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Synthesized activated rice husk ash as a heterogeneous catalyst for biodiesel production using waste cooking oil

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Abstract

Biodiesel has been globally recognized as the right replacement to reduce the effects of fossil fuel usage due to its renewability and eco-friendly nature. The cost of synthesizing biodiesel though transesterification process can be significantly reduced by using waste feedstock materials such as waste cooking oil with calcined rice husk ash activated using sodium hydroxide salt solution catalyst which forms the basis of this present study. A direct transesterification process was adopted in this study with the reduction of the free fatty acid value of the waste oil from 6.61 to a satisfactory ASTM value of 1.12 through multiple hot water washing and filtering. The characteristic study of activated rice husk ash using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), confirmed that the produced catalyst contains sodium silicate and undergo some morphological changes after impregnation with sodium hydroxide solution at a calcination temperature of 500 ºC for 4 h. The process parameters were optimized using one factor at a time (OFAT) to obtain the optimal yield of 86 % at the optimal conditions of methanol to oil molar ratio (9:1), process temperature (55 ºC), catalyst concentration (3.0 wt%), agitation speed (300 rpm) and process time (3 hrs). The characteristic properties of the produced biodiesel were determined using ASTM methods and obtained properties complied with the ASTM standards.

Keywords: Activated Rice Husk Ash, Waste Cooking Oil, Calcination, Transesterification, Optimization, Biodiesel Production.

1. Introduction

High fuel energy demand, environmental pollution, non-renewability, and shortage of non-renewable fuels have increased the reliance on renewable sources of fuels as a substitute to replace conventional fuels (Ganesan et al., 2021). The process of high energy demand has impacted the environment negatively as a result of industrialization, which has resulted to the fossil fuel depletion with the production of hazardous emissions from vehicles and industrial waste. Consequently, renewable energy sources are more appealing reserves and the production of hazardous emissions from vehicles and industrial waste. Consequently, renewable energy sources such as biofuels are more appealing (Nisar et al., 2017), and are classified according to the raw materials used in the production process (Ahmad et al., 2020). Biodiesel, as one of the most potential alternative energies to petro-diesel, is degradable, renewable, and economically friendly and has attracted much research attention in recent times due to its sustainability (Ajala, et al., 2014). Biodiesel production through the transesterification process is the most appropriate method for the synthesis of biodiesel, the process involves the mixture of fatty oil with alcohol in the presence of a catalyst to produce alkyl esters and by-products (Esonye, et al., 2019). The transesterification process can be achieved using virgin plant oils, animal fat, microalgae, and waste cooking oils as feedstock materials (Belewu et al., 2014). Methanol is the most widely used alcohol for the synthesis of biodiesel (Esonye, et al., 2019; Babagana et al., 2011).

Waste cooking oil (WCO) is a form of fatty acid-based glycerol ester obtained from virgin plant vegetable oils used severally for frying food for a period of time (Ali et al., 2018). Disposal of waste cooking oil to the surroundings negatively affects the environment while consumption of oxidized waste cooking oil over a long period might affect human health as a result of the formation of cancerous poisonous substances (Ganesan et al., 2021). In Nigeria, waste cooking oil is indiscriminately discharged to the surroundings in Nigeria causing environmental pollution considering the population of the country that uses vegetable oils for cooking/ frying different types of food. Hence waste cooking oil is considered a potential feedstock due to its availability within the country so as to reduce the cost of producing biodiesel (Busari, et al., 2013). In this research work, methanol was used as the reactant to produce biodiesel and glycerin.

To improve the transesterification process, different catalysts have been used to enhance the reaction rate as well as increase the yield by several researchers to obtain a more quality product (Adebayo et al., 2012). The homogenous catalytic process requires a large quantity of water during the washing process and lacks the reusability of catalyst properties due to the production of soap. These associated disadvantages with homogenous processes occur as a result of high free fatty acid value and increase production cost of biodiesel due to the purification steps involved in the separation (Betiku et al., 2013). However, production process using heterogeneous catalysts involves the use of lesser quantities of water during purification, due to the absence of a saponification which eventually reduces the overall cost of biodiesel production (Berrios et al., 2008). Thus, this research leverages on the advantages of heterogeneous catalysts by producing activated alkali metal-based catalysts from rice-husk ash that is used as an alternative to conventional homogenous catalysts.

Roschat et al., (2016), studied the transesterification of oils to biodiesel using sodium silicate-activated rice husk catalyst to achieve a low cost and high-performance biodiesel production at the optimal conditions. They further confirmed the optimal yield of 99.5% biodiesel using a Li-modified rice husk ash catalyst. Consequently, this research work aims to produce activated rice husk-based catalysts by impregnation using sodium silicate for biodiesel production from waste cooking oil under specified reaction parameters such as methanol: oil molar ratio, catalyst dosage, process time and temperature, and stirring rate, thereafter confirm the optimal yield of the process using one factor at a time optimization method at the designed experimental input factors.

