresponding fitted value. In this research work the lack of fit is not significant for the response with a P-value of 0.0500 (lack of fit is 11); this indicates that the model is fitted to all data (Not-significant, lack of fit is good). Adequate precision is a measure of signal to noise ratio; it compares the range of the predicted values at the design points to the average prediction error and as prerequisite of the model, a ratio of greater than 4 is desirable. In this model, the ratio of 13.058 indicates sufficient model discrimination.

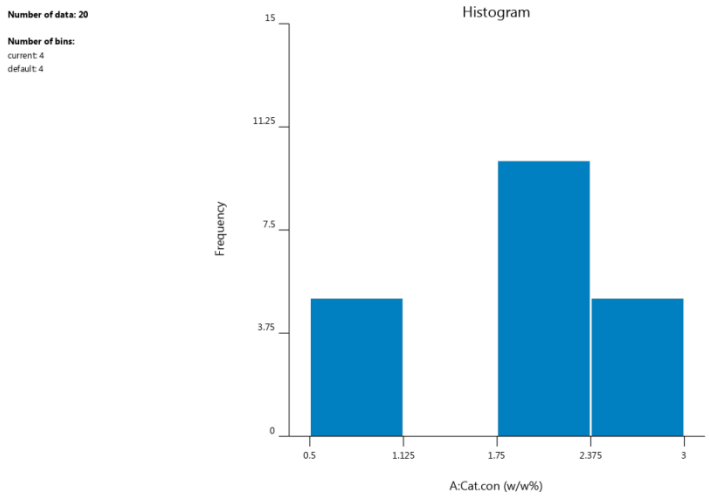
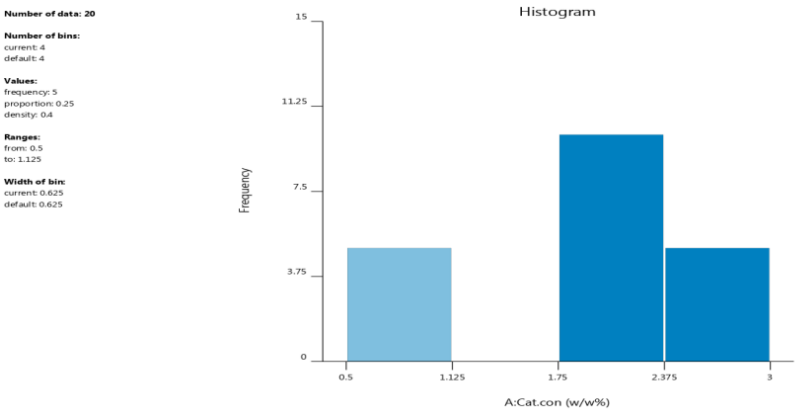



*Figure 2: Histogram showing frequency of occurance of concentration of catalyst in ww% of the 20 runs for production of Biodise*




*Figgure 3. Histogram showing range of 0.5 to 1.13 catalyst concentration (ww%), the said range appeared at the frequency of 4*

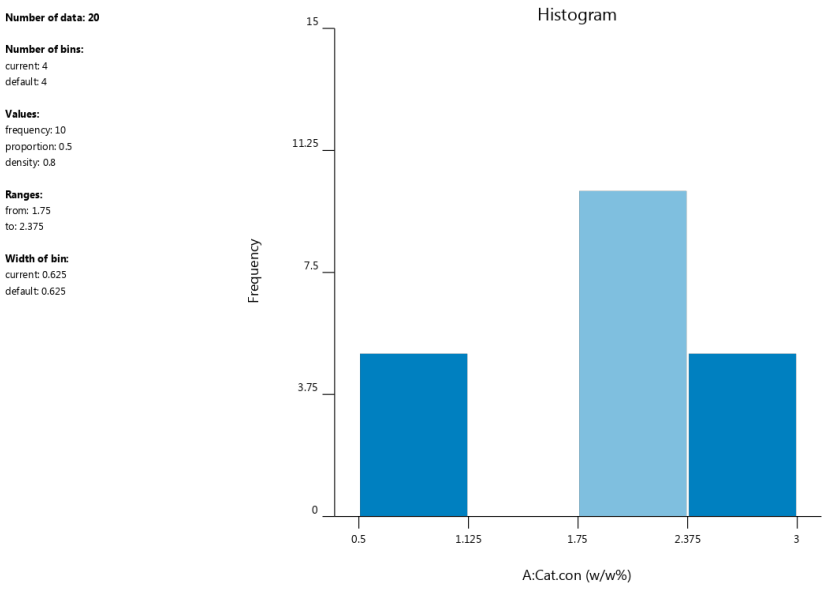



*Figure 4: Histogram showing range of catalyst concentration of 1.75 to 2.38 (ww%) which appears at frequency of 10*

