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# Green Synthesis and Chemically Enhanced *Rhynchophorus Phoenicis* Nano-Catalyst for Biodiesel Production from *Carica papaya* and *Citrullus lanatus* Oil

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**Abstract:** A cost-effective green process, simple recovery, and reusability are all facilitated by heterogeneous catalysts. In this research the trans-esterification process was used to produce biodiesel from *Carica papaya* (pawpaw) and *Citrullus lanatus* (water melon) seed oil. To compare reaction conditions for biodiesel production with the catalyst (homogeneous (KOH)) catalyst and heterogeneous (alumina-chitosan nano-composite biocatalyst), the percentage yield of biodiesel in the reaction parameters; molar ratio, and catalyst dose were experimented. To improve biodiesel performance, an environmental friendly novel catalyst that are effective and affordable helps to reduce the overall cost of producing biodiesel were produced and alumina-chitosan nano-composite a heterogeneous catalyst was compared to biodiesel production using a homogeneous catalyst potassium hydroxide (KOH). The alumina-chitosan nanocomposite was synthesized from hard shell of *Rhynchophorus phoenicis* using standard methods. The percentage yield (% wt/wt) of biodiesel range from 53.40 ± 0.55 - 72.36 ± 0.17%, 64.70 ± 0.40 - 86.40 ± 1.10%, 80.10 ± 0.40 - 97.00 ± 0.50%, 79.60 ± 0.55 - 97.10 ± 1.05%, 74.70 ± 0.45 - 95.40 ± 1.55.% and 77.40 ± 0.88 - 96.40 ± 0.95% ethyl ester yield of the biodiesels for 1g, 2g, 3g, 4g, 5g, and 6g respectively. The highest was recorded in *Carica papaya* seed oil with nano-composite catalyst whereas the lowest was seen in *Citrullus lanatus* seed oil with KOH catalyst. The optimum conditions for the transesterification process were a 12:01 molar ratio of ethanol to extracted oil and 4g catalyst dose.

**Keywords:** Mole Ratio, Heterogeneous Catalyst, Biodiesel, Synthesis

## 1. Introduction

The development of biodiesel as a liquid fuel derived from modified vegetable oil is currently gaining attention. In addition to competing with cooking oil, biodiesel made from edible oils is currently more expensive than traditional petroleum-based fuels. Consequently, attention has turned to using non-edible oils as a source of raw materials for biodiesel [1]. Popular non-edible oils being considered for biodiesel production include jatropha or seemaikattamankku (Jatropha curcas) [1], karanja or honge (Pongamia pinnata) [2], candlenut (Aleurites moluccana) [3], palm oil sludge [4]. According to [Gerpen, et al., 2005] [5], biodiesel production is through the chemical reaction of an animal fat or vegetable oil with an alcohol for instance methanol which requires the presence of a catalyst (usually a base) like potassium or sodium hydroxide which in turn produces new chemical compound called methyl esters.

Biodiesel offers many advantages such as: it is renewable, energy efficient, nontoxic, sulphur free and biodegradable, and also it usually takes cleaner combustion and reduces global warming gas emissions from the diesel engines.

Specifically, the combustion of vegetable oil biodiesel does not add to the net $CO_2$ in the atmosphere, because the next crop will reuse $CO_2$ to grow [6, 7]. The major drawback to the sustainability of the commercialization of biodiesel as a viable replacement for diesel (petroleum) includes limited quantity of non-edible feedstock, hence, the need to source for a feedstock that is both non-edible and available in abundance.

Variety of homogeneous and heterogeneous catalysts have been reported to enhance the recovery of biofuels, and due to their affordability, these catalysts have emerged as one of the best substitutes for enzyme-based catalysts [8]. Chitosan has been widely used recently for a variety of applications, such as biocatalysis and heterogeneous catalysis [9]. Chitosan is typically chosen as a catalyst in the production of biodiesel due to its promising qualities like biocompatibility, hydrophilic nature, safety, and physiological inertness [10]. Native chitosan, functionalized chitosan, and chitosan immobilized with enzymes have all been used successfully for the FAME conversion and biodiesel production, as previously mentioned [11].