2.0 Materials and Methods

2.1 Collection of WCO samples

Waste cooking oil used for this research work was gotten from a cafeteria in Ikwo local government area of Ebonyi State of Nigeria as a source of triglycerides for transesterification reaction. The initial analysis showed that the waste oil contains a high level of free fatty acid hence a pretreatment method was used to reduce the acid level.

2.2 Waste cooking oil pretreatment

50ml of the WCO sample was first filtered using Whatman filter paper and a funnel to reduce the residue from cooking processes, hence the waste oil was purified using the hot water washing method for several times. The washed WCO was further filtered using Whatmann filter paper and was heated in the laboratory oven for 10 mins at 110 ^oC. This process reduced the free fatty acid level to an acceptable level for the one-step transesterification process.

2.3 Waste cooking oil characterization

To determine the physiochemical properties of the pretreated oil, American standards and testing method (ASTM) was used to characterize the oil. The physicochemical properties of the waste cooking oil (WCO) and the biodiesel produced from waste cooking oil using activated rice husk catalyst (RWCOME) were compared with the ASTM standard (ASTM 6751) and presented in Table 1. For the produced waste cooking oil methyl ester, the specific gravity obtained was 0.942 which corresponds to the density of 942 kg/m^3. This value complies with the values obtained in literature by other researchers (Mushrush, et al., 2015). The result from this work shows a viscosity of 5.612 mm^2s^{-1} which is in accordance with the ASTM values and reported in literature (Yahaya, et al., 2016).

The value of the flash point obtained in this current work is approximately 168 ^oC and shows appreciable consistency with ASTM international standards for biodiesel and also reported in literature (Dantas, et al.,2011). The value of the flash point indicates that the presence of minimal quantity of methanol in the produced biodiesel. The value of the cetane number determines the ignition quality of fuel. The higher the value of the cetane number of the fuel, the faster the ignitability of the fuel as obtained in this research work

2.4 Catalyst preparation and characterization

Rice husk ash was washed to remove dirt and dried under the sun for a period of three days and further dried in a hot air oven at 105 ºC for 30 mins and sieved to obtain fine particles. The produced dried rice husk was further combusted in a muffle furnace at the calcination temperature of 500 ºC for 4hrs to remove organic compounds. This process allows complete conversion of the rice husk to rice hush ash silicate (SiO_2). The silica mixture of 10 g was mixed with 10 ml of 1N NaOH solutions in the ratio of 1:1(g/ml) through the process of impregnation and stirred at 300 rpm for homogeneity to form alkaline sodium-based rice husk silica ash slurry and then further heated at 110 °C using microwave oven to remove moisture. The activated rice husk ash was stored in a tight container to prevent moisture and further characterized for the structural, morphological, and elemental composition. The functional groups contained in the activated rice husk were analyzed using Infrared ray machine (FTIR).

2.5 Transesterification of WCO

The biodiesel was produced using direct transesterification process because of the low fatty acid content of less than 2 % obtain after purification of the waste oil. 50 ml of the WCO was measured and dried at 110 ºC to ensure that the sample was free from moisture. The mixture of the WCO and methanol at the ratios of methanol-to -oil of 3:1 – 15:1, was transferred into a three-neck conical flask, followed by the addition of 1.0 -3.0 w% of RHA prepared from activated rice husk. The agitation rate range of 100-500rpm was used for the transesterification process. A thermometer was inserted into the conical flask to determine the reaction temperatures of the process within the range of 45 – 65 ºC while the range of reaction time was 1-5 hrs. At the end of the process, the catalyst was separated from the mixture and the product allowed to settled for a period of at least 24 hrs in the separating funnel. The glycerol was withdrawn from the separating funnel and the fatty acid methyl ester is obtained as the product after washing and neutralizing using hydrochloric acid.

The product yield is calculated using equation (1) as follows:

$$\text{Yield (\%)} = \frac{Volume\ of\ Biodiesel(ml)}{Volume\ of\ WCO(ml)}\ x\ 100 \qquad (1)$$

2.6 Biodiesel Characterization

The percentage yield of the biodiesel and the physicochemical properties were determined. The characteristic results of the biodiesel product was compared to the ASTM values and it was confirmed that most of the properties fall within the range of the specified values of the ASTM standards. The physicochemical properties of

the produced biodiesel was analyzed using ASTM standards methods and the obtained values are compared with ASTM standards in Table 1.

