Boosting biodiesel production from waste vegetable oil water using Acid-Base Sequential Catalysis

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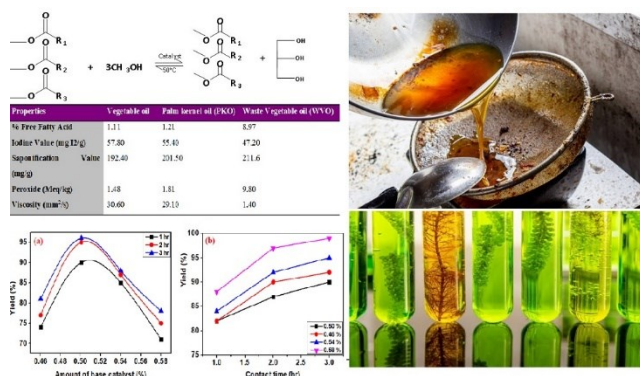
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Graphical abstract

Abstract

The use of active and recyclable catalysts is advantageous for catalytic biodiesel synthesis from waste vegetable oils which is in demand owing to frequent calls on environmental pollution and for clean renewable energy production. For this study, homogenous catalysts are effective at converting single-origin feedstocks low in free fatty acids (FFA) and water into biodiesel. Biodiesel production based on waste vegetable oil was carried out to establish an optimal catalyst régime. Acid-catalyzed transesterification and sequential base catalysis were used to convert waste vegetable oil to biodiesel at varying amounts of catalyst (0.46–0.58%) and different contact times (1–2 hr). Optimal yields were obtained at 2 hr contact time and 0.50% amount of catalyst. Characterization tests conducted were specific gravity (0.8718–0.8935), flash point (117–137°C), viscosity (4.29–6.09mm^2/s) and cetane index (40–43) values were within biodiesel specifications. The study, therefore, confirmed that acid-base sequential catalysis holds a lot of promise for the creation of affordable, environmentally friendly technologies. The biodiesel's characteristics were also in good agreement with American (ASTM D6571) fuel specifications. Therefore, the work recommends the utilization of acid (H_2SO_4) and base (NaOH) catalysis in the technologically enhanced conversion of waste vegetable oil into biodiesel.

1. Introduction

Nowadays, there are limited feedstocks that are depleted quickly and many anthropogenic activities that produce large amounts of carbon dioxide (CO_2) and greenhouse gas emissions (GHGs) which damage the environment and contribute to global warming (Akhmetshin *et al.* 2021; Zhao *et al.* 2023). Furthermore, these atmospheric gases contribute to climatic change that disrupts the ecosystem. Therefore, it is imperative to reduce these emissions by focusing on mitigation techniques, such as the use of renewable energy systems (Algarni *et al.* 2023). Consequently, it is expected to find an alternative non-fossil fuel-based energy economy that is sustainable, renewable, cost-effective, and environmentally responsible (Overland *et al.* 2022; Neupane 2023). As a widely accepted mitigation technique, biodiesel is researched as a traditional technology with minimal carbon emissions. Hence, the energy shift to biodiesel from petroleum fuels is a practical way to reduce CO_2 and other GHG emissions, especially in the transportation and industrial sectors (Yamashita and Villanueva 2023; Simon and Snyder 2022).

Biodiesel implementation is crucial for tackling environmental issues, global warming, and climate change (Semwal *et al.* 2011). It possesses low emission rates, non-toxic and biodegradable, and is often sourced from waste and recyclable matters. Chemically, biodiesel is made up of a variety of long-chain fatty acid alkyl esters. When converted into biodiesel, renewable sources like vegetable oils remove more carbon dioxide from the atmosphere during production than during the burning stage. As a result, it reduces the atmosphere's rising CO_2 level. By using biodiesel as a fuel substitute, concerns about localized air pollution and global warming brought about by excessive

