

The Potentials of Reaction Parameters on *Rhynchophorus Phoenicis* Nano-Catalysts Based Biodiesel Production from Waste Material Feedstocks

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Abstract: Heterogeneous catalysts are known to improve the trans-esterification Process in biodiesel production by eliminating the extra processing costs involved in homogeneous catalysis, as well as reducing the generation of pollutants. Heterogeneous catalysts promote easy recovery, reusability and a cost-effective green process. These catalysts tolerate high FFA and moisture content. In this research the trans-esterification process was used to produce biodiesel from *Carica papaya* (pawpaw) and *Citrullus lanatus* (water melon) seed oil. To improve biodiesel performance, an alumina-chitosan nanocomposite a heterogeneous catalyst synthesized from hard shell of *Rhynchophorus phoenicis* using standard methods was compare to biodiesel production using a homogeneous catalyst potassium hydroxide (KOH). Reaction parameters (reaction temperature and reaction time) were used for optimization of biodiesel production. The average values obtained for effect of time ranged from 42.30±0.20-63.10±1.30%, 49.30±1.50-64.70±1.00%, 71.40±0.70-79.80±0.20%, 80.46±0.20-97.10±0.30%, 81.20±1.20-86.10±1.60% and 79.39±0.40-83.90±0.50% for 30 minutes, 60 minutes, 90 minutes, 120 minutes, 150 minutes and 180 minutes respectively. Variation of temperature for the production of biodiesel from *Carica papaya* and *Citrullus lanatus* seed oil with KOH and Nanocomposite catalyst range from 63.09±0.60-95.20±1.55, 49.10±0.45-79.30±0.75, 66.00±1.00-97.10±0.45 and 59.20±0.95-83.40±0.85% for 40, 45, 50, 60, 80 and 90°C respectively. The optimum conditions for the trans=esterification process were 80°C reaction temperature, and 120 minutes reaction time.

Keywords: Reaction Parameter, Biocatalyst, Ethyl Ether, Seed Oil

1. Introduction

The demand for primary energy is anticipated to increase by 1.6% annually over the following ten years. While nuclear and renewable energy sources account for 7 and 5% of global energy consumption, respectively, a large portion of the primary energy used today comes from fossil fuel resources like crude oil (35%), coal (29%) and natural gas (24%) [1]. As a result, fossil fuels account for 88% of all energy consumption worldwide, making them the single largest energy source. Fossil fuel combustion on a large scale

produces air pollution, which has sparked research into finding alternatives. A technically viable, economically viable, environmentally friendly, and sufficiently accessible alternative to conventional petroleum diesel must also be available at a reasonable price. Vegetable oils, bio-alcohols, biogas, and biodiesel are all thought to be appropriate options in this situation [1, 2]. Biodiesel is one of these alternative fuels that is marketed as an additional fuel for diesel engines. Mono-alkyl esters of long-chain fatty acids derived from vegetable oil are used to make biodiesel [3]. Due to its adaptable physical and chemical properties, it can be used in compression-ignition (diesel) engines with little to no

modification and is renewable, non-toxic, biodegradable, and environmentally friendly. Additionally, compared to petroleum-based diesel fuel, it produces significantly less carbon monoxide, sulphur dioxide, and unburned hydrocarbons during combustion [3, 4]. Chitosan has been widely used recently for a variety of applications, such as biocatalysis and heterogeneous catalysis [5]. 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 [6]. Native chitosan, functionalized chitosan, and chitosan immobilized with enzymes have all been used successfully for the FAME conversion and biodiesel production, as previously mentioned [7]. Furthermore, straightforward chemical and physical alterations can increase chitosan's adaptability as a supporting material.

Nanocatalyst can be extensively studied by varying reaction conditions of the synthesis. Various morphology such as nanocrystals, nanosponges, and nanocubes, expose different active sites with rough and mesoporous structure, thus overall increasing the surface area and reactivity [8]. These highly developed nanocatalysts will eventually increase the production of biodiesel. Surface functionalization is prominent in increasing the overall acidity of nanocatalysts, eventually enhancing the catalytic activity, and introducing magnetic nanomaterials will help in easy separation recoverability and reusability [9, 10]. Besides development in nanocatalyst areas, physico-chemical properties of biodiesel are also essential in estimating the quality and quantity of production for biodiesel. It is mainly dependent on the type of feedstock and pre-treatment process it undergoes [11].

