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Synthesis of Alumina-Supported Chicken Eggshell Catalyst for Transesterification of Waste Cooking Oil

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Abstract

This research presents the synthesis of alumina-supported chicken eggshell for the transesterification of waste cooking oil. The major materials used in the research are from renewable sources because the research focuses on addressing issues associated with renewable energy and the environment. Biodiesel was produced from waste cooking oil using alumina-supported calcium oxide from chicken eggshell. The alumina was leached from kaolinite clay using hydrochloric acid while the eggshell was from chicken. The prepared catalyst was characterized using XRF, FT-IR, BET, and TGA. Using a 2^4 factorial design, the catalyst synthesis was optimized and the effect of the parameters used in catalyst synthesis such as the impregnation ratio and time, calcination temperature and time, on the yield of biodiesel from waste cooking oil were investigated. The optimization study showed that; impregnation ratio of 1.17:1, 1.32 hours of impregnation, calcination at 740.31°C for 2.62 hours gave the best results of 75.4% with 95% confidence level. The conditions for transesterification were methanol to oil molar ratio of 12:1, 6wt% catalyst, 60°C reaction time, and mixing speed of 250rpm for ninety minutes. The result of the characterization of the biodiesel produced using the $\text{CaO}/\text{Al}_2\text{O}_3$ produced proves that the biodiesel compares favourably with ASTM standards.

Keywords: Biodiesel, waste cooking oil, eggshell, kaolin, alumina, calcium oxide, transesterification, optimization.

1.0 Introduction

Rising world population has culminated higher demand for energy; unfortunately, this has not been met with higher supply of energy [1]. This increased demand has put a lot of pressure on fossil fuels which is the major source from which this global energy demand is met. Since these fuels are non-renewable, they are being depleted. In addition, global warming is another major environmental concern caused by the exploration and use of fossil fuels. Hence, the need for alternative renewable fuels that are environmentally friendly [2]. Among these alternatives are solar energy, wind energy, hydrogen (H_2) energy and most importantly biodiesel which is considered as a way out of the issues of energy sustainability and environmental pollution. Out of many methods for biodiesel synthesis from vegetable oils, transesterification happens to be widely used owing to its economy and simplicity. Transesterification is a reaction where the



alkoxy group present in an ester compound is exchanged by another alcohol in the presence of either an acid or base catalyst [3]. Several alcohols can be employed for the process; however, methanol and ethanol are the most commonly used. The feedstock for biodiesel production includes edible oils such as canola, rapeseed, sunflower, corn and vegetable oil [4]. However, the use of these edible oils been discouraged because of it competition as food [5]. Therefore non-edible oils such as *Jatropha*, neem, rubber seed and castor oil can provide an alternative because of its incredible potential for biodiesel product ion with low acid and good oxidation stability [6]. But the cost of these oils is also not sustainable as it results in the very high cost of the biodiesel produced. This has drawn attention to the potential of waste cooking oil as a potential feedstock for biodiesel production. Using the waste oil for biodiesel means recycling the oil, hence curbing the problem of improper disposal and high cost of biodiesel feedstock since these waste cooking oil is readily available [7].

Hitherto, the catalysts used in the synthesis of biodiesel via transesterification have been majorly homogeneous acid or alkaline based catalyst such as sulphuric acid and sodium hydroxide [8]. The advantage of this catalyst is that the ester yield is high and the reaction occurs at a comparatively fast rate. But in most cases, the resulting cost of production using homogeneous catalyst is high because of the need to wash off the soap formed during the production process, thereby increasing the total production cost and limiting biodiesel commercialisation [9]. In recent times, heterogeneous catalysts have gotten so much attention in the biodiesel production process because of their reusability, environmental friendliness, low cost, high quality yield and efficiency in transesterification of triglycerides when compared to their homogeneous counterparts. Even of greater interest is the fact that some of these heterogeneous catalysts could be sourced from both domestic and industrial wastes, as well as biological resources, [10]. Hitherto, these materials were regarded as waste and discarded. But with several research and developments in biodiesel production, they have been reported to be of great value in the production of biodiesel. This is because of the great advantages inherent in these materials as catalysts. They are biodegradable, they can be reused, and they produce a high quality biodiesel with high yield [11]. Because of their environmental acceptability, they are been regarded as green catalysts. Their use is economically sustainable because they occur in abundance in our environment [12]. Their use in biodiesel synthesis as catalysts provides a solution to the problem of disposal. Their production process is also not expensive thereby ensuring a cost effective biodiesel production process, [10]. Research has presented these locally sourced heterogeneous catalysts as good alternatives to the synthetic heterogeneous catalysts, since the biodiesel produced should compete favourably with petroleum diesel as against that produced using homogenous catalysts [13].