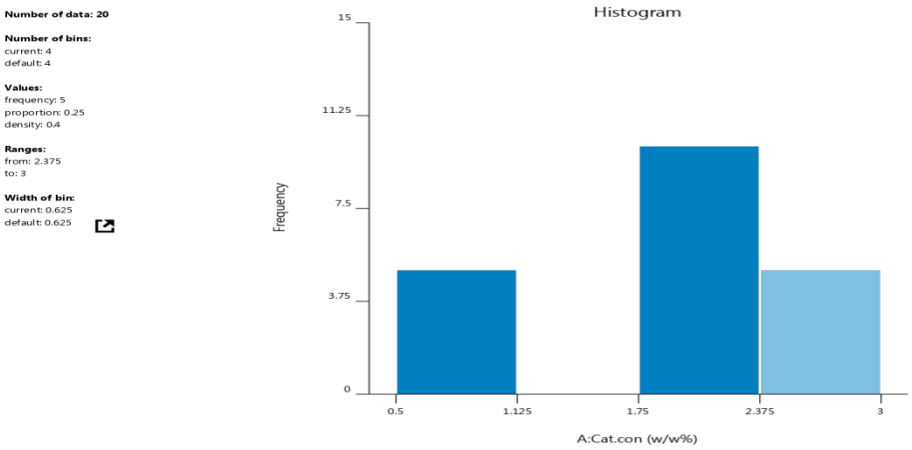



*Figure 5: Histogram showing the range between 2.38 to 3.00; of the catalyst concentration in (ww%) which appears at the frequency of 5*

**For a standard deviation**

Power calculations are performed using response type "Continuous" and parameters:

Power is evaluated over the -1 to +1 coded factor space.

Standard errors should be similar to each other in a balanced design. Lower standard errors are better.

The ideal VIF value is 1.0. VIFs above 10 are cause for concern. VIFs above 100 are cause for alarm, indicating coefficients are poorly estimated due to multicollinearity.

Ideal $R_i^2$ is 0.0. High $R_i^2$ means terms are correlated with each other, possibly leading to poor models.

If the design has multilinear constraints, then multicollinearity will exist to a greater degree. This inflates the VIFs and the $R_i^2$, rendering these statistics useless. Use FDS instead.

Power is an inappropriate tool to evaluate response surface designs.

Use prediction-based metrics provided in this program via Fraction of Design Space (FDS) statistics.

**Table 2:** Degrees of Freedom

| | |
|---|---|
| Model | 3 |
| Residuals | 16 |
| Lack of Fit | 11 |
| Pure Error | 5 |
| Corr Total | 19 |

At least 9 lack of fit DF is recommended and **4 pure error DF to ensure a valid lack of fit test.**

**Table 3: ANOVA for Quadratic model**

**Response 1: Yield**

Transform: Natural Log

Constant: 0

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 0.23 | 9 | 0.0223 | 9.67 | 0.0007 | significant |
| A-Cat.con | 0.0194 | 1 | 0.0194 | 8.41 | 0.0158 | |
| B-Molar ratio | 0.0054 | 1 | 0.0054 | 2.34 | 0.1570 | |
| C-Temp | 0.0006 | 1 | 0.0006 | 0.2473 | 0.6297 | |
| AB | 0.0069 | 1 | 0.0069 | 2.99 | 0.1143 | |
| AC | 0.0028 | 1 | 0.0028 | 1.20 | 0.2998 | |
| BC | 0.0016 | 1 | 0.0016 | 0.6812 | 0.4284 | |
| $A^2$ | 0.0460 | 1 | 0.0460 | 19.97 | 0.0012 | |
| $B^2$ | 0.0391 | 1 | 0.0391 | 16.98 | 0.0021 | |
| $C^2$ | 0.0152 | 1 | 0.0152 | 6.61 | 0.0278 | |
| Residual | 0.0230 | 10 | 0.0023 | | | |
| Lack of Fit | 0.0230 | 5 | 0.0046 | | | |
| Pure Error | 0.0000 | 5 | 0.0000 | | | |
| Cor Total | 0.2234 | 19 | | | | |

Factor coding is **Coded**.
Sum of squares is **Type III - Partial**
The **Model F-value** of 9.67 implies the model is significant. There is only a 0.07% chance that an F-value this large could occur due to noise. **P-values** less than 0.0500 indicate model terms are significant. In this case A, $A^2$, $B^2$, $C^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

**Table 4:** Fit Statistics

| | |
|---|---|
| Std. Dev. | 0.0480 |
| Mean | 4.22 |
| C.V. | 1.14 |
| $R^2$ | 0.8970 |
| Adjusted $R^2$ | 0.8042 |
| Predicted $R^2$ | 0.3442 |
| Adeq. Precision | 10.2063 |

The Predicted $R^2$ of 0.3442 is not as close to the Adjusted $R^2$ of 0.8042 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 10.206 indicates an adequate signal. This model can be used to navigate the design space.