3.0 Results and Discussions

3.1 Physiochemical properties of WCO and R-WCOME

This study shows that the cetane number of the produced biodiesel was 54.65 and the value obtained is in agreement with ASTM standard. This implies the waste cooking oil biodiesel produced has high ignition quality (Dantas, et al., 2011). Table 1 displays the characteristic properties of the waste cooking oil and waste cooking oil methyl ester compared with ASTM standards.

3.2 Catalyst Characterization

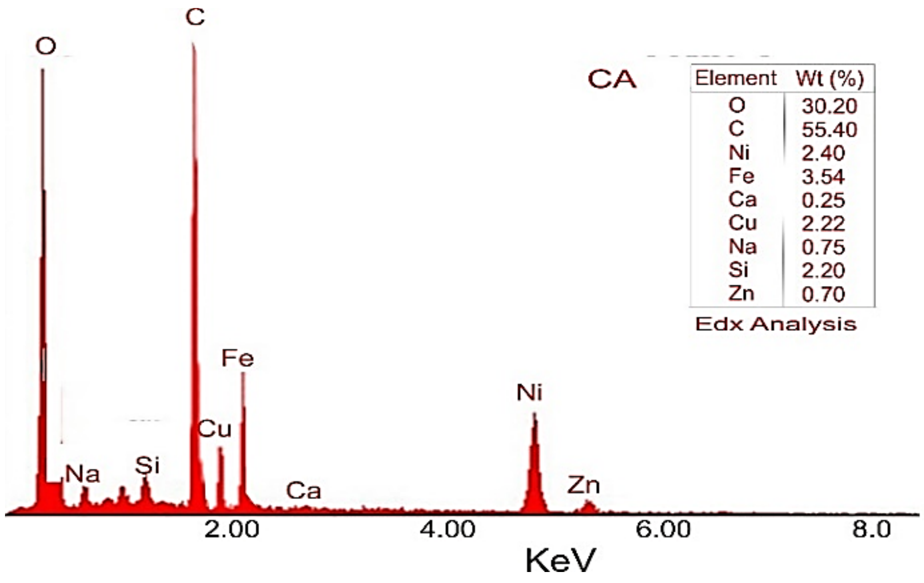
A sample of the calcined activated rice husk ash was analyzed by X-ray powder diffraction (XRD) using Rigaku Smartlab3kW X-ray diffractometer and Shimadzu GC QP-2010 gas chromatography with Cu Ka radiation (k = 1.5418 Å). Elemental compositions of the samples were analyzed by a PHILIPS Magi X wavelength dispersive X-ray Fluorescence (XRF) spectrophotometer with 1 kW Rh Ka radiation. Scanning electron microscopy SEM) was performed on Hitachi S-4700 scanning electron microscope. The sample was also characterized using a Fourier transform infrared (FTIR) spectroscopy Gas chromatography machine, Buck scientific infrared spectrophotometer Model (M530) in the range of 450–4000 cm^{-1} with resolution of 4 cm^{-1} using potassium bromide (KBr) medium.

Table 1: Results of WCO and WCO methyl ester (RWCOME) characterization compared with ASTM and European standard

Properties	WCO	RWCOME	ASTM D6751	EN 14214
Moisture Content (%)	1.049	0.028	< 0.03	0.02
Density (g/ml)	0.987	0.892	0.86–0.90	0.85
Viscosity at 40°C (mm^2/s)	43.40	5.612	1.9–6.0	3 .5–5.0
Flash point (ºC)	246	168	130min	120min
Acid value (mgKOH/g)	12.11	0.293	0.5 max	-
Free fatty acid (%)	6.06	0.116	0.5 max	-
Pour point	-	7.8	-15 – 10	-
Saponification value (mgKOH/g)	208	182	-	-
Iodine value mg/100g	73.58	101.63	48 – 60	-
Cetane Number	-	54.63	47 min	51 min
Heating Calorific Value (KJ/mol)	39.20	43.28	36 min	-
Cloud point	14	6.0	-3 - 12	-

3.2.1 Energy Dispersive X-ray Spectroscopy (EDS)

The elemental composition of the activated rice husk was determined using Energy-dispersive X-ray spectroscopy (EDS) as shown in Figure 1. The activated rice husk ash EDX result showed the presence of carbon, Oxygen, iron, Nickel, silicon and other oxides due to pretreatment and impregnation of sodium hydroxide to the feedstock structure. The peak spectra of the activated rice husk (Na/RHA) composite identified the elemental components, silicon (Si), copper (Cu), Iron (Fe), oxygen (O), Sodium (Na) and carbon (C). A high carbon value was obtained due to the calcination process and the presence of a silicon component with a relatively low calcium content was obtained using the EDS machine.



