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Production of Biodiesel from a Novel Combination of *Raphia Africana* Kernel Oil and Turtle Shell (*Centrochelys Sulcata*) Heterogenous Catalyst

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Abstract

This work investigated the viability of a non-edible oil obtained from *raphia africana* in the production of biodiesel using a novel heterogeneous catalyst derived from turtle shells (*Centrochelys sulcata*). The study also proposed the use of acetone as a co-solvent to enhance the solubility of the reacting mixtures. The turtle shells were calcined at 900°C for 3 hours, impregnated with KOH to improve their activity, and then supported with activated carbon produced from cassava peels to increase their surface area. The influences of KOH concentration, catalyst loading, catalyst/carbon mix ratio, and the concentration of acetone/methanol on the yield of biodiesel were investigated. The results obtained revealed that a maximum biodiesel yield of 93% was obtained from the bio-oil at a KOH concentration of 30% (w/w), catalyst loading of 6.5%, a solvent/methanol ratio of 0.4 and a catalyst/carbon weight ratio of 1.25. The activated carbon supported turtle shell catalyst has been found to possess very high catalytic activity, converting bio-oil with a high saturated fatty acid content to biodiesel with excellent fuel properties and a low saturated fatty acid profile.

Keywords: Biodiesel; Turtle Shells; *Raphia Africana*; Calcination; Catalyst, Fatty Acid.

1. Introduction

The emission of greenhouse gases from the burning of fossil fuels and their steady depletion coupled with increased industrialization and global population growth is a serious problem that requires immediate attention [1-3]. Other concomitant pollution problems associated with fossil fuels' exploration, processing, and distribution make their substitution inevitable [4]. This has made the consideration of different eco-friendly and renewable sources of energy, such as wind, solar, geothermal, wave, and biofuels, imperative [5-7]. Studies have shown that green or biofuel holds great potential as an alternative to liquid fossil fuel [8, 9]. Two major bio-based fuels that can potentially replace petroleum-based fuels are bio-ethanol and biodiesel [10–12]. Biodiesel is a good alternative to petroleum-based diesel fuel because of its distinct advantages. Some of these advantages are that it is not hazardous, it has a high flash point, it burns cleanly without soot, and it is safe because of its low flammability index and high lubricity [13]. Despite its

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low flammability index, biodiesel can effectively be used in internal combustion engines without any engine modification by blending it with a small quantity of petrol, diesel, and or ethanol to improve the flammability index [14–17]. Such a diesel blend is eco-friendly and exhibits better fuel properties such as high cetane number, high flash point, and high oxygen with low carbon dioxide emission [14, 18–21]. For example, Selaimia et al. [22] noted that the cetane number and other fuel parameters of biodiesel produced from waste cooking oil blended with a little petrol diesel show a great improvement over that of petrol diesel.

Biodiesel is obtained from some renewable biological materials like vegetable oils, animal fats, and microbial (e.g. microalgae) oils, mainly by reaction with short-chain alcohols in a process known as transesterification [23, 24]. Generally, transesterification reactions are carried out using acidic or basic homogeneous catalysts, which makes the reaction very slow, hence the low product yield. Biodiesel yield is also a function of the free fatty acid (FFA) content of the oil used. Due to their high FFA, edible vegetable oils, animal fats, palm oil, and palm kernel oil (PKO) have been found to give a high yield of biodiesel when transesterified using basic catalysts [15, 22, 23, 25, 26]. However, as a result of its serious threat to food security, the utilization of edible oils for biodiesel synthesis is not encouraged [27, 28].

The choice of catalysts in the transesterification reaction is of utmost importance as it determines the reaction rate as well as the yield of biodiesel. The biodiesel yield depends greatly on the FFA of the oil used. The alkali-based homogeneous catalysts most favoured for the transesterification reaction result in an undesired saponification reaction if the FFA content of the oil used is greater than 1% w/w and this is difficult to separate from the reaction products, leading to a low yield of biodiesel [24, 29]. Acid-based catalysts have been seen as alternative alkali-based catalysts since they do not form soap or other by-products. However, the reactions are extremely slow and corrode the reactors [30]. To mitigate the combined shortcomings of both the alkali-based and acid-base homogeneous catalysts, a heterogeneous catalyst has been proposed and research work has been going on to authenticate its seeming advantages. Since heterogeneous catalysts are solid catalysts, they do not react with the FFA of the oil used in the reaction, thereby improving the catalytic properties for both esterification and transesterification reactions [29, 31, 32]. Other distinct advantages of heterogeneous over the homogeneous catalyst are its ease of recoverability and regeneration after use as well as its ability to increase its activities over a wide range of feedstock during esterification and transesterification reactions due its turning ability to create acidic-basicity characteristics because of its porosity and surface area that does not require pre-treatment for FFA reduction [33, 34].