By removing the additional processing costs associated with homogeneous catalysis and lowering the production of pollutants, heterogeneous catalysts are known to improve the trans-esterification process [12]. High FFA and moisture content are tolerated by these catalysts. Due to the high energy demand from fossil fuels like coal, oil, and natural gas, which competes with the needs for feedstock for various chemical industries, we are currently experiencing an energy crisis. These non-renewable energy sources are increasingly in demand.

Due to its lack of sulfur and aromatics, biodiesel has several advantages over conventional fossil diesels, including renewability; biodegradability, non-toxicity, and low exhaust emissions [13]. Biodiesel can be considered to be a promising alternative to petroleum diesel and has attracted keen attention from many researchers all over the world [4]. Biofuels can be produced using lingo-cellulosic biomass, such as agricultural residues, byproducts of agricultural processing, and energy crops that don't compete with food and animal feed. The petrochemical industry currently consumes 75% of crude oil to meet the demand for liquid hydrocarbon fuels in the transportation sector. Considering the potential replacement of crude oil by biomass, this study revealed the synthesis and improved activity of nano-composite for biodiesel production from *Carica papaya (*pawpaw*)* and *Citrullus lanatus* (water melon) seed oil.

# 2. Materials and Methods

### *2.1. Synthesis of Chitosan and Its Alumina Nanocomposite*

*Rhynchophorus phoenicis* were collected from palm trees at Omuoko community in Aluu, Ikwerre Local Government Area, Rivers state, Nigeria, and identified at the Department of Animal and Environmental Biology, University of Port Harcourt, Rivers State, Nigeria. The samples were cleaned of adhering dirt and soft tissues, washed well with distilled water and kept in the oven at 50°C for two days. After drying, the dried samples were ground and sieved.

#### *2.1.1. Demineralization*

A 1000 mL beaker glass containing 650 mL of 1 M HCl solution was added 65g hard tissues of *Rhynchophorus phoenicis*. With a magnetic stirrer at room temperature for 3 hours, the mixture was stirred and then filtered with Whatman filter paper while constantly rinsed with distilled water until neutrality was achieved The residue was kept in an oven at 65°C until dry to steady weight [15, 16].

#### *2.1.2. Deproteinisation*

The residue was put into a 1000 mL glass beaker and added 650 mL of 1 M NaOH solution. The mixture was stirred and heated for 1 hour on a hotplate at 60°C and then sieved with filter paper. The residue were washed with distilled water until the pH was neutral, and then put in an oven at 65°C until dry to stable weight. The residue gotten at this step is chitin. [16].

#### *2.1.3. Deacetylation*

Deacetylation of chitin gives chitosan. The chitin was put into a glass beaker containing 50% NaOH solution at a ratio of 10: 1 (w/v) between NaOH solution and the isolated chitin. The mixture was stirred and heated for 2 hours on a hotplate at 110°C. The mixture was filtered and the residue were washed with de-ionized water until the chitosan was neutral. Chitosan was put in an oven at 65°C until it was dry to steady weight [16].

### *2.2. Synthesis of Alumina-Chitosan Nanocomposite*

120 mL of 10% oxalic acid was added to 6 g of chitosan and then heated at 55°C until it formed a gel. Then, 120 mL distilled water was added to the gel solution, and heated for 20 minutes at 45°C. Next, 12g of $Al_2O_3$ was added to the solution and stirred for 240 minutes at 250 rpm and left for 2 hours. The precipitate was filtered, cleaned and dried in an oven for 5 hours at 55°C [15, 17].