Element	Wt (%)
O	30.20
C	55.40
Ni	2.40
Fe	3.54
Ca	0.25
Cu	2.22
Na	0.75
Si	2.20
Zn	0.70

Figure 1: EDX analysis of Na / RHA @ 5000x

3.2.2 Scanning Electron Microscope (SEM)

The morphological surface of the activated rice husk was determined using scanning electron microscopy which shows that the surface is permeable, porous, and sphere-shaped in nature. The flaky morphological surface as shown in Figure 2, shows a loosely bound surface with hollow cavities thereby making them highly reactive and amorphous in nature (Ikhlaq, et al., 2013). Furthermore, the SEM micrograph shows the distribution of residual pores within the rice husk ash samples with surface outcrops depicting the embedded silica elements in the outer cells which produces highly active porous material as reported by Tenzin et al., (2017).

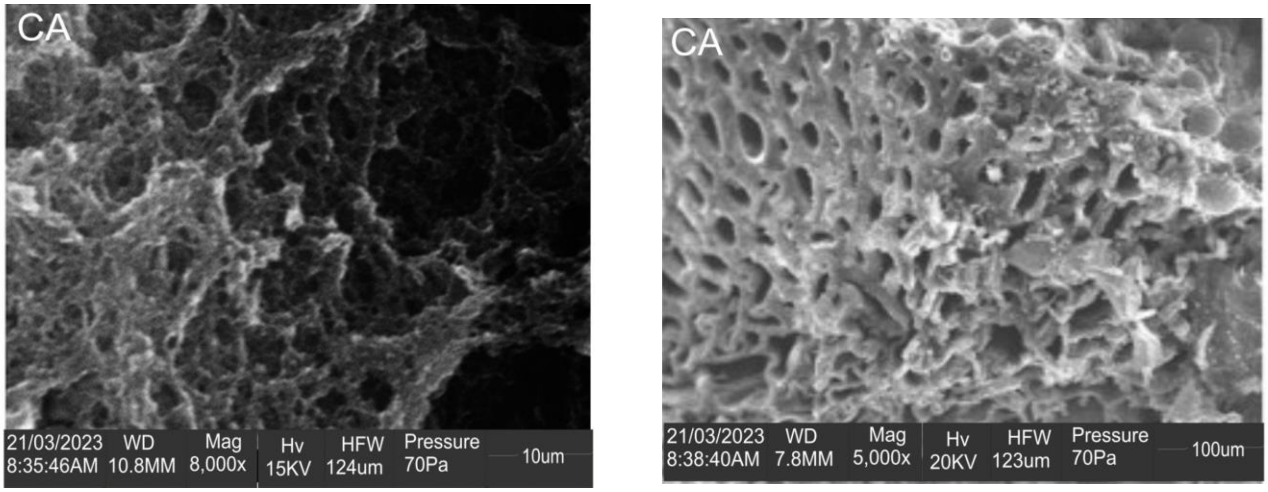


Figure 2: SEM Studies of Calcined Na/ RHA @ 5,000x and 8,000x

3.2.3 Fourier Transform Infra-Red Spectroscopy (FTIR)

Figure 3 displays the spectra of the synthesized Na/RHA catalyst using the sodium hydroxide impregnation method. Stretching modes of carboxylate ions were observed at peak 1856 cm^{-1} while the hydroxyl group stretching vibration of the broadband occurred at 2079.9 cm^{-1} due to O–H. This is attributed to the adsorbed surface water attached via Van der Walls bonds of a free hydroxyl group (Zaman, et al., 2018) during impregnation with sodium hydroxide. The broad band at 1100 cm^{-1} is responsible for Si-O-Si groups and which shows the presence of Silica as confirmed by Uprety et al., (2016). The peaks at 1561.8 cm^{-1} show the presence of SiO and CH_2 symmetric and asymmetric stretching occurs at 1457.4 cm^{-1}. The C–C stretching mode peaks were assigned at 998.9 cm^{-1} and attributed to Na – O stretching vibrations.