Various studies have shown that homogeneous catalysts developed from different materials like egg shells, crab shells, mollusk shells, and animal bones give a good yield of biodiesel [35-37]. Another excellent precursor of heterogeneous catalysts is calcium oxide, derived from marine shells and animal bones during heat activation [31]. However, this thermal activation process is expensive due to the high temperature required to attain the activation level. Earth metals have also proved to be an effective heterogeneous catalyst for biodiesel production from oil seed. For example, De Sousa et al. [38] carried out a study on the application of calcium oxide (CaO) obtained from calcined eggshells as a catalyst and obtained a 96% conversion of soybean oil to biodiesel at a moderate temperature. On the other hand, Putra [39] reported a 71% conversion of used cooking oil to biodiesel using pure CaO and a 91% conversion with CaO doped with silicon dioxide (SiO₂). Other workers also recorded excellent results using non-conventional heterogeneous catalysts. Sulaiman & Amin [40] studied the kinetics of waste cooking oil in the production of biodiesel using fish bones and obtained a significant biodiesel yield. Ali et al. [41] obtained an 84% biodiesel yield from the transesterification of waste cooking oil using calcined goat bones as catalysts. One major problem associated with the use of heterogeneous catalysts is their low surface area, but this can usually be increased by supporting them with compounds such as activated carbon or nanotubes or impregnating them with base solution [31, 32, 42, 43] However, activated carbon is preferred as a heterogeneous catalyst supporter because of its large surface area and its ease of separation from the product [42, 44]. Hadiyanto et al., [32] obtained a 95% biodiesel yield using a heterogeneous synthesized from green mussel shells calcined at 900°C for 3 hours, supported with activated carbon and impregnated in concentrated sodium hydroxide. Buasri et al. [42] obtained a 98% yield using calcium oxide calcined at 500°C for 5hrs supported with activated carbon and impregnated in potassium hydroxide. Zhang & Meng [44] obtained a 95% biodiesel yield using an activated carbon-supported heterogeneous catalyst derived from waste scallop shells calcined at 1000°C for 3 hours and impregnated in potassium hydroxide.

In the present study biodiesel is produced from raffia oil; a non-edible and poisonous oil with no known economic value using turtle shell; a non-convectional heterogeneous catalyst impregnated with potassium hydroxide (KOH). The combined use of raphia oil and impregnated turtle shell are novel initiative since to the best of our knowledge, no known study on this had been reported anywhere.

2. Materials and Method

2.1. Materials

The *Raphia africana* oil used in this work was extracted from raffia palm fruits obtained from Angalabiri community of Bayelsa State in the Niger Delta Area of Nigeria. Methanol, hexane, acetone and potassium hydroxide were obtained in analytical grade from Pyrex chemical stores in Benin City, Nigeria while the turtle shells were locally

sourced from fish farmers in Angalabiri and adjoining fishing communities. Activated carbon used as catalyst support was prepared locally from cassava peels.

2.2. Experimental Procedure

2.2.1. Preparation and Characterization of Heterogeneous Catalyst from Turtle Shells

The obtained turtle shells were washed in warm water several times in order to remove dirt and oily materials and dried for 3hrs in a dryer (DGH-9053) at 120°C to remove moisture. The shells were then subjected to heat activation at 900°C for 3hr. The choice of 900°C calcinations temperature was based on the fact that all carbon dioxide desorption on the turtle shell may have been completely eliminated at this temperature creating active sites for calcium oxide (CaO) which favours transesterification reaction [45, 46]. After the calcination step, the calcined sample was properly crushed using a mortar pestle and sieved to 80 mesh size. In order to study the influence of activated carbon support on the catalyst surface area, the catalyst was mixed with activated carbon prepared from cassava peels following the method of Oghenejoboh et al. (2016) [50]. The catalyst was then mixed with varying ratios of the prepared activated carbon on w/w basis before impregnating it with 15, 20, 25, 30, 35 and 40% (w/w) solutions of potassium hydroxide for 12hrs to improve the catalyst activity [32, 41]. The prepared catalysts were filtered using a filter paper, dried in an oven at 110°C for 4hrs and stored in a container containing silica gel to prevent it from absorbing atmospheric moisture from the surrounding. The catalyst was then subjected to FTIR analysis in order to study its morphology at the calcined conditions. The Buck scientific M530 USA FTIR equipped with a detector and beam splitter was used for the analysis. The spectra were obtained using the Gram A1 software. During measurement, FTIR spectrum was obtained at frequency regions of 4,000 – 600 cm⁻¹ with resolution of 4 cm⁻¹ from the accumulation of 32 scans.