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petroleum emissions are eliminated (Brännström *et al.* 2018). This sustainable, clean-burning liquid fuel called biodiesel can be produced by transesterifying biomass sources including used cooking oil, animal fat, and vegetable oil (Issariyakul and Dalai 2014). The cost of production and the high cost of the raw materials used for making biodiesel are the major challenges to its commercialization and market viability. As a result, the authors of this work have proceeded to contribute to this knowledge gap using local resources and technology that are appropriate for this study (Nwoko *et al.* 2019). For that reason, biodiesel made from ordinary foods is more expensive than gasoline and diesel, it is therefore crucial to concentrate on sourcing affordable and easily accessible feedstocks, alcohols, and catalysts to address this issue. A promising option for the production of affordable biodiesel is waste cooking oil (WCO) of which Topi (2020) advocated for a legislative ban on WCO disposal. The use of waste cooking oil in the production of biodiesel is advantageous in reducing environmental pollution and the cost of biodiesel treatment of used cooking oil (Yadav 2022; Asikin-Mijan *et al.* 2022).

Currently, researchers have continued to proffer solutions to alternative sources of energy (De Paola, Mazza, *et al.* 2021; Yogin Soodesh, Seriyala, *et al.* 2024) In a recent study, biodiesel yield of 94% was achieved by transesterification of vegetable oil which employed a nano-sized CaO catalyst at 60 °C for 120 min while maintaining a 1:12 oil to methanol molar ratio (Erchamo *et al.* 2021). Another study revealed that an alkaline catalyst was used to complete the transesterification reaction after lowering the free fatty acid (FFA) content of the vegetable oil to less than 1%. Owing to the low FFA concentration of the vegetable oil, the process was transesterified, using methanol as the alcohol and potassium hydroxide as a catalyst (Alptekin *et al.* 2014). Also using the biocatalytic model, the immobilised lipase was washed with tert-butanol over the course of 10 successive processes lasting 10 hours each at 30°C, and its activity dropped from 91.3% to 77.5%. When not rinsed with tert-butanol, immobilised lipase's activity dropped sharply from 91.3% to 61.9% (Ondul *et al.* 2015). Additionally, Zanthoxylum bungeanum seed oil (ZSO) with high free fatty acids (FFA) was used for biodiesel production by transesterification which employed calcium oxide (CaO) as an alkaline catalyst and ferric sulfate-catalyzed esterification. The ideal ratio of methanol to oil was 11.69:1, the catalyst amount was 2.52%, and the reaction duration was 2.45 hours. The conversion rate to biodiesel exceeded 96% under these ideal circumstances (Zhang *et al.* 2010). A base-catalyzed transesterification process that employs KOH or NaOH as the homogeneous catalyst and CH$_3$OH as the lower alcohol is a widely used method for the commercial production of biofuel from vegetable oils and fats (Kianimanesh, Abbaspour-Aghdam, *et al.* 2017; Mandari en Devarai 2022) The benefit of this method is the generation of methyl esters in very excellent yields under benign conditions where the reaction duration is about an hour (Najaf-Abadi, Ghobadian, *et al.* 2024). Many oils including palm oil, sunflower oil, and jatropha (Endalew *et al.* 2011; Nwoko *et* *al.* 2019; Mercuri *et al.* 2016) have undergone transesterification to produce biodiesel, Unfortunately, significant quality-related issues were identified which have been the challenges to commercial homogeneous catalyzed transesterification processes. For instance, the high costs of production were due to numerous washing and purification steps to achieve the required level of purity (Atadashi *et al.* 2013). The remaining K and Na traces in the product are also removed with great difficulty, and separating the glycerin poised additional technical difficulties. The overall cost of the process increased due to the greater volume of water used in washing and the subsequent treatment of the generated effluent (Adebisi *et al.* 2019; Ondul *et al.* 2015). Interestingly, the solubility of FFAs in water is very low ($\sim$1 μM), making it impracticable for simple aqueous diffusion to support metabolic processes. Likewise high levels of FFA in membranes potentially emulsifies the membrane into micelles (Stillwell 2016). On the other hand only a couple of studies dealing with solid acid catalysts for the biodiesel production have been recently published (Xie *et al.* 2024; Fiala, Thongjarad *et al.* 2024; Hasannia *et al.* 2024). Thus, research has been directed towards sustainable feedstocks that produces clean biodiesel while NaOH and H$_2$SO$_4$ were employed as catalysts to accelerate the reaction and compensate for the low reactivity of carboxylic acids, resulting in a wide range of ester compounds that were produced (Khan *et al.* 2021). Therefore, this study investigated the conversion of waste vegetable oil into biodiesel by a combined acid-base catalysis approach, its characterization, evaluation of experimental parameters for optimal yields, and optimal production of biodiesel using a programmed catalysis regime.