Calcium oxide is an example of a heterogeneous catalyst that is abundantly and cheaply available all around our environment. It occurs naturally in animal bones, and shells such as eggshells, oyster shells, and snail shells [14]. According to [11], eggshells are a rich source for calcium oxide as heterogeneous catalyst for the production of biodiesel. In as much as heterogeneous catalysts have the advantage of high conversion and yield, researchers have encountered the problem of catalyst leaching with the use of calcium oxide [15] Several authors have reported that after a few cycles, the solid catalyst leach into the reacting medium thereby reducing the quantity and quality of the ester produced [16]. In order to curb this challenge, several supports have been developed upon which these solid catalysts are anchored inorder to

reduce leaching and increase the number of times they can be reused for a reaction. Anchoring the catalyst on a support enhances the value of the catalyst and reduces the cost of production. Catalyst supports consist of different materials. Silica, alumina, potassium hydroxide and chromium have been used by different researchers. A study by [4] and [17] presents gamma-alumina as a good support for eggshell derived calcium oxide. The alumina used in this work was sourced from kaolinite clay.

Calcium oxide supported with alumina is an example of solid catalyst that can be synthesized with characteristics that permit catalytic properties that will improve the reaction [18]. In view of all these, this research attempts to explore the use of calcium oxide from eggshell with alumina support as heterogeneous catalyst in the production of biodiesel from waste cooking oil. The research also attempts to emphasize the use of local content as the catalyst produced is entirely from local materials.

2.0 Experimental

2.1 Catalyst synthesis

Kaolinite clay was gotten from Kutigi in Niger state. Alumina was extracted from kaolinite clay using hydrochloric acid by leaching [19], [20]. The waste chicken eggshells were collected from a local restaurant in Minna, Niger state; washed thoroughly, dried at 100°C for 12 hours, grinded to 125µm mesh size and calcined at 900°C for 4 hours. The calcium oxide was dissolved in 50ml of distilled water containing 10g of alumina. The quantity of the calcium oxide used was in ratios of 1:1 and 2:1 with the alumina. The slurry was stirred for a period of 1 and 2 hours at room temperature using a magnetic stirrer. After which the slurry was oven dried at 100 °C for 12 hours and the dry sample was calcined over a temperature range of 650 to 750 °C over a time range of 2 to 3 hours. The impregnation ratio, time, calcination temperature and time were varied using 2⁴ factorial design. The catalyst was characterized using FT-IR, XRF, BET, and TGA, [17].

2.2 Transesterification

100ml of the waste cooking oil was pre-treated before it was poured into a conical flask and heated to a temperature of 60°C. A mixture of concentrated H₂SO₄ (1 % w /w) with methanol (30 % v/v) was separately heated at (60°C) and added to the heated oil in the flask. The mixture was stirred for 1 hour and allowed to settle for 2 hours in a separating funnel. The clean oil was then withdrawn. 30 ml of pre-treated waste cooking oil was poured into a conical flask and heated in a water bath until the oil attained a temperature of 60°C. 50 ml of methanol and 6 wt. % catalyst was added to the oil and the mixture was returned back to the water bath at 60°C and mixture stirred as 250 rpm for 90 minutes. The methanol to oil ratio was 12:1, [17]. The conical flask was equipped with a stopper to prevent the escape of methanol by evaporation. After 90 minutes the mixture was removed and the catalyst was separated by filtration. The liquid was then poured into a separating funnel and left overnight for separation of the biodiesel from the glycerol by gravity. The glycerol which formed the lower layer was collected and the biodiesel yield was determined, [21]. The catalyst reusability was tested for 5 runs under the same conditions of

reaction, [12]. The biodiesel was characterized to determine the physicochemical properties and the fatty acid profile was determined by gas chromatography.