### *2.3. Collection and Preparation of Vegetable Oil*

*Carica papaya* and water melon was purchased from a local market as a source of vegetable oil for transesterification reaction. The alcohol selected was methanol (99.8%, Sigma-Aldrich). Other utilized chemicals for transesterification process are of analytical grades such as sodium hydroxide (99%, Sigma-Aldrich), acetic acid (98%, Sigma-Aldrich), and tetrahydrofuran (ACS GRADE, 99%, Right Price Chemicals). and Alumina-chitosan nanocomposite.

The vegetable oil was first filtered using a glass Büchner funnel filtration system and then it was subjected to an acid catalyzed esterification process in order to maintain free fatty acid content lower than 1% [18].

### *2.4. Biodiesel Production Process*

In this study, the trans-esterification process was used to

produce biodiesel from oil synthesised from pawpaw and water melon seed in the presence of Alumina-chitosan nanocomposite. A reflux condenser was used to prevent methanol evaporation and better control of the reaction temperature. Then, 50 g of the oil extracted from the rotten carrot and watermelon seed were transferred into a 250-mL three-neck round-bottom flask each. The flask was placed on a heater to raise the oil temperature to the desired value. Then, the mixture of methanol and the catalyst (initially 1 wt.% for checking the effect of methanol/oil molar ratio) was added to the oil and a magnet was applied to blend the mixture. The time of mixing the oil with methanol and catalyst was recorded as the starting time of the experiment. Also, the temperature was controlled by a heater equipped with a magnetic stirrer. The solution temperature was checked every 5 min by a thermometer and kept at the desired temperature (60°C for checking the effect of methanol/oil molar ratio). After the reaction time (2 h) was completed, the biodiesel was produced.

At the end of the reaction, the produced biodiesel was transferred to the decanter funnel for separation and after 24 h, the solution in the funnel was converted into three phases including biodiesel, glycerol, and catalyst, respectively.

The yield of biodiesel was calculated using Eq. (1):

$$\text{Biodiesel yield\%} = (\text{weight of produced biodiesel (g)}/\text{initial weight of oil (g)}) \times 100 \quad (1)$$

## 3. Results and Discussion

In this study, the effect of different parameters such as reaction temperature, and contact time, on the biodiesel production was investigated. To determine the best conditions for biodiesel production, one of the parameters was varied and other factors were kept constant. The trans-esterification reaction was initially evaluated at different mole ratio (3:01, 6:01, 9:01, 12:01, and 14:01) and dose of catalyst 1, 2, 3, 4, 5, and 6g was also evaluated at the optimized conditions.

The ethanol to oil ratio is one of the most important factors affecting the trans-esterification reaction process. The reaction temperature is set at 80°C. The stoichiometric molar ratio of alcohol triglyceride is 3:01, 6:01, 9:01, 12:01 and 14:01 as shown in table 1. The percentage yield ranged from 49.50 ± 1.65 - 78.30 ± 0.40, 58.00 ± 0.75 - 81.40 ± 0.60, 76.30 ± 1.70 - 94.60 ± 0.30, 81.20 ± 0.55 - 97.10 ± 0.95 and 78.04 ± 2.55 - 96.40 ± 1.05 for 3:01, 6:01, 9:01, 12:01 and 14:01 mole ratio of ethanol to extracted oil respectively. The highest was recorded in *Carica papaya* seed oil with nanocomposite as catalyst whereas the lowest was seen in *Citrullus lanatus* seed oil with KOH as catalyst.