2. Materials and methods

The samples collected were *turkey vegetable oil*, *palm kernel oil from Old Market* located in Douglas Road, Owerri and *waste vegetable oil* taken from Mr. Biggs Fast Foods, Okigwe Road, Owerri, Imo State, Nigeria. The following instruments were used such as Stuart magnetic Stirrer (ST-200-MP model), hot plate (UC152D model), pensky-martens closed cup tester (Flash Point Koehler K16000 model), redwood apparatus (Viscosity EIE -PTLT-148E1 model), 150 – I717 normal flow viscometer (Metler PN-163) and citizen weighing balance (CX 165 model), hydrometers (HB-Durac B61891; range 0.850–0.900 and 0.900–0.950). The following characterization tests were carried out on the different oils: viscosity, % free fatty acids, iodine number, saponification number and peroxide value. Figure 1 describes the mechanism of the reaction while the study findings are shown in Tables 1–6 and Figures 1–4.

2.1. Purification (Drying) of Methanol

200 cm^3 of methanol was measured into a 500 cm^3 round bottom flask and heated under a distillation set-up, through an efficient fractionating column. Anhydrous methanol was then obtained from the methanol distillate by standing over a type 3A molecular sieve. The pure methanol had a boiling point of 65°C/ at 760 mmHg and a 95% recovery. The average of triplicate results was reported.
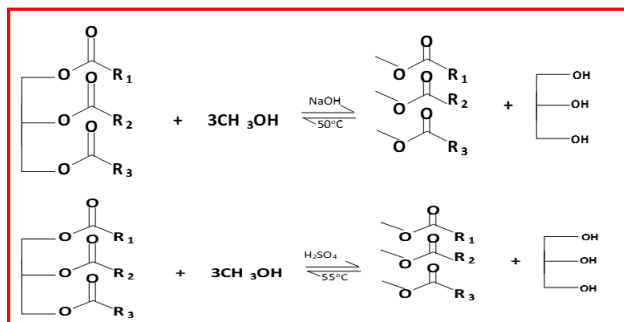
Figure 1. Mechanism of transesterification of oil by NaOH and H_2SO_4

2.2. Base-Catalyzed Transesterification

A measured 75 cm^3 volume of dry methanol was transferred into a 250 cm^3 conical flask, and 1.25 g of NaOH was dissolved in the alcohol. The mixture in the flask was stirred until the NaOH was completely dissolved in the methanol. Then 250 cm^3 of turkey vegetable oil was measured into a 500 cm^3 round-bottomed flask and heated to about 50°C. The mixture in the conical flask was then poured into the preheated oil and the reaction mixture was heated (45 ± 5°C) under reflux in a water bath with stirring for 1 hr. The resulting mixture was then left to stand for 24 hr, and two distinct layers separated by gravity were formed. The lower layer containing the glycerol and impurities was decanted, while the upper layer containing the ester was washed with 25 cm^3 distilled water and 10% vol of oil. The lower aqueous layer was discarded and yellow-coloured upper organic layer liquid was obtained. The resulting liquid was measured and found to be 210 cm^3, representing a yield of 84%. The procedure was repeated by varying concentrations or amounts of catalyst at 1.15 g (0.46%), 1.35 g (0.54%), and 1.45 g (0.58%) and the reaction time of each reaction was extended to 2–3 hr respectively. This experiment was repeated using palm kernel oil (PKO). The resulting liquid was measured and found to be 200 cm^3, representing a yield of 80% and the results were recorded.

2.3. Biodiesel Production Using Sodium Hydroxide Catalyst

About 75 cm^3 of dry methanol was weighed into a 250 cm^3 conical flask, and 1.25 g of sodium hydroxide was dissolved in it. The mixture was stirred till the sodium hydroxide was completely dissolved in the methanol. 250 cm^3 of used oil weighed into a 500 cm^3 round-bottomed flask was heated to about 50°C and treated with the methoxide ion solution previously prepared. The reaction was heated under reflux in the water bath with stirring for 1 hr. The temperature was maintained at 45 ± 5°C and the resulting mixture turned into a semisolid gel.