3.0 Results and Discussion

3.1 Catalyst Analysis

The X-ray fluorescence carried out on the $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst showed that CaO and alumina were present as major components in the catalyst in nearly equal amounts. While other oxides like silicon oxide, zinc oxide, titanium oxide, and iron oxide were present in very minute quantities as impurities, the alumina and calcium oxide have the largest percentage compositions of 46.163% and 45.472% respectively. This result reflects the 1:1 ratio of impregnation used in preparing the catalyst. For the FTIR, in the O–H stretching region, the sample shows prominent bands at $3672 - 3996\text{cm}^{-1}$ corresponds to Al–OH stretching. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets, give the absorption at 3672cm^{-1} . A strong band at 3620cm^{-1} is related to the in phase symmetric stretching and a weak absorption at 3561cm^{-1} is assigned to out-of-plane stretching vibrations. The band observed at $3063 - 3562\text{cm}^{-1}$, assigned to the high amount of water physisorbed on the surface of the clay [22]. In the bending region mode, the catalyst show a series of IR bands with peak maxima at 1065, 1427 and 1512cm^{-1} . The peak at 1512cm^{-1} is quite intense and can be attributed to the bending vibration mode of physisorbed water on the surface of catalyst produced due to leaching [23]. The 1065 and 1427cm^{-1} bands is due to the stretching vibrations of the CO_3^{2-} which is as a result of the complete decomposition of the CaCO_3 in the chicken eggshell [24]. IR peaks at $2654 - 2809\text{cm}^{-1}$ and $2021 - 2577\text{cm}^{-1}$ can be assigned to the Al–Al–OH and Si–O–Al vibration of the catalyst sheet. Again well resolved strong bands in the 525 and 578cm^{-1} regions are due to Si–O stretching in the catalyst. Strong IR spectral lines characteristic for CaO are placed in the far-infrared range ($\sim 400\text{cm}^{-1}$ and 290cm^{-1}) and one weak band is in the range from 500cm^{-1} to 560cm^{-1} . This peak is due to the formation of amorphous catalyst produced.

The summary of the BET analysis revealed a very high surface area of $340\text{m}^2/\text{g}$ for the alumina supported calcium oxide catalyst with a pore volume and mean pore radius of $0.1351\text{cm}^3\text{g}^{-1}$ and 7.208 \AA respectively. The surface area is actually high compared to the previous studies reported in various literatures. A study by [25] reported a surface area of $83.77\text{m}^2\text{g}^{-1}$ for alumina supported calcium oxide catalyst, though the alumina loading was just 30% unlike the 100% loading used in this research. This result also varies with the report by [17] where the surface area for the calcium oxide supported with alumina in a 1:1 ratio was $82.74\text{m}^2\text{g}^{-1}$. A study by [26] reported that alumina has very large specific area which enhances high dispersion of active sites. According to [27], a combination of high surface area, large pore volume and smaller pore sizes allows triglycerides of different sizes to enter the pores of the catalyst, and as well gives a large surface for proper transesterification. This combination therefore makes for a highly active catalyst.

The thermal stability of the catalyst was determined via thermo gravimetric analysis (TGA). A plot of the results obtained showed three different stages of weight loss with increasing temperature. At the first stage, the weight of the catalyst was seen to have reduced steadily between temperature ranges of $60^\circ\text{C} - 160^\circ\text{C}$. This was followed by a second stage

between 160°C and 360°C which showed a drastic weight loss with increasing temperature. According to [24], this weight loss could be attributed to loss in organic matter. The last stage of weight loss was similar to the first stage, the weight loss occurred steadily between 360°C and 600°C. Above 600°C, the catalyst maintained a constant weight. This means that the catalyst is thermally stable above 600°C. Figure 1 is a TGA plot of the CaO/Al₂O₃ catalyst.

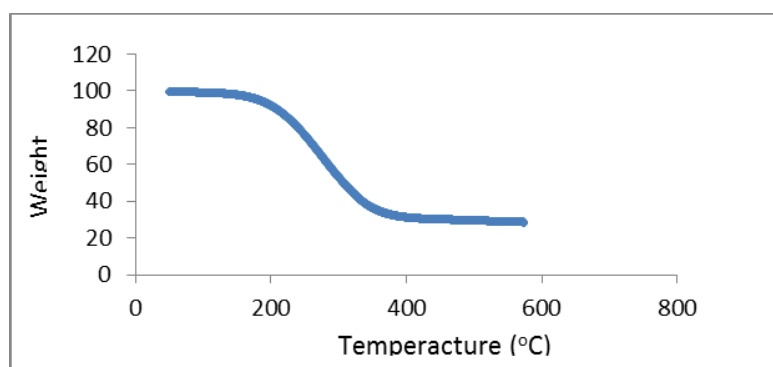


Figure 1: TGA Plot of the CaO/Al₂O₃ Catalyst.