2.2.2. Extraction and Characterisation of Raphia Seed Oil

Raphia seeds were detached from raphia palm bunches collected from the swampy area of Angalabiri in Bayelsa State of Nigeria. The seeds were dried for two weeks before cracking them open to obtain the oil-bearing kernels. The kernels were thoroughly washed and subjected to size reduction by crushing using a mortar and pestle. The solvent extraction method using a soxhlet and analytical grade hexane as solvent was then used to extract the oil from the crushed kernels. The Buck M910 Scientific gas chromatography coupled to FID with detector (USA) having column dimensions 100m × 0.25 mm ID × 0.20 µm film thickness was used to determine the constituents of the produced bio-oil and the resultant biodiesel. The experimental conditions were as follows: inlet temperature of column was 60°C for 1min, then at a gradient of 15°C/min up to 165°C for 20 min, a gradient of 2 °C/min up to 225°C. The injector volume was 1µL while the injector/detector temperature was 250°C. Carrier gas was helium and its flowrate was 0.8mL/min. The sample's contents were identified by comparing their retention time against standards.

2.2.3. Transesterification Experiment

The transesterification reactions were performed in a 250ml conical flask with pre-determined small volume of acetone added as co-solvent. The choice of acetone over other co-solvents such as diethyl ether (DEE) and dichlorobenzene (CBN) as co-solvent systems was based on its distinct advantages as reported by Alhassan et al. [47]. Based on oil weight, a predetermined mass of catalyst was measured and added into a conical flask containing a predetermined mass of methanol and stirred at 60°C for 30min. This was to allow proper dispersion of the catalyst before adding the oil. A predetermined mass of oil preheated to 60°C was measured and poured into the catalyst/methanol mixture and this was quickly followed by adding the acetone co-solvent (in basis of the methanol volume). It has been widely reported that increasing the reaction temperature, increasing stirring speed and increasing methanol/oil ratio increase biodiesel yield, however, variation of these three variables were not considered in this study. In all the experiments, reaction temperature of 65°C, stirring speed of 300rpm [40], methanol/oil ratio of 1:2 (w/w) and reaction time of 3hr [32] were used except in the reactions to investigate influence of the co-solvent where time was 30 minutes. The influences of four major variables- Catalyst/carbon ratio (w/w), catalyst weight per weight of oil, concentration of potassium hydroxide and co-solvent/methanol ratio (v/v) were considered in this research. Catalyst/carbon ratio was varied between 0.5 and 1.75 (w/w); catalyst concentration 2-10 wt%, KOH concentration of 15-40% (w/w) and co-solvent/oil ratio of 0-0.8 (v/v). At the end of a reaction, the reaction mixture was poured into a separating funnel through a filter paper in order to separate the catalyst. After 6 hours, the methyl ester phase was carefully separated, washed with warm distilled water at 45°C in order to remove impurities (excess glycerol and methanol), dried for 24hr at room temperature. The percentage volume yield of the biodiesel was calculated according to Equation 1.

$$\%Biodiesel\ yield = \frac{vol\ of\ FAME\ produced - vol\ of\ acetone\ cosolvent}{vol\ of\ oil\ used} \times 100 \quad (1)$$

3. Results and Discussion

3.1. Catalyst Characterization

The prepared turtle shell catalyst was characterized using the FTIR analysis to determine its morphology. Figure 1 show the spectra of turtle shell catalyst calcined at a temperature of 900°C for a period of 3hr.