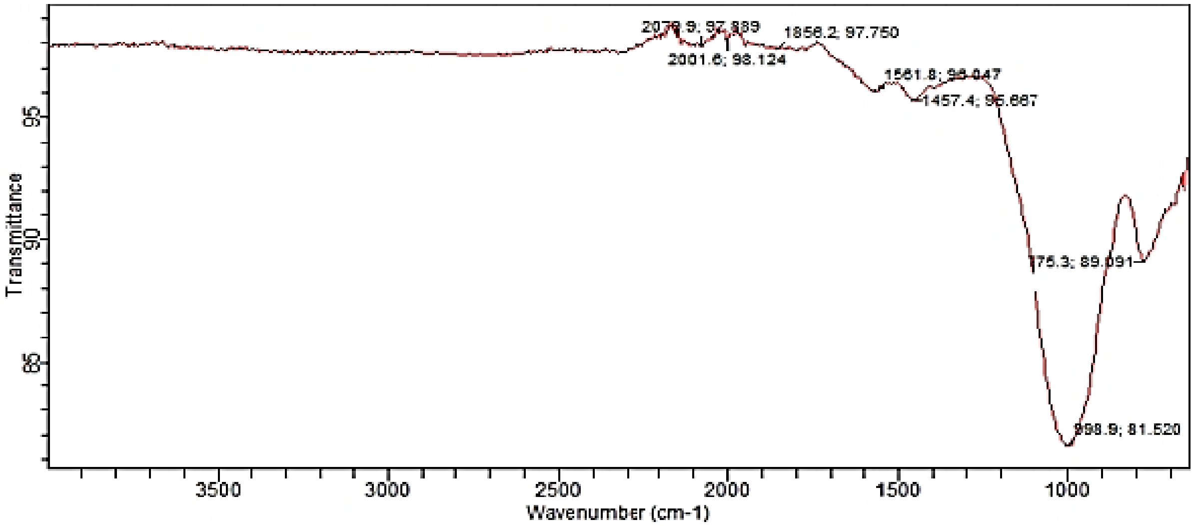


Figure 3: FTIR Spectra of Synthesized Na/RHA

3.2.4 X-ray Diffraction Analysis (XRD)

Figure 4 shows the X-ray diffraction (XRD) crystallographic properties of the activated rice husk sample. The crystalline pattern of Na/RHA exhibits the existence of Quartz Hp (SiO_2), Osumilite, Brushite, Lime (CaO), Biotite and Hanksite, with the highest silicate diffraction line appearing at peak 2θ of approximately 23° and highest peak of Silico Oxide peaks at 36°. Table 2 shows the qualitative analysis of the prepared Rice husk Ash.

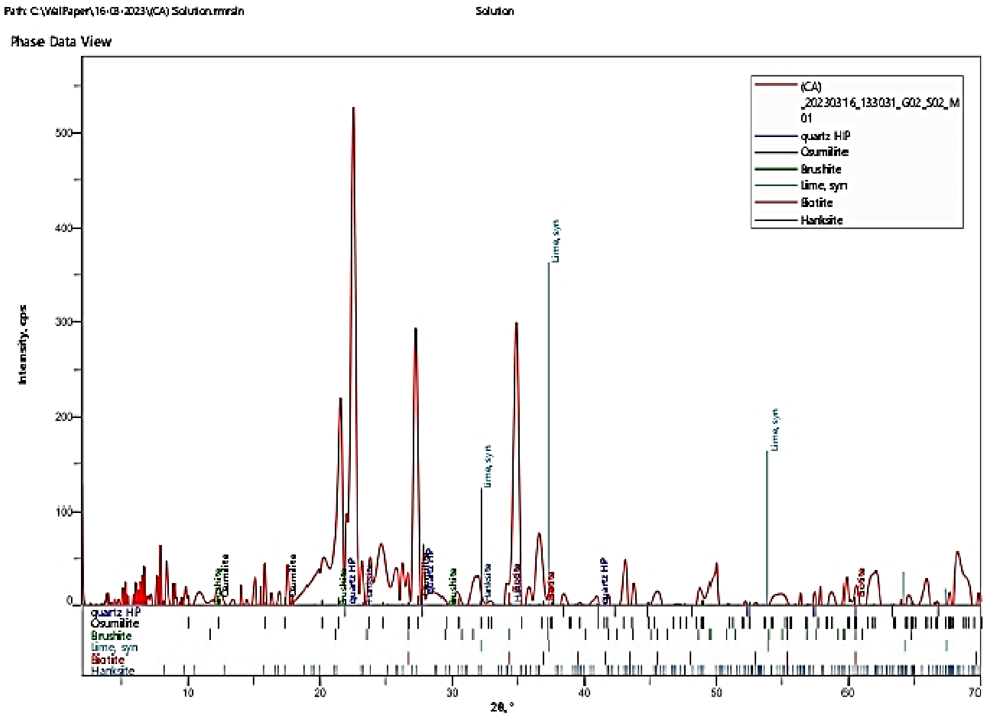


Figure 4: XRD Patterns of Na / RHA Catalyst.

