ISSN:2584-2706 DOI: https://doi.org/10.5281/zenodo.21990862

Alumina–Chitosan Nanocomposite as a Heterogeneous Catalyst for Biodiesel Production from Carica Papaya and Citrullus Lanatus Seed Oils

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Abstract
Growing interest in renewable fuels has increased the need for efficient, recoverable and environmentally preferable catalysts for biodiesel production. This study evaluated an alumina–chitosan nanocomposite as a heterogeneous catalyst for transesterification of seed oils obtained from Carica papaya (pawpaw) and Citrullus lanatus (watermelon), with potassium hydroxide (KOH) used as the homogeneous-catalyst comparator. Chitosan was prepared from the hard tissues of Rhynchophorus phoenicis and incorporated with alumina to form the nanocomposite. The synthesized materials were characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). FTIR showed characteristic chitosan functional groups with shifts after alumina incorporation; SEM showed that the nanocomposite had smaller particles and a more porous surface than chitosan; and XRD confirmed distinct crystalline features. The seed oils were converted to biodiesel by transesterification, and the effects of alcohol-to-oil molar ratio, catalyst dose, reaction temperature and reaction time were evaluated. The optimum conditions identified in the thesis were a 12:1 alcohol-to-oil molar ratio, 4 g catalyst dose, 80 °C reaction temperature and 120 min reaction time. Under the molar-ratio experiment, Carica papaya with the nanocomposite reached 97.10 ± 0.95% yield, compared with 92.04 ± 0.55% with KOH; Citrullus lanatus reached 83.40 ± 1.45% with the nanocomposite and 81.20 ± 0.55% with KOH. The nanocomposite generally produced higher biodiesel yields than KOH, while Carica papaya gave the strongest overall performance. These findings support alumina–chitosan nanocomposite as a promising heterogeneous catalyst for biodiesel production from underutilized seed-oil feedstocks.

Keywords:
alumina–chitosan nanocomposite; biodiesel; heterogeneous catalyst; Carica papaya; Citrullus lanatus; transesterification; Rhynchophorus phoenicis

1. Introduction

Dependence on fossil fuels has intensified concerns about air pollution, greenhouse-gas emissions, energy security and the long-term availability of petroleum resources. Biodiesel is an attractive renewable alternative because it is biodegradable, comparatively non-toxic and can be used in compression-ignition engines with limited modification. However, the economic and environmental performance of biodiesel depends strongly on feedstock selection and the catalyst used for transesterification.

Conventional homogeneous catalysts such as KOH can provide rapid conversion, but catalyst separation, wastewater generation, sensitivity to free fatty acids and difficulties in product purification can increase processing burdens. Heterogeneous catalysts offer advantages including easier

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separation, potential recovery and reuse, and reduced downstream treatment. Chitosan is particularly attractive as a catalyst-support material because of its functional groups and its potential to be obtained from biological residues.

The underlying doctoral research therefore investigated a waste-derived alumina–chitosan nanocomposite for biodiesel production using Carica papaya and Citrullus lanatus seed oils. The work combined catalyst synthesis and characterization with a direct comparison against KOH and optimization of major transesterification variables. The objective of this article is to present the catalyst-development and biodiesel-performance findings as a focused journal paper.

2. Materials and Methods

2.1 Preparation of chitosan

Rhynchophorus phoenicis specimens collected from palm trees in Omuoko village, Aluu, Ikwerre Local Government Area, Rivers State, Nigeria, were identified by the Department of Animal and Environmental Biology, University of Port Harcourt. Hard tissues were cleaned, washed with distilled water, dried at 50 °C for two days, crushed and sieved. For demineralization, 65 g of the prepared material was treated with 650 mL of 1 M HCl for 3 h at room temperature, filtered, washed to neutrality and dried at 65 °C. Deproteinization was carried out with 650 mL of 1 M NaOH at 60 °C for 1 h with stirring, followed by filtration, washing to neutrality and drying. The resulting chitin was deacetylated using 50% NaOH at a solution-to-chitin ratio of 10:1 (w/v) at 110 °C for 2 h, then washed to neutrality and dried at 65 °C.