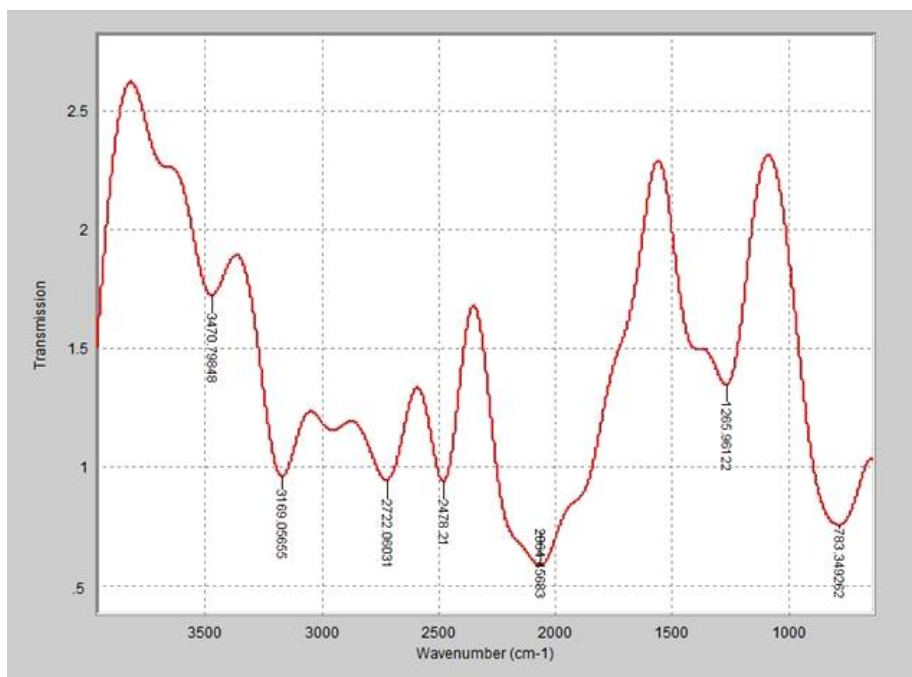


Figure 1. FTIR spectrum of the shell calcined at 900°C for 3hr

As shown in Figure 1, the FTIR spectrum of the turtle shell calcined at 900°C for 3 hours produces sharp bands at 3470, 3169, 2722, 2478, 2064, 1265 and 783 cm⁻¹. Most of these bands correspond to the production of calcium containing compounds with terminal amines. For example, the peak at the 3470 cm⁻¹ produces N–H stretch; a secondary amine group. This may be as a result of the oily nature of turtle shell; however, this is temporary as indicated by the symmetric CH₃ and CH₂ stretches at the 2722 and 2478 cm⁻¹ peak respectively culminating into a bending (rocking) motion associated with a long chain band of four or more CH₂ groups. The wide and strong band produced at the 2064 cm⁻¹ wavelength band indicates the appearance of the Ca–O bond which shows the complete elimination of carbon dioxide from the turtle shell, thereby producing the required CaO active site for effective transesterification reaction. This finding is in agreement with that of Wembabazi et al. [45] and Birla et al. [36], working with eggshells and snail shells calcined at 900°C for 3 and 4 hours respectively. Turtle shell calcinations temperature lower than 900°C gives incomplete carbonization as shown by the results of Xie et al. [48] who carried out turtle shell carbonization at a temperature of 200 – 700°C. The results obtained by these workers may be as a result of the formation of carbonate group (CO₃²⁻) represented by asymmetric C–O band in the FTIR analysis.

3.2. Bio-oil and Biodiesel Characterization

The fatty acid profiles of the oil and the produced biodiesel are presented in the chromatographs shown in Figures 2 and 3 with the results summarized in Tables 1 and 2 respectively.