Table 2: Qualitative analysis of XRD

Phase name	formula	Value
Quartz Hp	$Si O_2$	3.581
Osumilite	K – Na – Ca – Mg- Fe – Al-..	2.117
Brushite	$Ca H P O_4 – 2H_2O$	2.850
Lime, syn	Ca O	2.770
Biotite	2(Mg, Fe +2) O. (k, H)2…	2.946
Hanksite	Na22k Cl $(CO_3)_2$ $(S O_4)_9$	2.058

3.3 Optimization of process parameters of the transesterification process

For this study, a factor at a time (OFAT) optimization process was utilized to determine the most favourable conditions for the transesterification process using five-factor five-level process parameters as the preliminary study to ensure a good experimental design for the process before proceeding with other analytical tools such as response surface methodology (RSM), artificial neural network (ANN), adaptive neuro-fuzzy inference system (ANFIS), support vector machine (SVM) and linear regression and was reported by same authors, Ogbodo, et al.,(2024). The interactions of the process parameters such as methanol to oil ratio (3:1- 15:1), process temperature (45- 65 ºC), process time (1-5 hrs), and catalyst dosage (1-5 wt%) at the agitation rate (100 – 500 rpm) were determined for the optional biodiesel production. The statistical analysis using different modeling tools will be reported in subsequent publications using analytical parameters such as coefficient of determination (R^2), adjusted R^2, root mean error analysis (RMSE) e.t.c

3.3.1 Methanol to oil molar ratio effects on biodiesel yield

Figure 5 presents the effect of the molar ratio of methanol to WCO on the optimal biodiesel yield of 86 % was achieved at the ratio of 9:1 while further increase in the molar ratio above 9:1 affects the yield negatively as seen in the one-factor-at-time- a time plots with decreased yield and also confirmed in literature (Nasution, et al., 2019). The decrease in biodiesel production beyond the optimal condition occurs as a result of the excess methanol-to-oil ratio which hinders glycerol separation (Uprety et al., 2016; Obadiah, et al., 2012).

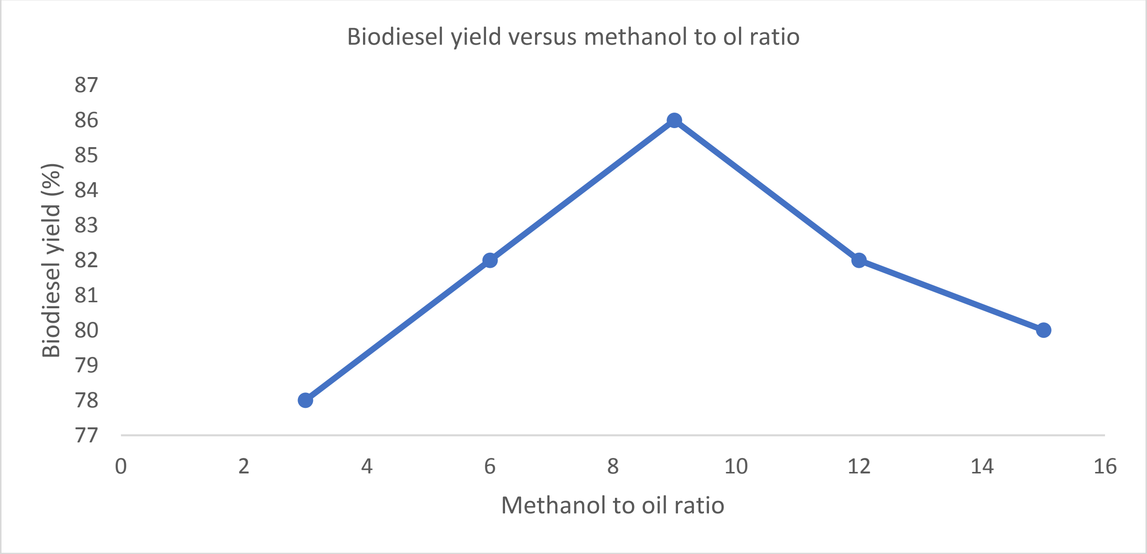


Figure 5: Plot of methanol to oil vs biodiesel yield.

3.3.2 Reaction temperature effects on biodiesel yield

Figure 6 contains the plot of the process temperature ranges from (45 – 65 °C) at a catalyst concentration of 3.0 wt%. From the plot, it was observed that as the temperature increased from (45 – 65 °C) the conversion rate of biodiesel also increased significantly to optimum temperature while the biodiesel yield started reducing with further increase in temperature. The optimum reaction temperature for this process occurred at 55 °C with a maximum yield of approximately 86 %