2.4. Biodiesel Production Using Sulphuric Acid Catalyst

About 250 cm^3 of waste vegetable oil (WVO) was measured into a 500 cm^3 round-bottomed flask and then heated to about 55°C. Then 75 cm^3 of dry methanol was measured and added to the preheated oil and stirred for 10 min. Afterwards, 1.25 cm^3 of H_2SO_4 was added to the mixture. The reaction mixture was heated at 55°C under reflux in a water bath with stirring for 1 hr. The resulting mixture was allowed to stand for 24 hr, during which time two distinct layers were formed and separated by gravity. The lower layer containing the glycerol and impurities was decanted, while the upper layer containing the ester was washed with 25 cm^3 of hot distilled water. The lower aqueous layer was discarded and the yellow-coloured upper organic layer liquid was stored. The resulting liquid was measured and found to be 140 cm^3, representing 56% yield. This experiment was repeated at a reaction time of 2 hr and by varying amounts of catalyst used 1.15 cm^3, 1.35 cm^3 and 1.45 cm^3 and results were recorded.

2.5. Production of Biodiesel from Acid and Base Catalysis

A 250 cm^3 of waste vegetable oil (WVO) was measured into a 500 cm^3 round-bottomed flask and heated to about 55°C. About 75 cm^3 of dry methanol was measured and added to the preheated oil and stirred for 10 min. Then 1.25 cm^3 of H_2SO_4 was added to the mixture and the reaction mixture was heated at 55°C under reflux in the water bath with stirring for 1 hr. The resulting mixture was poured into a 500 cm^3 round-bottomed flask and preheated to about 50°C. Afterwards, 1.25g of NaOH dissolved in 75 cm^3 dry methanol was poured into the reaction mixture and heated under reflux in the water bath with stirring for 1 hr. The temperature was maintained at 45 ± 5°C and the resulting mixture was allowed to stand for 24 hr giving two distinct layers separated by gravity. The lower layer was separated and the upper layer was washed with 25 cm^3 of hot distilled water (10% vol. of oil). The lower aqueous layer was discarded and the upper organic layer liquid was obtained and measured to be 180 cm^3, representing a yield of 72%. The experiment was repeated at a reaction time of 2 hr by varying amounts of catalyst used 1.15, 1.35 1.45. cm^3 and results were noted.

2.6. Biodiesel Characterization Using American (ASTM D6571) Fuel Standards.

A normal flow 150, I717 viscometer was cleaned by rinsing with benzene and acetone and passed through a current of clean, dry air to remove traces of solvents. Only 10 ml of the biodiesel sample was introduced into the viscometer. The water bath was heated to 40°C and the thermostat was adjusted to maintain that temperature. The clamped viscometer was placed in the water bath at 40°C and allowed 10 min for the temperature of the sample to equilibrate with the temperature of the bath. A gentle suction was applied to the mouth of the viscometer tube using a vacuum pump to bring the sample level above the two marks on the viscometer. As the sample level reached the first mark on the viscometer, the timer was started and stopped as the sample level got to the second mark. The timer reading obtained was multiplied by the viscometer constant to give the viscosity of the sample. This experiment was repeated for the various samples of the biodiesel produced.

In another test, the biodiesel sample (100 cm^3) was poured into a 500 cm^3 cylindrical flask. A hydrometer of the range 0.850 - 0.900 was introduced and left for some time to float. The reading at the top meniscus of the sample level was read off from the hydrometer at a specific. temperature. This

experiment was repeated for all the samples of the biodiesel produced and readings were recorded.

Also, 70 ml of biodiesel was added to the top mark of the closed cup tester. The test cover and other parts of the apparatus were mounted so that the locking device was properly closed. The thermometer was inserted into its holder the test flame lit and the heating apparatus switched on. The ignition source was rotated over the tester cup containing the sample until there was a brief flash. The observed flash point was recorded from the thermometer and the procedure was repeated for all samples.