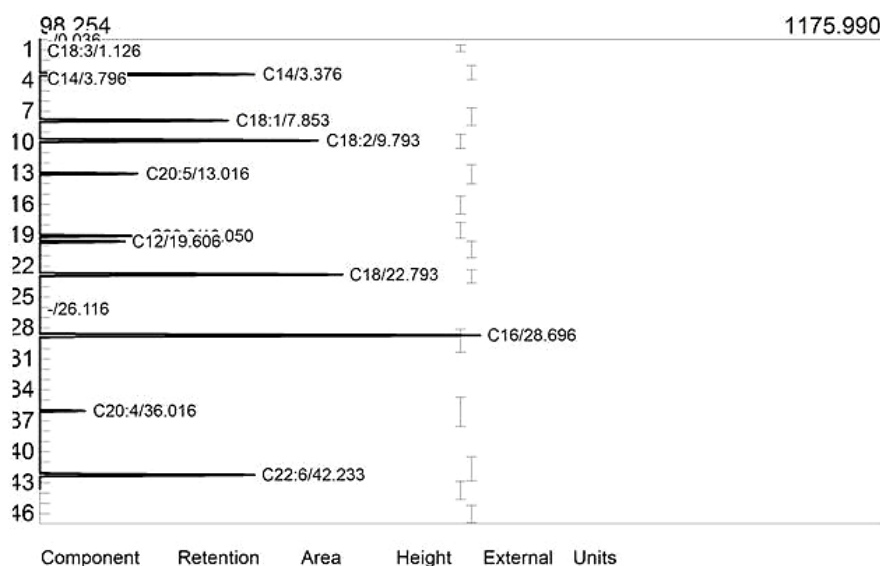


Figure 2. GC-FID spectrum of the bio oil

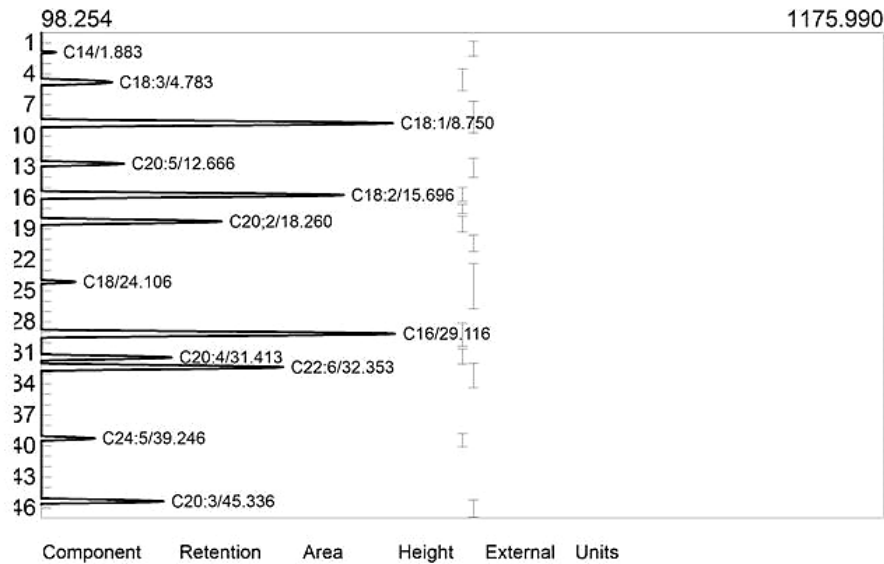


Figure 3. GC-FID spectrum of the produced biodiesel

Table 1. Summary of the fatty acid profile of the bio-oil

Component	Name	RT (min)	% composition
C18:3	Linolenic acid	1.126	0.178532
C14	Myristic acid	3.376	0.801708
C18:1	Oleic acid	7.853	7.652005
C18:2	Linoleic acid	9.793	14.30198
C20:5	Eicosapentanoic acid	13.016	3.657381
C20:2	Gondoic acid	18.936	7.628529
C12	Lauric acid	19.606	2.653383
C18	Stearic acid	22.793	17.0026
C16	Palmitic acid	28.696	36.19833
C20:4	Arachidonic acid	36.016	3.511181
C22:6	Osbond	42.233	6.294317

Table 2. Summary of the fatty acid profile of the produced biodiesel

Component	Name	RT (min)	% composition
C14	Lauric acid	1.883	3.140543
C18:3	Linolenic acid	4.783	8.469609
C18:1	Oleic acid	8.750	13.45768
C20:5	Eicosapentanoic acid	12.666	3.554962
C18:2	Linoleic acid	15.696	16.61874
C20:2	Gondoic acid	18.260	11.96552
C18	Stearic acid	24.106	5.490978
C16	Palmitic acid	29.116	19.7915
C20:4	Arachidonic acid	31.413	6.18783
C22:6	Osbond	32.353	7.303004
C24:5	Nervonic acid	39.246	1.500221
C20:3	Dihomolinenic acid	45.336	2.506957

From the fatty acid profile of the oil obtained from the raffia palm fruit shown in Table 1, the percentage composition of the saturated fatty acids (C4:0-C24:0) is 56.66%, the prominent saturated fatty acids being palmitic acid (36.198%) and stearic acid (17.003%). The percentage composition of the unsaturated fatty acids is 43.34% and the prominent unsaturated fatty acid is linoleic acid (14.302%). The ratio of the bio-oil polyunsaturated to saturated