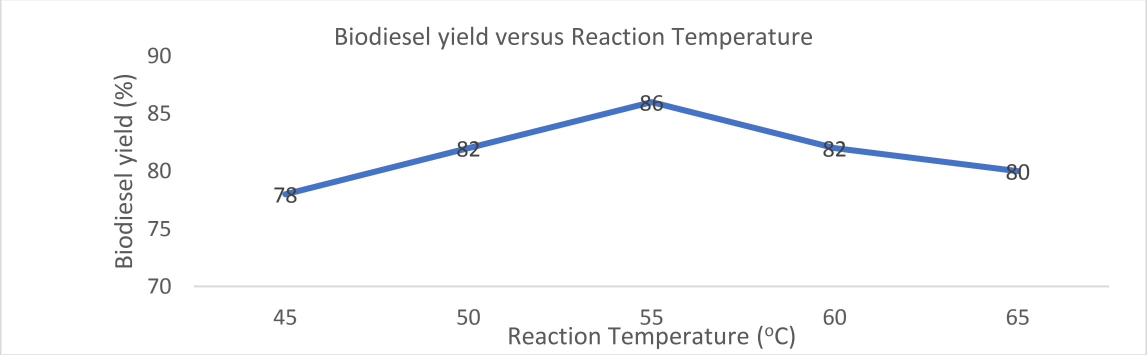


Figure 6: Plots of reaction temperature vs biodiesel yield.

3.3.3 Catalyst concentration effects on biodiesel yield.

Figure 7 comprises the catalyst concentration versus the biodiesel yield at the catalyst dosage ranges of 1 – 5 wt%. From the graph, it was observed that a significant increase in biodiesel yield percentage was achieved within 1-3 wt% catalyst and thereafter the yield reduced when the concentration was above 3.0 wt % of the activated rice husk.

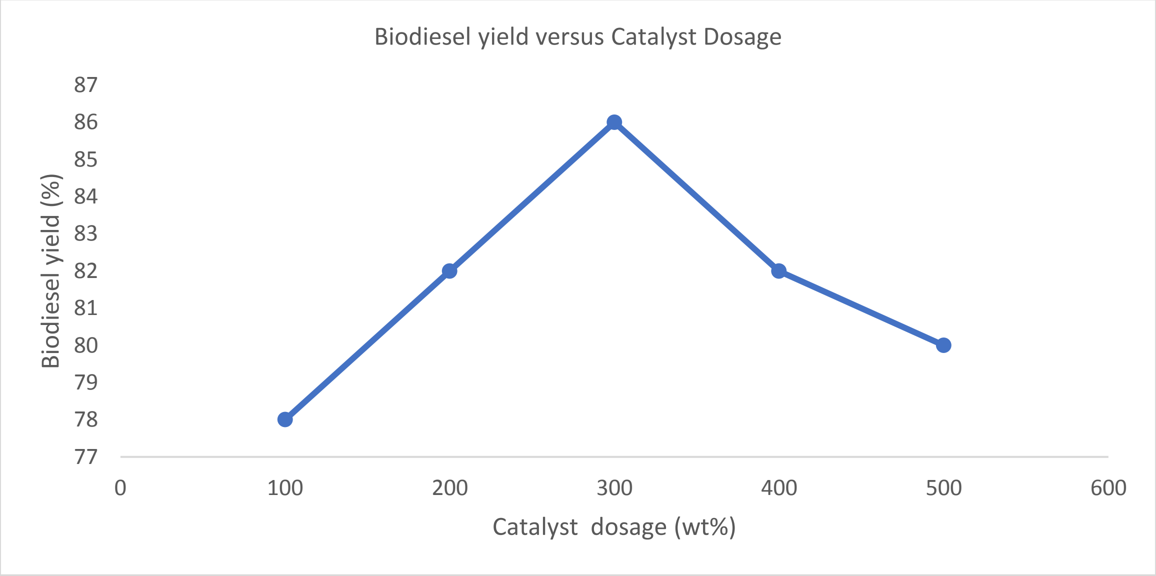


Figure 7: Plot of catalyst dosage vs biodiesel yield.

3.3.4 Reaction time effects on biodiesel yield

Figure 8 shows that the optimum transesterification time for WCO with the maximum yield of 86 % obtained at 3 hrs. reaction time. At first few minutes, the reaction was slow as a result of dispersal interaction between molecules. As the reaction time increases, the yield increases due to a highly effective collision occurring between the molecules of the waste cooking oil. Beyond the reaction time of 3 hrs, a decrease in the yield of the product was observed which confirms that 3 hrs is the optimum reaction time for the transesterification process as confirmed in literature.