3.2 Design of Experiment

The design of experiment was done using a 2⁴ experimental design to investigate the effect of the process variables on the yield of the biodiesel. Table 1 shows the experimental design and the results obtained.

Table 1: Experimental Design Catalyst

Std	Run	F1	F2	F3	F4	Response 1	Response 2
1	7	1:1	1	650	2	82.59	40.03
2	11	2:1	1	650	2	87.63	23.2
3	3	1:1	2	650	2	85.04	48.51
4	12	2:1	2	650	2	81.80	28.62
5	2	1:1	1	750	2	74.30	76.83
6	10	2:1	1	750	2	77.63	50.02
7	15	1:1	2	750	2	73.01	85.89
8	14	2:1	2	750	2	79.92	57.02
9	9	1:1	1	650	3	84.09	68.07
10	5	2:1	1	650	3	88.72	37.23
11	8	1:1	2	650	3	78.27	71.06
12	1	2:1	2	650	3	83.54	34.05
13	16	1:1	1	750	3	79.20	82.40
14	6	2:1	1	750	3	81.71	48.23
15	13	1:1	2	750	3	76.67	90.10
16	4	2:1	2	750	3	78.05	55.71

*where; F1 = Catalyst impregnation ratio, F2 = Impregnation time (hours), F3 = Calcination temperature ($^{\circ}\text{C}$) and F4 = Calcination time (hours). Response 1 = Percentage catalyst yield; Response 2 = Percentage Biodiesel yield.

3.3 Analysis of Variance (ANOVA) on Yield of Biodiesel

The adequacy and significance of the experimental data obtained from the investigations of the effect of process parameters used in catalyst production on the yield of biodiesel was emphasized using the analysis of variance (ANOVA). Tables 2 and 3 give the details of the analysis of variance for the 2^4 factorial design for the effect of process parameters used in calcium oxide-alumina as a catalyst on the yield of biodiesel.

Table 2: ANOVA for 2^4 Factorial Design on the Yield of Biodiesel

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	6625.89	13	509.68	624.53	0.0016	Significant
A-Impregnation Ratio	3272.13	1	3272.13	4009.44	0.0002	
B-Impregnation Time	126.28	1	126.28	154.74	0.0064	
C-Calcination Temp.	2387.06	1	2387.06	2924.93	0.0003	
D-Calcination Time	367.97	1	367.97	450.88	0.0022	
AB	8.28	1	8.28	10.15	0.0860	
AC	24.18	1	24.18	29.63	0.0321	
AD	121.06	1	121.06	148.33	0.0067	
BC	19.21	1	19.21	23.53	0.0400	
BD	14.01	1	14.01	17.16	0.0536	
CD	250.98	1	250.98	307.54	0.0032	
ABC	3.02	1	3.02	3.70	0.1944	
ACD	20.82	1	20.82	25.51	0.0370	
BCD	10.91	1	10.91	13.36	0.0674	
Residual	1.63	2	0.82			
Cor Total	6627.52	15				

The Model F-value of 624.53 implies that the model is significant. There is only a 0.16% chance that a Model F-value this large could occur due to noise (induced variation under normal operating conditions by uncontrollable factors).

Prob > F values less than 0.0500 indicates model terms are significant. In this case A, B, C, D, AC, AD, BC, CD, ACD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. In this experiment, only one model term; ABC has a value above 0.1000 which is the only insignificant term in the developed 2^4 factorial model. The values of R^2 , adjusted- R^2 and standard deviation give an understanding of the accuracy of the model that has been developed. R^2 reflects the extent to which the model perfectly estimated the experimental data points. In this case, there is a reasonable agreement between the predicted R-squared value of 0.9842 and the adjusted R-squared value of 0.9982. This close agreement between the predicted R-squared value and the adjusted R-squared value reflects the closeness of the experimental data to the predicted values and also the extent of accuracy of the developed model, its correctness and applicability. Adequate precision gives the ratio of signal to noise. Usually, a ratio above 4 is desirable, which means that the 78.98 ratio gotten from this model is an indication of an accurate signal. This model can therefore be used to navigate the design space. Determining the value of the coefficient of variance is of utmost importance because the value gives the ratio of the standard error of estimate to the mean value of the observed response as a percentage and also helps to measure the reproducibility of the model. The coefficient of variance for this model was found to be 1.61%. This value is less than 10% of the biodiesel yield which makes the model reproducible. Table 4 gives details of the statistical parameters obtained from the analysis of variance (ANOVA).