***Table 1.*** *Effect of the Molar Ratio of Ethanol to Extracted Oil on Ethyl Ester Yield. catalyst/Oil Mass Ratio, 3.0g; Reaction Temperature, 80°C.*

| Molar Ratio | *Carica papaya* seed oil with KOH catalyst | *Citrullus lanatus* seed oil with KOH catalyst | *Carica papaya* seed oil with Nanocomposite catalyst | *Citrullus lanatus* seed oil with Nanocomposite catalyst |
|---|---|---|---|---|
| 3:01 | 72.15 ± 0.70 | 49.50 ± 1.65 | 78.30 ± 0.40 | 54.60 ± 2.75 |
| 6:01 | 79.25 ± 0.50 | 58.00 ± 0.75 | 81.40 ± 0.60 | 63.20 ± 1.05 |
| 9:01 | 89.30 ± 0.40 | 76.30 ± 1.70 | 94.60 ± 0.30 | 81.60 ± 0.80 |
| 12:01 | 92.04 ± 0.55 | 81.20 ± 0.55 | 97.10 ± 0.95 | 83.40 ± 1.45 |
| 14:01 | 90.20 ± 0.85 | 78.04 ± 2.55 | 96.40 ± 1.05 | 79.20 ± 1.45 |

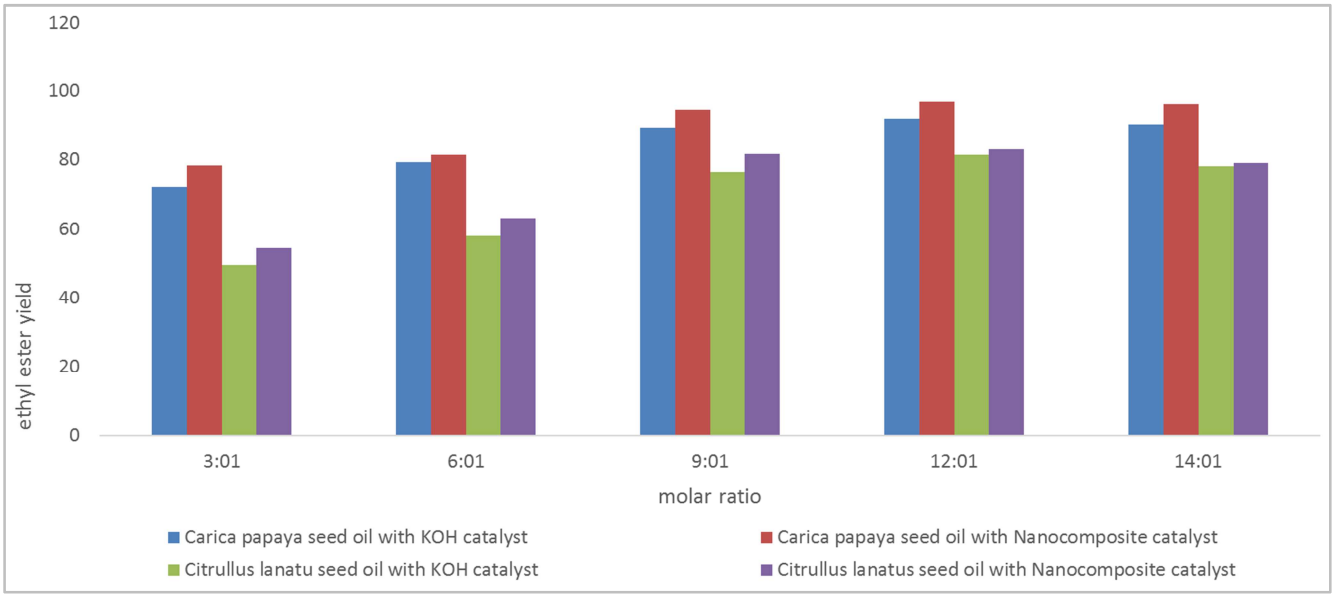


***Figure 1.*** *Effect of the Molar Ratio of Ethanol to Extracted Oil on Ethyl Ester Yield. catalyst/Oil Mass Ratio, 3.0g; Reaction Temperature, 80°C.*