**Table 5:** Coefficients in Terms of Coded Factors

| Factor | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|---|---|---|---|---|---|---|
| Intercept | 4.30 | 1 | 0.0165 | 4.27 | 4.34 | |
| A-Cat.con | -0.0440 | 1 | 0.0152 | -0.0778 | -0.0102 | 1.0000 |
| B-Molar ratio | 0.0232 | 1 | 0.0152 | -0.0106 | 0.0570 | 1.0000 |
| C-Temp | 0.0075 | 1 | 0.0152 | -0.0263 | 0.0413 | 1.0000 |
| AB | -0.0293 | 1 | 0.0170 | -0.0671 | 0.0084 | 1.0000 |
| AC | 0.0185 | 1 | 0.0170 | -0.0192 | 0.0563 | 1.0000 |
| BC | 0.0140 | 1 | 0.0170 | -0.0238 | 0.0518 | 1.0000 |
| $A^2$ | -0.1293 | 1 | 0.0289 | -0.1937 | -0.0648 | 1.82 |
| $B^2$ | -0.1192 | 1 | 0.0289 | -0.1837 | -0.0547 | 1.82 |
| $C^2$ | 0.0744 | 1 | 0.0289 | 0.0099 | 0.1389 | 1.82 |

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multicolinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

**Optimization**
To ascertain the reliability of the model, the data achieved predicted with reasonable accurateness by the model in comparison with the experimental data. The figure below
represents the predicted and the experimental value for the two-steps transesterification process using the developed model equation.
In figure 6, for the two-step alkali-catalyzed transesterification reaction showed that the model was able to successfully and adequately capture the correlation between the process parameters and the response (%R).

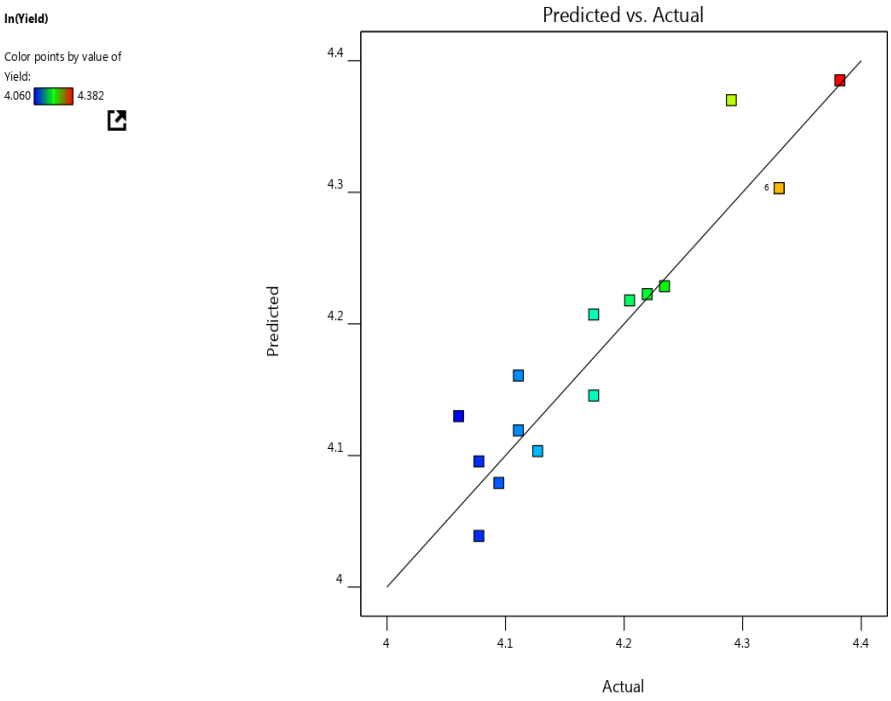



*Figure 6: Correlation between predicted and actual*

**Table 6:** Overall optimization results and model evaluation

| Temp ($^{o}$C) | Time (Min) | Cat. Conc. (%) | %R (Yield) | |
|---|---|---|---|---|
| | | | Predicted | Experimental |
| 60 | 70 | 1.75 | 96.245 | |

## Conclusion

A cost effective catalyst i.e. calcium oxide nanoparticle was successfully synthesized which was used to catalyze the reaction for esterification for the production of liquid fuel (biodiesel). It is clear that chicken eggshell contains calcium which is not only important for biological system but also very important substance for catalysis which can be used in industrial and small scale productions. The statistical analysis of variance (ANOVA) was carried out using the software (Design-Expert 12 software – the latest version (Stat-Ease Inc., USA) so as to evaluate the precision of the model, the fitness and the significance of the model, the effects of the individual parameters and interaction effects on the response.

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