Table 3: Statistical Parameters Obtained from the Analysis of Variance (ANOVA) on Biodiesel Yield

Variable	Biodiesel
Standard deviation	0.9
Mean	56.06
Coefficient of variation (%)	1.61
PRESS	104.46
R- Squared (R^2)	0.9998
Adjusted- R^2	0.9982
Pred. R^2	0.9842
Adeq. Precision	78.98

The model equation in terms of coded factors for biodiesel yield is given as;

$$Y = +56.06 - 14.30 * A + 2.81 * B + 12.21 * C + 4.80 * D - 0.72 * A * B - 1.23 * A * C - 2.75 * A * D + 1.10 * B * C - 0.94 * B * D - 3.96 * C * D + 0.43 * A * B * C + 3.69 * A * C * D + 1.14 * A * C * D + 0.83 * B * C * D \quad (1)$$

But values greater than 0.1000 indicates that the values are insignificant and as such ABC is insignificant which tends to zero and the final model equation for biodiesel yield is given as;

$$Y = +56.06 - 14.30 * A + 2.81 * B + 12.21 * C + 4.80 * D - 0.72 * A * B - 1.23 * A * C - 2.75 * A * D + 1.10 * B * C - 0.94 * B * D - 3.96 * C * D + 3.69 * A * C * D + 1.14 * A * C * D + 0.83 * B * C * D \quad (2)$$

Equation 2 describes how the yield of biodiesel was affected by the parameters used in the production of the calcium oxide-alumina catalyst.

3.4 Influence of parameters used in catalyst production on yield of biodiesel.

The analysis of the experimental data obtained showed that all the four factors had a considerable effect on the biodiesel yield with the impregnation ratio and the calcination temperature being of greater effect because of their F-values. But in terms of interaction of the factors, the interaction between the calcination temperature and calcination time had the greatest effect on the yield of biodiesel as shown in Table 3 above. There should be a better response in the percentage yield of biodiesel when the calcium oxide-alumina catalyst is calcined at a higher temperature and time with lower impregnation ratio and time. This result agrees with the study done by [4] and [17] where calcium oxide from chicken eggshell impregnated with gamma alumina in a 1:1 ratio and calcined at 718°C gave the optimum biodiesel yield of 98%.

The three-dimensional response for the effect of the interactions of these parameters, according to the 2^4 factorial design is shown in Figures 2a to 2f which clearly represents the effect of the interactions of the process variables used in the production of the catalyst on the yield of the biodiesel.

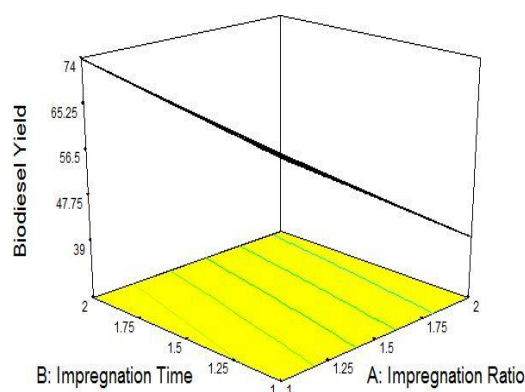


Fig. 2a: Effect of impregnation ratio and impregnation time on biodiesel yield.

High yields of biodiesel were gotten with a combination of lower impregnation ratio and higher impregnation time. From the model equation of biodiesel response, (Eqn. 1) impregnation ratio alone has a significant negative effect on the biodiesel response while the impregnation time has a significant positive effect. Since the impregnation ratio-time term of the biodiesel yield model equation is a linear term, the effect of the impregnation ratio will be more pronounced on the response. This means that loading a higher quantity of the calcium oxide on the alumina will require more time for impregnation in order to get a higher biodiesel yield. Lower biodiesel yields at lower impregnation time and high impregnation ratio could be due to improper mixing since the time of impregnation is shorter and catalyst loading higher. This result also agrees with the report by [17] that once the loading of calcium oxide on alumina increases beyond a ratio of 1:1, the yield of biodiesel begins to drop because of blockage of catalyst pore spaces by the precursor.