The use of an appropriate catalyst in accordance with the nature of the oil is one of the key challenges facing the biodiesel production process. The functional efficacy and adverse effects of catalysts during trans-esterification have attracted extensive research and discussion. This paper revealed the reaction parameters for optimal yield of biodiesel using heterogeneous catalyst.

2. Materials and Methods

2.1. Synthesis of Chitosan and Its Alumina Nanocomposite

Rhynchophorus phoenixis 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 phoenixis*. 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 [12, 13].

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. [13].

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 [13].

2.1.4. 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 Al₂O₃ 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 [12, 14].

2.2. 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% [15].

2.3. 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

3.1. The Effect of Reaction Parameters on Biodiesel Production

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 transesterification reaction was initially evaluated at reaction temperature (40, 50, 60, 70, and 80°C) and reaction time of 30, 60, 90, 120, 150 and 180 minutes was also evaluated at the optimized conditions.

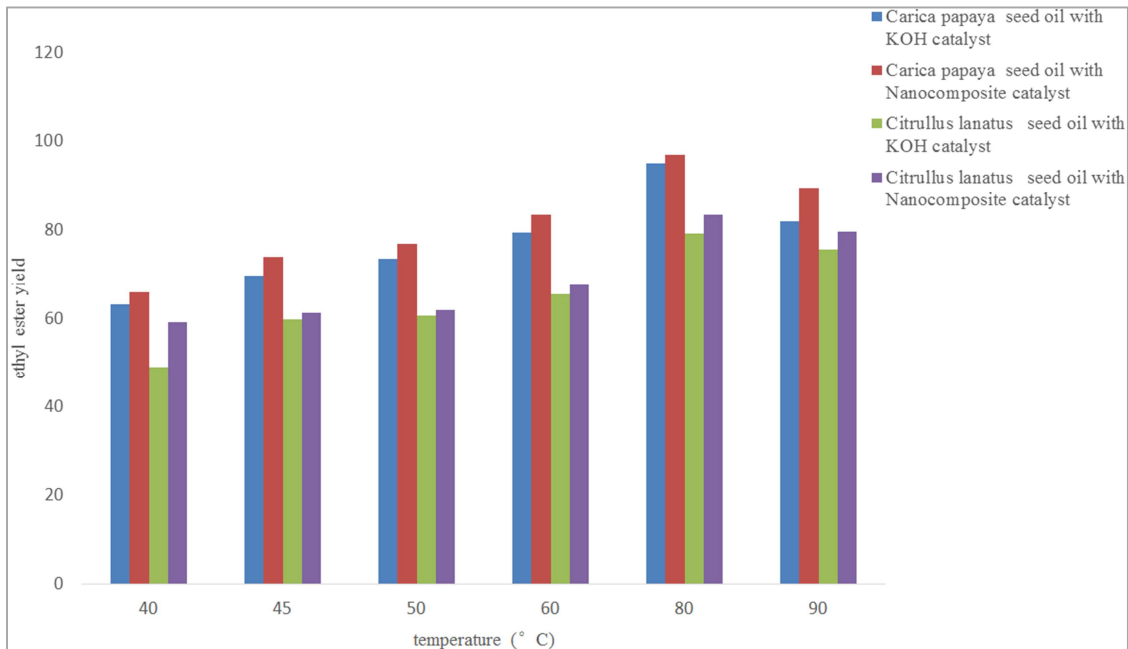


Figure 1. Variation of Reaction Temperature for Optimization of Ethyl Ester Yield (Biodiesel).

Table 1. Variation of Reaction Temperature for Optimization of Ethyl Ester Yield (biodiesel).