(P/S) is 0.79 which shows that the oil is unsuitable for human consumption. It had been reported that the higher the P/S value of an oil, the better it is for human consumption [49-51]. From this analysis, the bio-oil seems not to be a good feedstock for biodiesel production because of its high content of saturated fatty acids. Vegetable or seed oils with high composition of saturated fatty acids such as palmitic and stearic acids produces biodiesel having low cold flow properties [52]. As noted by Bello et al. [53], biodiesel with low cold flow properties results in the formation of gum and crystallization of fuel particles at high temperatures resulting in damages to engine parts such as pumps and injectors as well as clogging of fuel lines and fuel filters. However, the results of the produced biodiesel fatty acid profile presented in Figure 3 and summarized in Table 2 gives the percentage of saturated fatty acid as 28.343%, the prominent ones being palmitic acid (19.792%) and stearic acid (5.491%) while the percentage of the unsaturated fatty acids was 71.657%, the prominent ones being linoleic acid (16.619%) and oleic acid (13.458%). Studies had shown that biodiesel with these unsaturated fatty acids possess good cold flow performance as a result of better pour and cloud point of the fuel. This is as a result of the presence of double bonds in the linoleic and oleic acids that forms a cis-cis configuration which eventually reduces the intermolecular attraction that lowers the melting point of the fuel [52, 54]. The production of biodiesel with low saturated fatty acid component from bio-oil with high saturated fatty acid components may be as a result of the novel heterogeneous catalyst produced from turtle shell and its configuration. The contribution of the combination of the process variables may also be responsible for the results obtained. Comparison of the fuel properties of the produced biodiesel with that of petroleum diesel, shows that the biodiesel exhibit better fuel characteristics as can be seen in Table 3 below

Table 3. Fuel properties of the biodiesel and petroleum diesel

Physicochemical property	Produced biodiesel	Petroleum diesel	Test method
Density (g/cm ³)	0.91	0.835	ASTM D9448-1972
Kinematic viscosity @40°C (cst)	6.43	2.83	ASTM D445
Flash point (°C)	186	70	ASTM D7215
Pour point (°C)	-2	3	ASTM D2500
Cloud point (°C)	0.00	6.4	ASTM D97
Cetane number (N)	69	48	ASTM D6890

3.3. Effect of Process Variables on Product Yield

3.3.1. Effect of KOH Concentration on Biodiesel Yield

Figure 4 shows the effect of the concentration of KOH used as impregnator for the catalyst on the yield of biodiesel. The objective of the impregnation was to increase the catalyst basic strength. As can be seen from Figure 4, increasing the concentration of KOH in the impregnation process increased the biodiesel yield due to the increased basicity of the catalyst and increased active sites. A maximum biodiesel yield of 93% was recorded at an optimum KOH concentration of 30% (w/w). Further increase of KOH concentration above the optimum appeared not to favour biodiesel yield. The reduced biodiesel yield at higher KOH concentrations may be due to the exhaustion of the active sites on the catalyst surface as reported by Singh et al. [43] and Hadiyanto et al. [32].

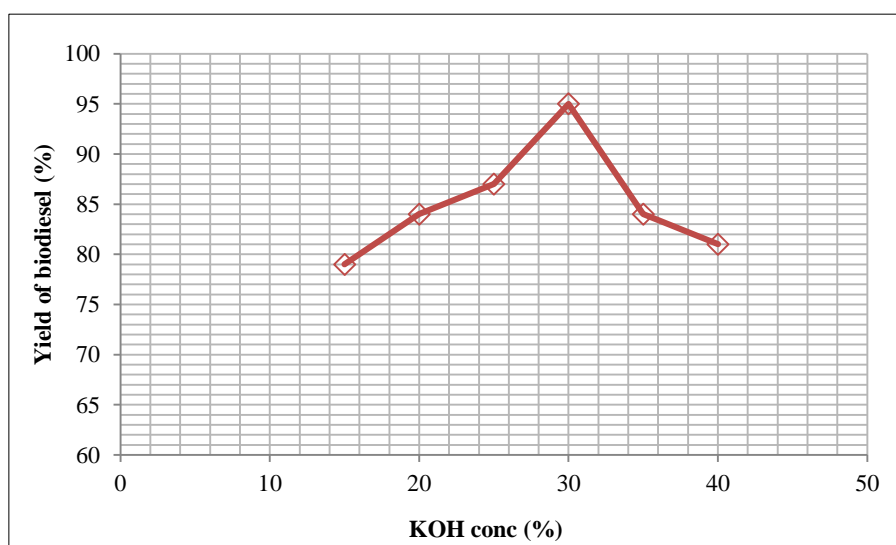


Figure 4. Effect of KOH concentration on biodiesel yield

3.3.2. Effect of Catalyst Loading on Biodiesel Yield

Figure 5 shows the effect of catalyst loading on the yield of biodiesel using 30% (w/w) of KOH concentration. Biodiesel yield increases to a maximum of 92% as catalyst loading increases up to 6.5wt%. This marginal linear increase may be due to increased catalytic driving force as reported by Akhiero et al., [23], however, as the catalyst loading increases beyond 6.5%, biodiesel yield began to decline. The decline in biodiesel yield at higher catalyst loadings may be as a result of increased in viscosity caused by catalyst overload which limits the reaction rate. This is in agreement with the results of both Chen et al. [24] and Ali et al. [41].