***Table 2.*** *Effect of Dose of catalyst on the Percentage Yield (% wt/wt) of Biodiesel.*

| Dose (g) | *Carica papaya* seed oil with KOH catalyst | *Citrullus lanatus* seed oil with KOH catalyst | *Carica papaya* seed oil with Nanocomposite catalyst | *Citrullus lanatus* seed oil with Nanocomposite catalyst |
|---|---|---|---|---|
| 1 | 68.15 ± 0.55 | 53.40 ± 0.45 | 72.36 ± 0.17 | 54.60 ± 0.85 |
| 2 | 81.60 ± 1.67 | 64.70 ± 0.40 | 86.40 ± 1.10 | 67.90 ± 0.70 |
| 3 | 94.10 ± 0.20 | 80.10 ± 0.40 | 97.00 ± 0.50 | 83.40 ± 0.90 |
| 4 | 95.00 ± 0.95 | 79.60 ± 0.55 | 97.10 ± 1.05 | 82.9 ± 0.65 |
| 5 | 93.10 ± 1.45 | 77.40 ± 0.80 | 96.40 ± 0.95 | 78.00 ± 0.50 |
| 6 | 90.40 ± 0.55 | 74.70 ± 0.45 | 95.40 ± 1.55 | 76.80 ± 0.65 |

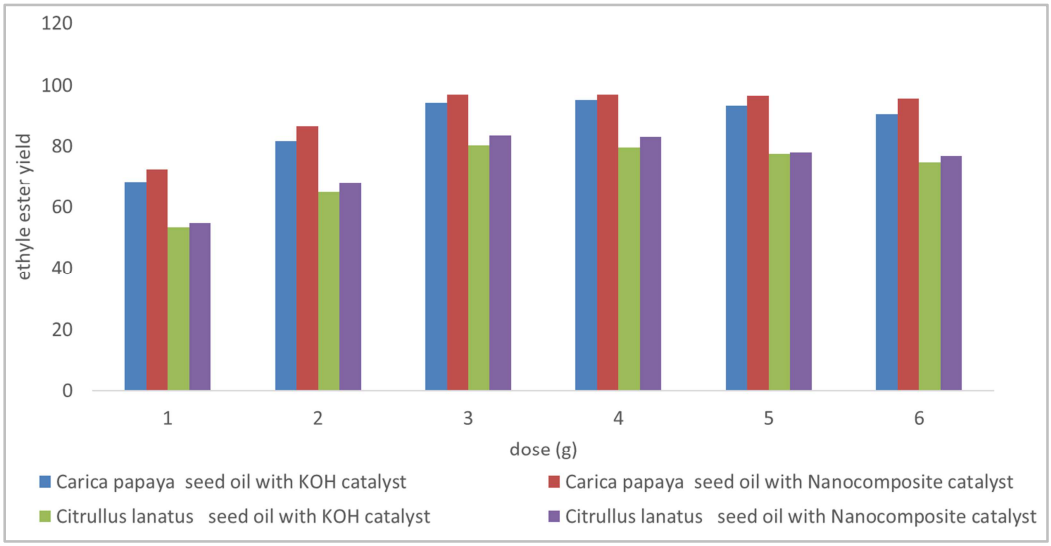


***Figure 2.*** *Effect of Dose of catalyst on the Percentage Yield (% wt/wt) of Biodiesel.*

The molar ratio of ethanol to extracted oil on ethyl ester yield showed that molar ratio 12:01 was at its optimum and was highest at that point compare to other molar ratios. The lowest yield was seen in the molar ratio of 3:01.

Figure 1 shows the ethyl ester yield increases as the quantity of ethanol was increased up to an optimal value of 12:01 molar ratio of ethanol to extracted oil and at that point a maximum yield of 97.10 ± 0.95% > 92.10 ± 0.55% > 83.40 ± 1.45% and 81.40 ± 0.55% was observed for *Carica papaya* with nanocomposite as catalyst > *Carica papaya* with KOH as catalyst > *Citrullus lanatus* with nanocomposite as catalyst > *Citrullus lanatus* with KOH as catalyst. This observation was seen for the entire molar ratio across all the samples and the performance decreased in the order already described as shown in table 1. Biodiesel produced with *Carica papaya* with nanocomposite as catalyst was observed to have a higher yield among the molar ratio performed and is recommended for production of biodiesel for industrial process and application.