Temperature (°C)	<i>Carica papaya</i> seed oil with KOH catalyst	<i>Citrullus lanatus</i> seed oil with KOH catalyst	<i>Carica papaya</i> seed oil with Nanocomposite catalyst	<i>Citrullus lanatus</i> seed oil with Nanocomposite catalyst
40	63.09±0.60	49.10±0.45	66.00±1.00	59.20±0.95
45	69.70±0.50	59.90±0.75	73.90±0.55	61.30±0.95
50	73.60±0.70	60.60±0.56	77.00±0.90	62.00±0.55
60	79.5±0.78	65.5±0.46	83.4±1.05	67.6±0.85
80	95.20±1.55	79.30±0.75	97.10±0.45	83.40±0.85
90	82.00±0.15	75.60±0.55	89.70±0.65	79.70±1.55

Table 2. Variation of Reaction Time for Optimization of Ethyl Ester Yield (Biodiesel).

Time (min)	<i>Carica papaya</i> seed oil with KOH catalyst	<i>Citrullus lanatus</i> seed oil with KOH catalyst	<i>Carica papaya</i> seed oil with Nanocomposite catalyst	<i>Citrullus lanatus</i> seed oil with Nanocomposite catalyst
30	59.20±0.30	42.30±0.20	63.10±1.30	43.30±0.50
60	61.55±0.60	49.30±1.50	64.70±1.00	51.60±0.40
90	78.20±1.10	71.40±0.70	79.80±0.20	70.80±1.10
120	96.15±0.50	80.46±0.20	97.10±0.30	83.40±1.20
150	84.10±1.30	81.20±1.20	86.10±1.60	83.10±0.30
180	79.39±0.40	79.80±1.40	83.90±0.50	81.90±0.50

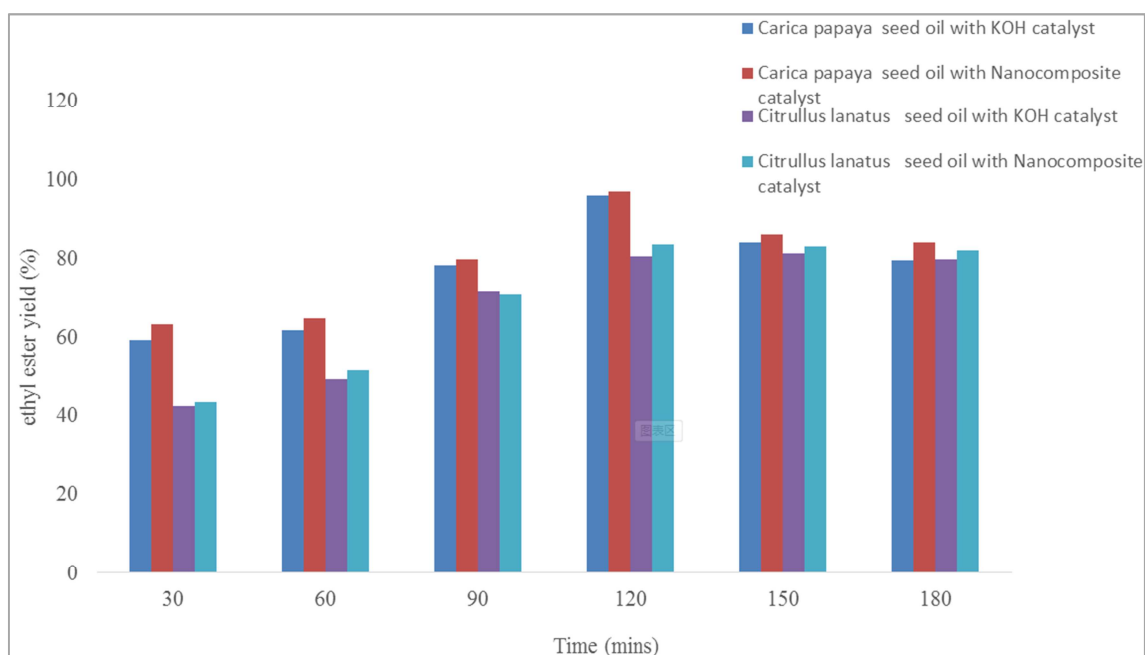


Figure 2. Variation of Reaction Time for Optimization of Ethyl Ester Yield (Biodiesel).

3.2. Effect of Reaction of Temperature

The reaction temperature was optimized by carrying out transesterification reaction in the temperature range of 40 to 90°C at constant oil to ethanol molar ratio and catalyst concentration. From this study, it was observed that there is a steady increase in percentage yield of biodiesel with increasing reaction temperature up to 80°C beyond which the percentage yield starts decreasing as shown in figure 1. The decrease in percentage yield beyond 90°C was due to the methanol vaporization and formation of bubbles that slows down reaction on the three-phase interface [16].