About 100 cm^3 of the sample was weighed into a 250 cm^3 round-bottomed flask and distilled using a distillation unit. Recovery was monitored at 10% intervals and the different temperatures were recorded (D$_{86}$). The Specific gravity of the sample was recorded. The results were then compared to 50%, 90%, and 10% recovery using standard graph extrapolations and the specific gravity. The extrapolation results were added up to get the calculated cetane index, which gives the cetane number of the biodiesel sample. This procedure was repeated for all biodiesel samples and the results were recorded.

3. Results and discussion

The transesterification process requires anhydrous conditions of the raw materials used. The pure methanol was left over a type 3A molecular sieve, hence dry

methanol was obtained and determined oil properties shown in Table 1.

From the results, it was seen that the percentage of fatty acid in waste vegetable oil was the highest (8.97) due to the degradation of the oil by heat after prolonged use. Also, for iodine value, the samples were observed to decrease, 57.80, 55.40 and 47.20, from the vegetable oil > palm kernel oil (PKO) > waste oil, respectively. The Lower reading of iodine value for waste vegetable oil is attributed to the presence of higher levels of peroxides in the sample than in other oil samples. The saponification and peroxide values were observed to increase progressively from vegetable oil to palm kernel oil and highest with waste vegetable oil. High amounts of peroxide in (WVO) showed that the oil had been degraded by free radicals and would produce aldehydes and ketones (Zhang *et al.* 2021), which makes the oil smell musty and rancid. Moreover heat, light, and air from the reacting circumstances speed up these reactions. Likewise, WVO has the shortest fatty acid chain and lowest molecular weight (Ivanova *et al.* 2022). Furthermore, the viscosities of the different oil samples varied differently and WVO has a lower viscosity than PKO and vegetable oil, which allowed more free flow at low temperatures. Tables 2–4 and 6 presented in this study showed the different amounts of catalysts used and the corresponding experimental yield and equivalent % yield obtained from the study at 1–3 hr duration.

Table 1. Properties of different oil sources

Properties	Vegetable oil	Palm kernel oil (PKO)	Waste Vegetable oil (WVO)
% Free Fatty Acid	1.11	1.21	8.97
Iodine Value (mg I2/g)	57.80	55.40	47.20
Saponification Value (mg/g)	192.40	201.50	211.6
Peroxide (Meq/kg)	1.48	1.81	9.80
Viscosity (mm^2/s)	30.60	29.10	1.40

Table 2. Biodiesel yield from 250 cm^3 of vegetable oil via base-catalyzed transesterification

Catalyst (%)	Amt of NaOH (g)	Experimental yield obtained (cm^3)			Percentage yield (%).		
		1 hr	2 hr	3 hr	1 hr	2 hr	3 hr
0.46	1.15	210.00	215.00	217.00	84.00	86.00	86.80
0.50	1.25	225.50	227.50	230.00	89.00	91.00	92.00
0.54	1.35	215.00	217.00	219.00	86.00	87.00	87.60
0.58	1.45	210.00	212.50	214.00	84.00	85.00	85.80

Table 3. Biodiesel yield from 250 cm^3 of waste vegetable oil via acid-catalyzed transesterification

Catalyst (%)	Vol of H$_2$SO$_4$ (cm^3)	Experimental yield obtained (cm^3)		Percentage yield (%).	
		1hr	2hr	1hr	2hr
0.46	1.15	140.00	145.00	56.00	58.00
0.50	1.25	150.00	157.50	60.00	63.00
0.54	1.35	145.00	150.00	58.00	60.00
0.58	1.45	142.00	147.50	57.00	59.00

Table 4. Biodiesel yield from 250 cm^3 of palm kernel oil via base-catalyzed transesterification

Catalyst (%)	Amt of NaOH (g)	Experimental yield obtained (cm^3)			Percentage yield (%).		
		1hr	2hr	3hr	1hr	2hr	3hr
0.46	1.,15	200.00	207.50	210.00	80.00	83.00	84.00
0.50	1.25	210.00	219.00	221.75	84.00	87.60	88.70
0.54	1.35	205.00	210.00	212.50	82.00	84.00	85.00
0.58	1.45	202.50	207.50	209.50	81.00	83.00	83.80