When the quantity of ethanol was increased further then the yield of ethyl ester drastically reduced at 14.01 molar ratio (figure 1). The separation of esters from glycerol becomes difficult when the ethanol to oil ratio is increased above 12:01 molar ratio of ethanol to extracted oil. The presence of unreacted ethanol can suppress the gravity decantation, so that the apparent yield of biodiesel decreases because traces of glycerol may remain in the biodiesel phase. The glycerol remaining in the solution drives the equilibrium back to the left side of the reaction produced in the lower yield of esters. Similar results were also obtained by [Chakraborty and Baruah, 2013] [19].

The average values of the effect of dose (1, 2, 3, 4, 5 and 6g dose) of nano composite on the percentage yield (% wt/wt) of biodiesel are represented in Table 2.

The percentage yield (% wt/wt) of biodiesel range from 53.40 ± 0.55 - 72.36 ± 0.17%, 64.70 ± 0.40 - 86.40 ± 1.10%, 80.10 ± 0.40 - 97.00 ± 0.50%, 79.60 ± 0.55 - 97.10 ± 1.05%, 74.70 ± 0.45 - 95.40 ± 1.55.% and 77.40 ± 0.88 - 96.40 ± 0.95% ethyl ester yield of the biodiesels for 1g, 2g, 3g, 4g, 5g, and 6g respectively. The highest was recorded in *Carica papaya* seed oil with nano-composite catalyst whereas the lowest was seen in *Citrullus lanatus* seed oil with KOH catalyst.

Furthermore, The highest% ethyl ester yield was recorded in 4g dose of nanocomposite catalyst for *Carica papaya* and *Citrullus lanatus* with% yield of 97.10 ± 1.05 and 82.9 ± 0.65 also with 4g of KOH catalyst for *Carica papaya* 95.00 ± 0.95% respectively. while, 3g dose of KOH was observed only for *Citrullus lanatus* 80.10 ± 0.40%. Whereas the lowest was seen in 1g of catalyst across all the samples.

A plot of percent biodiesel yield against catalyst concentration in figure 2 showed a peak at catalyst concentration of 4 g of nanocomposite catalyst was optimal in the reaction for both *Carica papaya* and *Citrullus lanatus*, while 3g and 4g of KOH was optimal in the reaction for *Carica papaya* and *Citrullus lanatus* respectively as shown in

table 2. It is clearly seen that 4 g of nanocomposite while 3g and 4g of KOH was optimal for producing the ethyl esters of biodiesel. Excess amount of catalyst will opt to form emulsion, which will increase the viscosity and lead to the formation of gels. The formation of emulsion will therefore block the reaction [20].

# 4. Conclusion

The alumina-chitosan nanocomposite was synthesized from hard shell of *Rhynchophorus phoenicis* using standard methods and were used as a catalyst for the Production of biodiesel using *Carica papaya* (pawpaw) and *Citrullus lanatus* (water melon) seed oil (transesterification process). To improve the performance of the biodiesel the alumina-chitosan nanocomposite a heterogenous catalyst used was compare to the production of biodiesel with homogenous catalyst potassium hydroxide (KOH).

The optimum conditions for the transesterification process were compared using different reaction conditions (molar ratio, and dose of catalyst) for production of biodiesel with homogeneous catalyst (KOH) and heterogeneous biocatalust (alumina-chitosin nanocomposite). The optimum conditions for the transesterification process were Molar Ratio of Ethanol to Extracted Oil of 12:01, dose of 4g of catalyst. A higher percentage yield was recorded in the biodiesel produced with alumina-chitosin nanocomposite as biocatalyst for all the reaction condition experimented and the highest yield was seen using *Carica papaya* (pawpaw) ethyl ester.

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