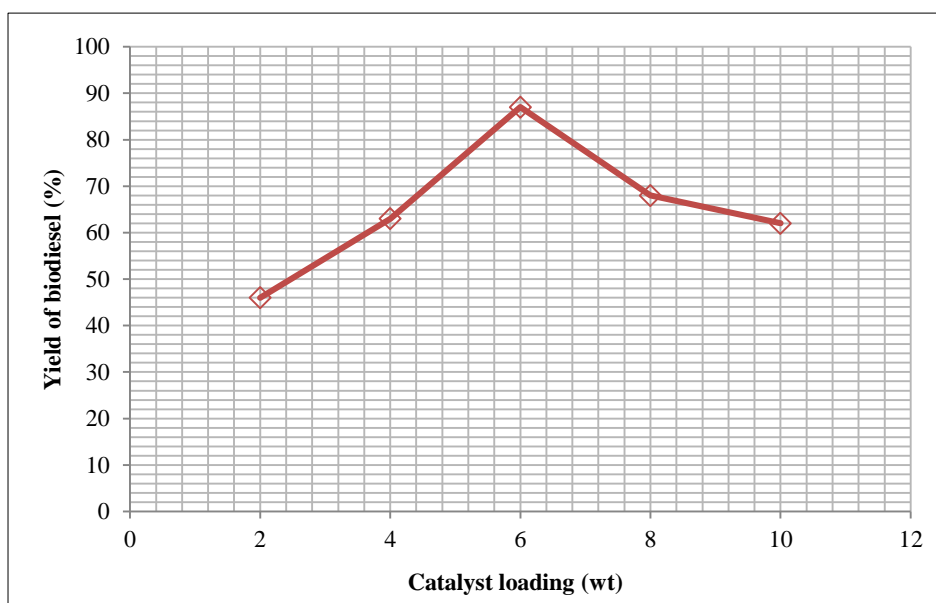


Figure 5. Effect of catalyst loading on biodiesel yield

3.3.3. Effect of Acetone Co-solvent/methanol Ratio on Biodiesel Yield

Using KOH concentration of 30% (w/w) and catalyst loading of 6.5% (w/w), the influence of acetone co-solvent/methanol ratio on biodiesel yield was studied and the result is presented in Figure 6. The primary aim of adding a co-solvent in a transesterification process is to improve miscibility of the reacting species so as to reduce reaction time. The reaction time was reduced from 5hr to 0.5hr in order to ascertain the impact of the co-solvent on the reaction rate. As can be seen from the figure, biodiesel yield increases as acetone/methanol ratio increases up to 0.4 at a maximum yield of 65%. Further increase in acetone/methanol ratio showed marginal decline in biodiesel yield and this may be due to over-dilution of the methanol by acetone. Similar result was obtained by Elkady et al. [29].