The results of the transesterification reaction are shown in **Table 2–4**. The amount of catalyst, sodium hydroxide used

varied in the range of 0.46 to 0.58% (weight of NaOH/weight of oil) and vol of H$_2$SO$_4$ (1.15–1.45 cm^3). The

contact time of reaction was varied for 1–3 hr based on the nature of the sample. The effects of these experimental factors on biodiesel yields are shown in **Figure 2(a-d).** According to Tables 2–4, the results obtained using palm kernel oil are similar to the results from vegetable oil, but with slightly lower yields. This was attributed to the slightly higher percentage of free fatty acid in palm kernel oil than that of vegetable oil (Brännström *et al.* 2018). Furthermore, the result obtained from palm kernel oil and vegetable oil as plotted in is shown in **Figure 2(c-d)** showed the effects of the amount of catalyst and contact time on the yields of biodiesel produced from both feedstocks.
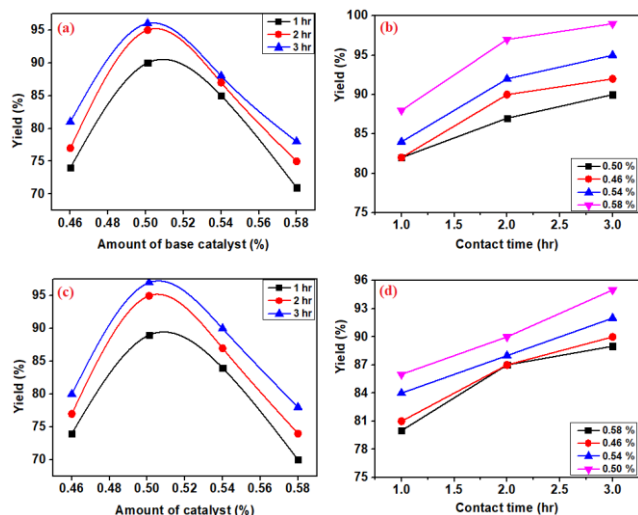

Figure 2. Effect of different parameters on the feedstocks (a) effect of base catalysis on vegetable oil yield (b) effect of contact time on vegetable oil yield (c) effect of base catalysis on palm kernel oil yield (d) effect of contact time on palm kernel yield

Although the reaction conditions using waste vegetable oil are the same as those of fresh vegetable oil, the differences were due to the different courses of their reactions. As the waste vegetable oil and methoxide ion formed from methanol, the sodium hydroxide mixture was stirred and

heated till the reaction mixture began to foam. Hence, the desired products were subjected to different mechanisms that affected the mass, volume and kinematic viscosity now attributed to the consumption of NaOH catalyst by the high percentage of free fatty acid of the used oil. Thus the findings of this investigation revealed that the total polar matter content of waste cooking oil has a significant impact on the kinematic viscosity of the biodiesel (Adhikesavan *et al.* 2022).

From the graphs, it was observed that the optimum yield of biodiesel was ≥ 88% achieved at 0.50% of NaOH, while the increase in the contact time increased the biodiesel yield (3 hr) for both palm kernel oil and vegetable oil as previously observed (Ali and Tay 2013; Amenaghawon *et al.* 2021). The results of the characterization of biodiesel produced from vegetable oil, are shown in **Table 5** which confirmed the fuel properties of the different oil sources. Their properties were within the standard biodiesel specifications. Standard diesel fuels have cetane numbers 40 - 70 corresponding to their ignition values, viscosity between 1.9 - 6.1 mm^2/s, a flash point above 100°C and specific gravity of 0.87 - 0.90. These properties project the biodiesel produced as a good diesel substitute

Results of the characterization of biodiesel produced as shown in **Table 5** were close approximations to the standard values of the fuel properties. The fuel qualities of acquired biodiesel generated by NaOH and H_2SO_4 synthesized from vegetable oil, waste vegetable oil and palm kernel at optimum process conditions were determined using the American Society for Testing and Material method (ASTM). The data showed that biodiesel produced using all procedures displayed high-quality fuel characteristics that were within the parameters of the biodiesel standard and were also in line with earlier results (Sajjadi *et al.* 2016; Adhikesavan *et al.* 2022; Veza *et al.* 2022).