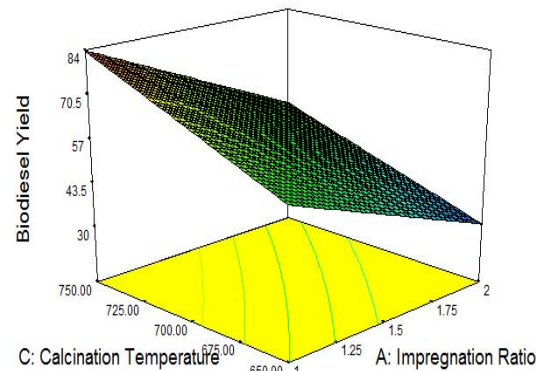


Fig. 2b: Effect of impregnation ratio and calcination temperature on biodiesel yield.

This represents the effect of the interaction of calcination temperature and impregnation ratio on the yield of biodiesel. The biodiesel yield can be seen to have increased with an increase in temperature and a decrease in impregnation ratio. This means that in order to get a higher yield, a combination of lower ratio of impregnation and a higher temperature of calcination is suitable.

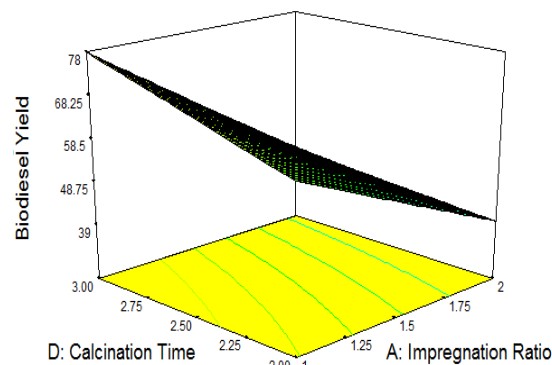


Fig. 2c: Effect of impregnation ratio and calcination time on biodiesel yield.

From the plot, a better biodiesel response is observed with a combination of longer hours of calcination and a lower impregnation ratio. It can also be seen that between two to three hours of calcination, the response is high with low impregnation ratio. But as the impregnation ratio is increased, the response begins to drop even with long hours of calcination. This can be explained from the model equation for biodiesel yield (Equation 1), while calcination time has a significant positive effect on the biodiesel response, the impregnation ratio has a significant negative effect on the response and a combination of these terms gives a significant negative effect on the yield of biodiesel. This means that the ratio used in impregnation is of utmost importance as it has a strong effect on the biodiesel response [4].

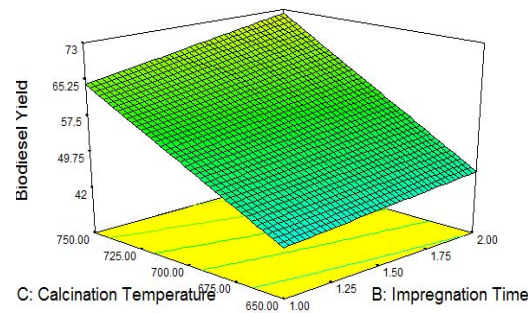


Fig. 2d: Effect of impregnation time and calcination temperature on biodiesel yield.

It is observed that the yield of biodiesel increased with increase in calcination temperature and impregnation time. Worthy of note is the fact that there seems to be a very slight difference in the yield at lower impregnation time and that at the higher. From the plot, there seems to be a greater effect on the yield from the calcination temperature than that from the hours used in impregnation. From Equation 1, the calcination temperature-impregnation time term of the equation is linear and has a positive term. This implies that the interaction of these factors has a significant positive effect on the biodiesel response. This means that when the catalyst is impregnated for longer hours and calcined at higher temperatures, the yield will be higher.

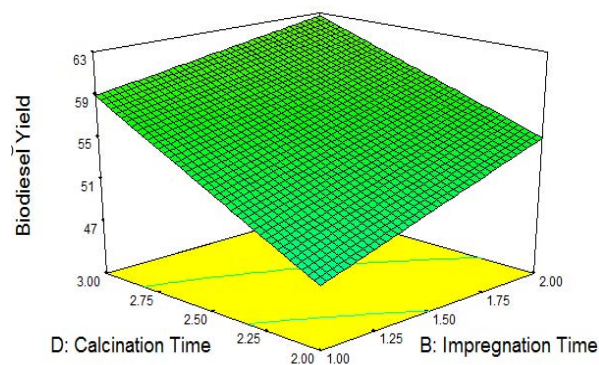


Fig. 2e: Effect of impregnation time and calcination time on biodiesel yield.