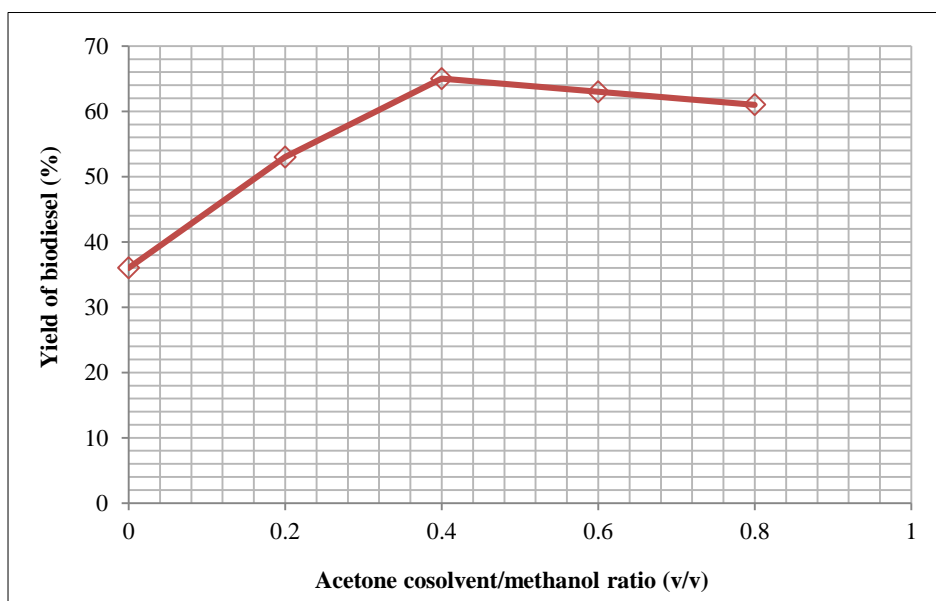


Figure 6. Effect of acetone co-solvent/methanol ratio (v/v) on biodiesel yield

3.3.4. Effect of Catalyst/Carbon Ratio on Biodiesel Yield

Using KOH concentration of 30% (w/w), catalyst loading of 6.5% and acetone co-solvent/methanol ratio of 0.4, the effect of catalyst/carbon ratio on biodiesel yield was studied and the result is presented in Figure 7. The catalytic property of a heterogeneous catalyst is highly dependent on its surface area which can be increased by supporting the catalyst with activated carbon [55]. However, an appropriate mix ratio is needed to obtain the desired catalytic activity. As can be seen from the figure, at a low catalyst/carbon weight ratio, biodiesel yield was low because of the availability of less active components. Increasing the ratio was seen to greatly improve biodiesel yield, and the maximum yield of 93% was obtained at a ratio of 1.25. Further increase of catalyst/carbon ratio led to a slight decline in biodiesel yield as a result of reduced surface area. Singh et al. [43] and Hadiyanto et al. [32] reported similar results in their work.

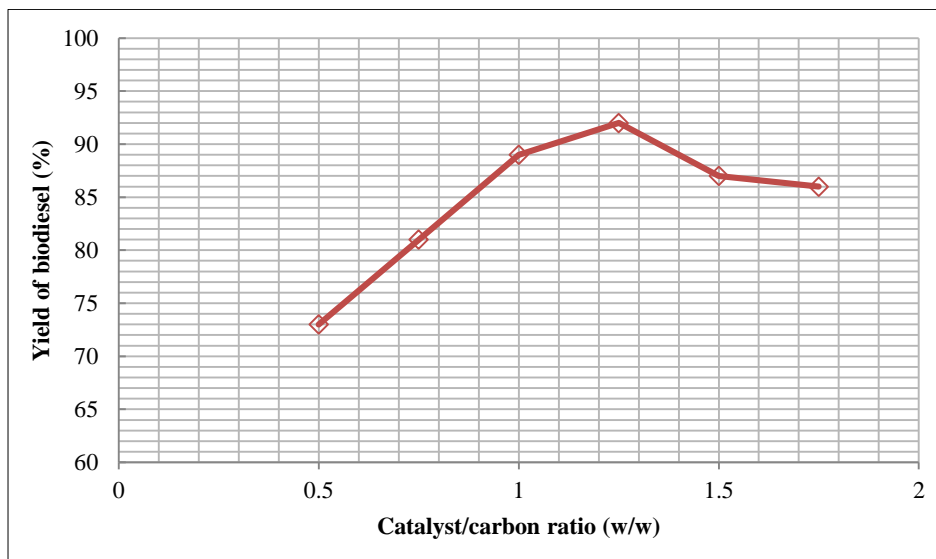


Figure 7. Effect of catalyst/carbon ratio (w/w) on biodiesel yield

4. Conclusion

The possibility of producing biodiesel from a non-convictional source, raphia africana oil, using a heterogeneous catalyst derived from turtle shells supported with activated carbon produced from cassava peels, has been carried out. The present study, which is novel in nature, shows that bio-oil with a high content of saturated fatty acids can be used to produce biodiesel with high fuel quality and a low saturated fatty acid profile. The application of acetone as a co-solvent in the transesterification reaction is another factor that improves the yield of the resultant biodiesel. Turtle shells and raphia palms that are prevalent in the riverine areas of Nigeria's Niger Delta are, therefore, ready feedstock for biodiesel production.

5. Declarations

5.1. Author Contributions

Conceptualization, H.E.O. and K.M.O. methodology, H.E.O., K.M.O. and U.M.O.; software, U.M.O.; validation, H.E.O., K.M.O. and O.E.O.; formal analysis, U.M.O.; investigation, K.M.O. and H.E.O.; resources, K.M.O., and O.E.O.; data curation, K.M.O., H.O.O. and U.M.O.; writing—original draft preparation, H.O.O., and U.M.O.; writing—review and editing, K.M.O., and O.E.O.; visualization, K.M.O.; supervision, K.M.O.; project administration, K.M.O.; funding acquisition, K.M.O. and O.E.O. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available in article.

5.3. Funding

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5.4. Acknowledgements

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5.5. Institutional Review Board Statement

Not applicable.

5.6. Informed Consent Statement

Not applicable.

5.7. Declaration of Competing Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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