Table 5. Characterization results on properties of biodiesel

Property	Testing procedure	Palm kernel oil methyl ester	Pure vegetable oil methyl ester	Waste vegetable oil methyl ester	Pet. diesel
Specific Gravity	ASTM D4052	0.8772	0.8718	0.8935	0.8150
Viscosity @ 40°C (mm^2/s)	ASTM D445	4.29	6.04	6.09	2.98
Flash Point (°C)	ASTM D93	122	137	117	55
Cetane Index	ASTM D4737	41	43	40	47

Table 6. Biodiesel Yield from 250 cm^3 of waste vegetable oil by acid-catalyzed transesterification

Catalyst (%)	Vol of H_2SO_4 (cm^3)	Experimental yield obtained (cm^3)		Percentage yield (%)	
		1hr	2hr	1hr	2hr
0.46	1.15	140.00	145.00	56.00	58.00
0.50	1.25	150.00	157.50	60.00	63.00
0.54	1.35	145.00	150.00	58.00	60.00
0.58	1.45	142.00	147.50	57.00	59.00

The results of the reaction obtained from waste vegetable oil by acid-catalyzed transesterification are shown in **Table 6**. From the data above, the optimum production yield was obtained at 0.50% (1.25 cm^3) of the H_2SO_4 catalyst. While

an increase in contact time increased biodiesel yield as shown in **Figure 3(a-b)**.
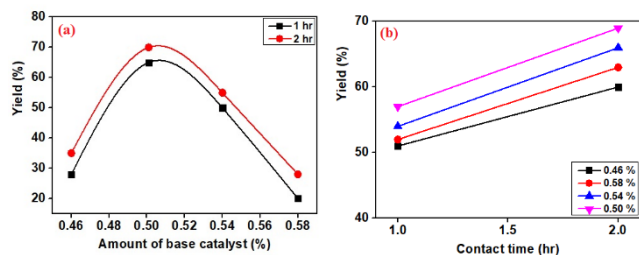
Figure 3. Effect of parameters on waste vegetable oil (a) effect of amount of acid catalyst on waste vegetable oil yield (b) effect of contact time on waste vegetable oil yield

The calculated reaction rate constants, k, for the base-catalyzed reaction, are higher than that for the acid-catalyzed reaction. Hence acid-catalyzed reaction is slower and the yields are lower than that of the base-catalyzed reaction, as observed from the results. According to the findings, both the esterification of H_2SO_4 and NaOH reactions are first-order rate reactions, with reaction rate constants of 0.00261 min^{-1} and 0.00548 min^{-1}, respectively, confirming that the former is the slower among the two processes as had been similarly observed in previous studies (Ding *et al.* 2012; Jain *et al.* 2011)

In the mechanism of base-catalyzed transesterification, the methoxide ion formed attacked the carbonyl carbon, but for acid catalysis, the lone pairs of oxygen of the carbonyl group of the oil captured the hydrogen ion of the acid. The resulting tetrahedral intermediate (tetrahedral carbon) on rearrangement becomes very electrophilic because of the positive charge on it. Likewise, the lone pairs of oxygen of the methanol attack the intermediate resulting in the formation of fatty acid ester and diglycerides. This stepwise conversion gave three moles of ester and glycerol. For waste vegetable oil containing free fatty acids, the commercially used base catalysis was not successful. The consumption of the base by the free fatty acids in waste oil indicated that the saponification reaction occurred faster than the desired transesterification reaction (Jain *et al.* 2011; Zhang *et al.* 2010; Keera *et al.* 2011).

Owing to the lower yield observed in acid-catalyzed transesterification, sequential catalysis involving an acid (H_2SO_4) and then a base (NaOH) was used on the waste vegetable oil to improve the yield of the product. The reaction conditions were the same as the other reactions carried out. Acid catalysis was first performed and then the resulting mixture of ester and glycerol was subjected to base catalysis. The results of the reactions are shown in **Table 7** It was observed that biodiesel yields were higher than that of acid catalysis. The effects of the amount of catalyst and the contact time on yield are shown in **Figure 4(a-b)**.