Figure 2e shows a positive effect on the response from the interaction of calcination time and impregnation time. This can be seen as the biodiesel yield increased linearly with increase in calcination time and impregnation time.

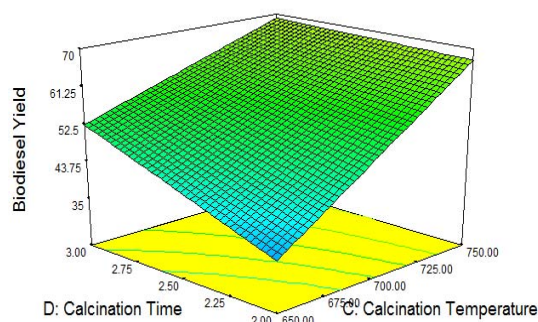


Fig. 2f: Effect of calcination temperature and calcination time on biodiesel yield.

There is a similar occurrence as observed in Figure 2e, the biodiesel yield increased from low to high with increase in calcination time and calcination temperature with calcination temperature giving a greater effect on the response.

Table 4.12: Results of the model evaluation

Run	Impreg. Ratio	Impreg. Time (hr)	Cal. T. (°C)	Cal. Time (hr)	Biodiesel Yield (%)	
					Experimental	Predicted
1	1.17:1	1.32	740.31	2.62	76.02	75.4

Cal=Calcination; T=Temperature; Impreg=Impregnation

Comparing the results obtained in table 4.12 above, the error margin between the experimental and predicted biodiesel yields is 0.62%, it can be conclusively said that the developed model is accurate and precise enough to predict the amount of biodiesel yield at any point in time using the produced catalyst.

4.0 Conclusion

The interaction between the calcination temperature and calcination time had the greatest effect on the yield of biodiesel. There could be a better response in the percentage yield of biodiesel when the calcium oxide-alumina catalyst from chicken eggshell and kaolinite clay is calcined at a higher temperature and time with lower impregnation ratio and time.

Optimum conditions of the reaction obtained were; impregnation ratio of 1.17:1, 1.32 hours of impregnation, calcination at 740.31°C for 2.62 hours. The biodiesel yield from these optimum conditions was predicted to be 75.4% with 95% confidence level. The conditions for transesterification were 12:1 methanol to oil molar ratio, 6wt% catalyst, 60°C reaction time, and mixing speed of 250rpm for ninety minutes. This result closely agrees with the reports from previous literature.

REFERENCES

- [1] Jakeira, M. R., Fazal, M. A., and Haseeb, A. S. (2014). Influence of different factors on the stability of biodiesel: A review. *Renewable and Sustainable Energy Reviews*, 154-163.
- [2] Tinwala, F., Mohanty, P., Parmar, S., Patel, A., and Pant, K. K. (2015). Intermediate pyrolysis of agro-industrial biomasses in bench-scale pyrolyser: Product yields and its characterization. *Bioresource Technology*, 258-264.
- [3] Sajjadi, B., Raman, A. A., and Arandiyani, H. (2016). A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. *Renewable and Sustainable Energy Reviews*, 62-92.
- [4] Zabeti, M., Wan Daud, A. W., and Aroua, M. K. (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, 770-777. doi:doi:10.1016/j.fuproc.2009.03.0
- [5] Verma, P., and Sharma, M. P. (2016). Review of process parameters for biodiesel production from different feedstocks. *Renewable and Sustainable Energy Reviews*, 1063-1071.
- [6] Baroi, C., Yanful, E. K., and Bergougnou, M. A. (2009). Biodiesel Production from *Jatropha curcas* Oil Using Potassium Carbonate as an unsupported catalyst. *International Journal of Chemical Reactor Engineering*, 7, 1-20.
- [7] Acquah, N., Obeng, G., and E., M. (2016). Repetitive use of vegetable cooking oil and effects on physico-chemical properties - case of frying with red fish (*Lutjanus fulgens*). *Journal of science and technology*, 6(1), 4-14.
- [8] Sharma, Y. C., Singh, B., and Korstad, J. (2010). Application of an Efficient Nonconventional Heterogeneous Catalyst for Biodiesel Synthesis from *Pongamia pinnata* Oil. *Energy Fuels*, 1-9.
- [9] Fadhil, A., Aziz, A. M., and Al-Tamer, M. H. (2016). Biodiesel production from *Silybum marianum* L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification. *Energy Conversion and Management*, 255-265.
- [10] Sanjay, B. (2013). Heterogeneous catalyst derived from natural resources for biodiesel production: A review. *Research journal of chemical sciences*, 3(6), 95-101.
- [11] Jagadale, S., and Jugulkar, L. (2012). Review of various reaction parameters and other factors affecting on production of chicken fat based biodiesel. *international journal of modern engineering research*, 2(2), 407-411.
- [12] Tan, Y., Abdullah, M., Nolasco-Hipolito, C., and Taufiq-Yap, Y. (2015). waste ostrich- and chicken eggshells as catalyst for biodiesel production from waste cooking oil: Catalyst characterization and biodiesel yield performance. *Applied energy*, 160, 58-70.
- [13] Semwal, S., Arora, A. K., Badoni, R. P., and Tuli, D. K. (2011). Biodiesel production using heterogeneous catalysts. *Bioresource Technology*, 2151-2161. doi:doi:10.1016/j.biortech.2010.10.080