Variation of temperature for the production of biodiesel from *Carica papaya* and *Citrullus lanatus* seed oil with KOH and Nanocomposite catalyst range from 63.09±0.60-95.20±1.55, 49.10±0.45-79.30±0.75, 66.00±1.00-97.10±0.45 and 59.20±0.95-83.40±0.85% for 40, 45, 50, 60, 80 and 90°C respectively as shown in table 1. The highest yield of the biodiesel was recorded in temperature of 80°C whereas the lowest was seen in temperature of 40°C for the *Carica papaya* and *Citrullus lanatus* seed oil with KOH and nanocomposite catalyst respectively. The trend of the biodiesel yield shows an increasing order of *Citrullus lanatus* with KOH catalyst > *Carica papaya* with KOH catalyst > *Citrullus lanatus* with nanocomposite catalyst > *Carica papaya* with nanocomposite catalyst. Furthermore, *Carica papaya* and *Citrullus lanatus* with nanocomposite catalyst shows a higher yield among the KOH catalyst of the seed oil used for the study whereas *Carica papaya* with nanocomposite catalyst showed a higher yield when compared.

The variation of reaction time for production of ethyl ester yield (biodiesel) is shown in Figure 2. The average values obtained for effect of time ranged from 42.30±0.20-

63.10±1.30%, 49.30±1.50-64.70±1.00%, 71.40±0.70-79.80±0.20%, 80.46±0.20-97.10±0.30%, 81.20±1.20-86.10±1.60% and 79.39±0.40-83.90±0.50% for 30 minutes, 60 minutes, 90 minutes, 120 minutes, 150 minutes and 180 minutes respectively.

For time of 30 minutes, the highest percentage yield was recorded in *Carica papaya* seed oil with synthesized nano-composite as catalyst whereas the lowest was seen in *Citrullus lanatus* seed oil with KOH as catalyst. This trend was observed for 60 minutes, 90 minutes and 150 minutes except at 180 minutes in which the highest percentage yield was recorded in *Carica papaya* seed oil with nano-composite as catalyst whereas the lowest was seen in *Carica papaya* seed oil with KOH as catalyst.

Furthermore, as time increases, the percentage yield increases. The highest percentage yield value obtained was at 120 minutes and decreased as time increased above 120 minutes. This study revealed that the use of nano-composite synthesized from hard tissues of *Rhynchophorus phoenixis* optimizes the yield of biodiesel.

Reaction time is required for the completion of homogeneous/heterogeneous-catalyst trans-esterification, which depends not only on the reaction temperature, but also on the degree of mixing in the process. From the figure 1 above, it is seen that the yield of biodiesel is less at the beginning and reaches a maximum at the reaction time of 120 minutes and relatively decreases afterward. The reaction time of the product yield after more than 120 minutes has no significant effect on the conversion of triglycerides, but leads to a reduction in the product yield. This is because a longer reaction time enhances the hydrolysis of esters (reverse reaction of trans-esterification), which results in the loss of esters besides causing more fatty acids to form soap. The gradual increase of reaction time after 120 minutes shows the

negative effect on product yield.

4. Conclusion

The use of *Carica papaya* (pawpaw) and *Citrullus lanatus* (water melon) seed oil as biodiesel was carried out by using the trans-esterification process. To improve the performance of the biodiesel the alumina-chitosan nano-composite a heterogeneous catalyst used was compare to the production of biodiesel with homogenous catalyst potassium hydroxide (KOH).

In order to compare reaction condition for production of biodiesel with homogeneous (KOH) catalyst and heterogeneous (alumina-chitosin nanocomposite) biocatalyst, the percentage yield of biodiesel in the reaction parameters (reaction temperature, and reaction time) was studied. The optimum conditions for the transesterification process were 80°C and 120 minutes for reaction temperature and reaction time respectively. A higher percentage yield was recorded in the biodiesel produced with alumina-chitosin nanocomposite as catalyst for all the reaction condition studied and the highest yield was seen *Carica papaya* (pawpaw) ethyl ester.

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