Generally, the percentage yields of biodiesel from vegetable oil were higher than those from PKO and waste vegetable oil. This can be explained by the findings from the analyses of the oils. The % fatty acids and saponification values for waste vegetable oil were higher than those of the PKO and the vegetable oil, hence affecting their yields. After being used for frying, the saponification values of waste vegetable oils varied from 192.4 for vegetable oil to 201.5 for palm kernel oil
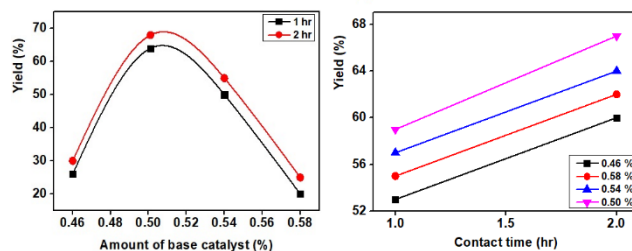

Figure 4. Effect of parameters on waste vegetable oil, (a) amount of catalyst on sequential acid/base catalysis on waste vegetable oil (b) effect of contact time on sequential catalysis on waste vegetable oil

Table 7. Biodiesel yield from 250 cm^3 of waste vegetable oil on sequential acid/ base catalyzed

Catalyst (%)	Amt. Of Catalyst	Experimental yield obtained (cm^3)		Percentage yield (%).	
		1hr	**2hr**	**1hr**	**2hr**
0.46	1.15	180.00	185.00	72.00	74.00
0.50	1.25	192.50	205.00	77.00	82.00
0.54	1.35	185.00	190.00	74.00	76.50
0.58	1.45	182.50	187.50	73.00	75.00

The higher saponification numbers, on the other hand, can indicate that the mean fatty acid molecular weight is larger or that there are more ester linkages. This may suggest that the fat molecules interacted with one another (Gbadamosi *et al.* 2020). Likewise, It is also recommended to use an emerging technique that is quick and convenient for calculating the saponification value from spectroscopic data, not based on regression equations, and calibration from a database. Some methods, like the use of NMR spectroscopy, are directly and independently computed from the product and can be used for further studies (Ivanova *et al.* 2022). In addition, the results of the characterization of biodiesel produced from the study showed that its characteristics are similar to the characteristics of standard diesel. All the fuel properties were within specifications. However, an improved result of the cetane number can be obtained by using a test engine to determine the cetane number rather than the calculated cetane index. Finally, the findings from this work were compared to similar studies that utilized NaOH and H_2SO_4 and the yield % was all significantly higher than 75%. (Chinglenthoiba *et al.* 2020; Abd-Rabu *et al.* 2013; Suzihaque *et al.* 2022 Sahar *et al.* 2018) Furthermore, it was similarly concluded that H_2SO_4 can give higher yield and purity as it steers transesterification reactions towards more fatty acid methyl ester, while the necessary conversion rate using an alkali-catalyzed transesterification must be between 0.5% and 3% FFA concentration in the raw materials

4.   Conclusion

Biodiesel was produced from waste vegetable oil by acid-catalyzed transesterification and with sequential base catalysis at optimal conditions, hence improving its yields. The iodine value of the samples decreases from 57.80 > 55.40 > 47.20, for vegetable oil, palm kernel oil (PKO) and waste oil, respectively. While the viscosities varied differently with WVO having the lowest viscosity.

Esterification results of palm kernel oil were similar to the results from vegetable oil, but of lower yields and the total polar matter content of WVO had a substantial impact on the kinematic viscosity of the biodiesel. Furthermore, the optimum yield of biodiesel was ≥ 88% achieved at 0.50% of NaOH, while the increase in the contact time improved the biodiesel yield at 3 hr for both palm kernel oil and vegetable oil. Also, the esterification of H_2SO_4 and NaOH reactions are 1st-order rate reactions, with reaction rate constants of 0.00261 min^{-1} and 0.00548 min^{-1}, respectively. The saponification values obtained for WVO were 192.4 lower than 201.5 for palm kernel oil. The cetane number of our products was between 40–43 while the flash points were 117 to 137. The data showed that biodiesel produced using all procedures displayed high-quality fuel characteristics that were within the parameters of the biodiesel standard. To this end, the study identified optimal conditions for the biodiesel production process. It is therefore recommended that a more comprehensive optimization study, possibly employing a design of experiments approach to systematically explore the interaction effects between variables be carried out.

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