- [14] Pandit, P., and Fulekar, M. (2017). Eggshell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology. *journal of environmental management*, 198, 319-329.
- [15] Elizabeth J. Eterigho, T. S. Farrow and S. E. Ejeigbe (2017), "Sulphated Zirconia Catalyst Prepared from Solid Sulphates by Non-aqueous Method", Iranica Journal of Energy and Environment, Vol. 8, Issue 2, pp 142 – 146 www.IJEE.net
- [16] Singh, V. y. (2017). Effect of co-solvent on biodiesel production using calcium aluminium oxide as a reusable catalyst and waste vegetable oil. *Fuel*, 203, 360-369.
- [17] Zabeti, M., Daud, W. M., and Aroua, M. K. (2010). Biodiesel Production using alumina supported calcium oxide: An optimization study. *Fuel processing technology*, 91, 243-248.
- [18] Muthu, K., and Viruthagiri, T. (2015). Study on solid base calcium oxide as a heterogeneous catalyst for the production of biodiesel. *Journal of advanced chemical sciences*, 1(4), 160-163.
- [19] Ajemba, O. R., and Onukwuli, O. D. (2012). Kinetic model for Ukpok clay dissolution in Hydrochloric acid solution. *Journal of emerging trends in engineering and applied sciences*, 3(3), 448-454.
- [20] Olaremu, A. (2015). sequential leaching for the production of alumina from nigerian clay. *International journal of engineering technology, management and applied sciences*, 3(7), 103-109.
- [21] Mahesh, S., Ramanathan, A., Begum, K., and Narayanan, A. (2015). Biodiesel production from waste cooking oil using KBr impregnated CaO as catalyst. *Energy conversion and management*, 91, 442-450.
- [22] Madejova, J. (2003). FTIR Techniques in Clay Mineral Studies. *Vibration Spectroscopy*, 31, 1-10.
- [23] Dudkin, B., Loukhina, I., Avvakumov, E., & Isupov, V. (2004). Application of Mechanochemical Treatment of Disintegration of Kaolinite with Sulphuric Acid. *Chem.Sust. Dev.*, 12, 327-330.
- [24] Rohazriny, R., Razi, A., Naimah, I., Nasrul, H., and Abidin, C. (2014). Characterization of Calcium oxide catalyst from eggshell waste. *Advances in Environmental Biology*, 8(22), 35-38.
- [25] Asri, N., Diah, A., Puspita, S., Bambang, P., and Suprpto. (2015). Utilization of Waste Cooking Oil for Biodiesel Production Using Alumina Supported Base Catalyst. *3rd International Conference on Biological, Chemical & Environmental Sciences* (pp. 59-63). Kuala Lumpur, Malaysia: BCES.
- [26] Theodoro, P., Pedro, A., & Silva, E. A. (2017). Synthesis of bifunctional calcium oxide supported on gamma alumina for biofuel production from the transesterification of crambe oil . *Acid base catalysis*, 7-10.
- [27] Sulaiman, N. B. (2017). Response surface methodology for the optimum production of biodiesel over Cr/Ca/r-Al₂O₃ catalyst: catalytic performance and physicochemical studies. *Renewable energy*, 113, 697-705.