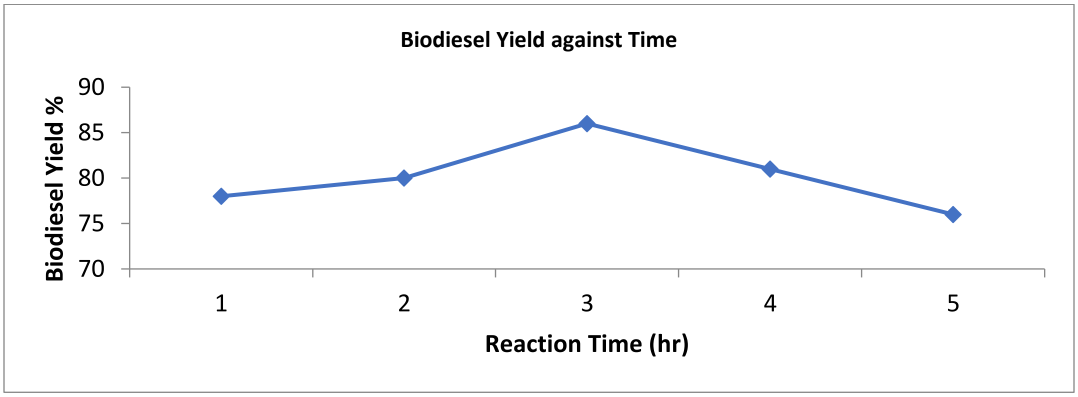


Figure 8: Plot of reaction time vs biodiesel yield.

3.3.5 Agitation rate effects on biodiesel yield

Figure 9 shows the effect of agitation speed on the transesterification reaction of WCO. The result from this study shows that the agitation speed increases from 100 rpm to 500 rpm and the maximum biodiesel yield was obtained at 300 rpm but decreases at a higher stirring speed. This is due to the reverse behavior of the transesterification reaction.

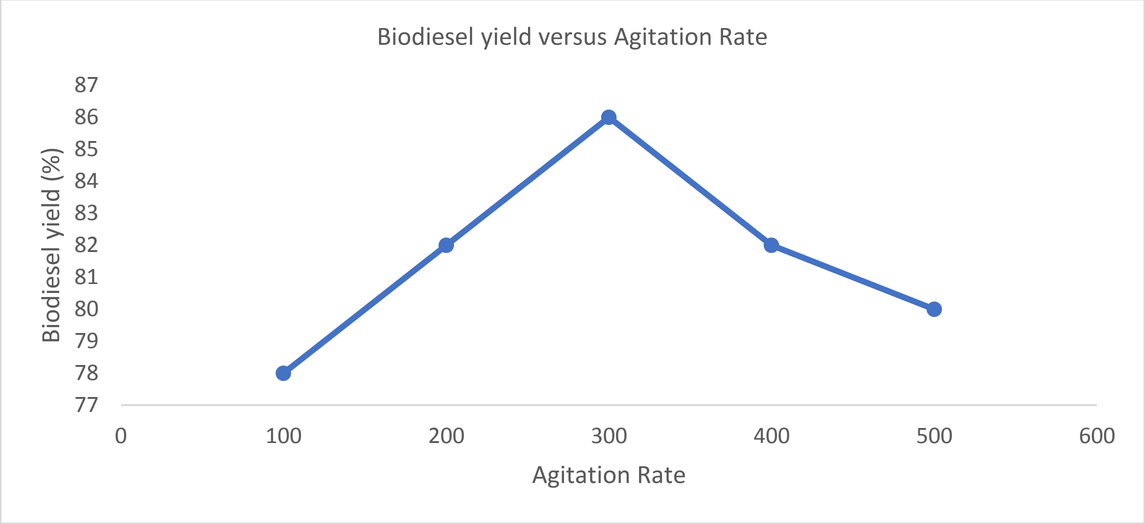


Figure 9: Plot of agitation speed vs biodiesel yield.

4.0 Conclusion

For this research work, an effective heterogeneous catalyst was developed by impregnating rice husk with sodium hydroxide solution and combustion through the calcination process. The pretreatment step was achieved through the hot water washing method to reduce the FFA from 6.61 to an acceptable value of 1.12. A biodiesel yield of approximately 86 % was obtained through a one-step transesterification reaction at the optimal conditions of methanol to oil molar ratio of 9:1, reaction temperature of 55 ^{o}C, catalyst concentration of 3 wt%, reaction time of 3 hrs and agitation rate of 300 rpm. The physiochemical characterization confirms the suitability of waste cooking oil for the production of biodiesel using the activated rice husk ash due to the presence of sodium silicate catalytic properties which improve the catalytic properties and can be adopted as alternative feedstocks. The characteristic properties of the biodiesel produced complied with the ASTM international standards.

5.0 Recommendations

For further studies, the optimization analysis should be done using different analytical tools to determine the performance of the heterogeneously activated biodiesel process parameters using waste cooking oil.

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Nomenclature

C–C- Carbon bonding
CH_2 – Methyl group
Na – O – Sodium /Oxygen bonding
Na/RHA Sodium activated rice husk ash
O–H – Hydroxyl group
SiO- Silicon oxide
RWCOME- Rice husk activated catalyst waste cooking oil methyl ester
WCO- Waste cooking oil.

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