2.2 Synthesis and characterization of alumina–chitosan nanocomposite

A gel was prepared by combining 6 g chitosan with 120 mL of 10% oxalic acid at 55 °C. After addition of 120 mL purified water, the mixture was heated at 45 °C for 20 min. Alumina (Al_2O_3; 12 g) was then added and the mixture agitated at 250 rpm for 240 min. The precipitate was filtered, washed and oven-dried for 5 h at 55 °C. FTIR spectra were obtained over 4000–600 cm^{-1} using an FTIR-8400S instrument. XRD measurements were obtained using an ARL X'TRA diffractometer, while surface morphology was examined using a Pro-X scanning electron microscope.

2.3 Feedstock preparation and biodiesel production

Pawpaw and watermelon seed feedstocks were obtained from waste fruits sourced from a local market. The oils were filtered and subjected to acid-catalyzed pretreatment to reduce free fatty acids before transesterification. Biodiesel production was conducted in a 250 mL three-neck round-bottom flask fitted with a reflux condenser and magnetic stirring. A 50 g oil charge was heated to the required temperature and reacted with alcohol and catalyst. After reaction, the mixture was transferred to a separating funnel and allowed to settle for 24 h to separate biodiesel, glycerol and catalyst phases. Biodiesel yield was calculated as the mass of biodiesel obtained divided by the mass of oil used, multiplied by 100.

2.4 Process-variable evaluation

The study evaluated the effects of alcohol-to-oil molar ratio, catalyst dose, reaction temperature and reaction time by varying one parameter while holding the others constant. The thesis reports molar ratios of 3:1, 6:1, 9:1, 12:1 and 14:1; catalyst doses from 1 to 6 g; reaction temperatures from 40 to 90 °C; and reaction-time experiments extending beyond 120 min. KOH and the alumina–chitosan nanocomposite were compared for both feedstocks.

3. Results and Discussion

3.1 Catalyst characterization

FTIR analysis of chitosan showed O–H, N–H, C–H, C–N and C–O-related bands. In the alumina–chitosan nanocomposite, O–H bands occurred at approximately 3841.21, 3826.90, 3742.03 and 3626.29 cm^{-1}, while N–H stretching was observed near 3495.13 and 3363.97 cm^{-1}. A C–H vibration was observed near 2931.9 cm^{-1} and a C–O band near 1080.17 cm^{-1}. The changes in band positions and intensities after alumina incorporation were consistent with interaction between alumina and chitosan functional groups.

SEM images showed that chitosan consisted mainly of relatively large, regular crystalline particles with few pores, whereas the alumina–chitosan nanocomposite contained smaller particles and a highly porous surface. XRD further differentiated the materials: chitosan showed broad features around 22°

ISSN:2584-2706 DOI: https://doi.org/10.5281/zenodo.21990862

and 16°, while the nanocomposite showed clearer features around 25° and 17°. Together, FTIR, SEM and XRD supported successful formation of a material distinct from the starting chitosan.

3.2 Feedstock and biodiesel properties

The extracted Carica papaya and Citrullus lanatus oils showed saponification values of 182.8 and 204.1, iodine values of 133.2 and 124.7, acid values of 7.4 and 6.3, and viscosities of 30.6 and 33.7 cSt, respectively. Following transesterification, viscosity decreased substantially to 4.70 cSt for Carica papaya ethyl ester and 3.96 cSt for Citrullus lanatus ethyl ester. The corresponding biodiesel densities were 868.4 and 879.8 kg/m³, while flash points were approximately 173 and 180 °C. The marked viscosity reduction demonstrates the expected conversion of high-viscosity triglyceride feedstock to lower-viscosity alkyl esters.

3.3 Effect of alcohol-to-oil molar ratio

Molar ratio	C. papaya + KOH (%)	C. lanatus + KOH (%)	C. papaya + nanocomposite (%)	C. lanatus + nanocomposite (%)
3:1	72.15 ± 0.70	49.50 ± 1.65	78.30 ± 0.40	54.60 ± 2.75
6:1	79.25 ± 0.50	58.00 ± 0.75	81.40 ± 0.60	63.20 ± 1.05
9:1	89.30 ± 0.40	76.30 ± 1.70	94.60 ± 0.30	81.60 ± 0.80
12:1	92.04 ± 0.55	81.20 ± 0.55	97.10 ± 0.95	83.40 ± 1.45
14:1	90.20 ± 0.85	78.04 ± 2.55	96.40 ± 1.05	79.20 ± 1.45

The yield increased as the alcohol-to-oil ratio increased to 12:1, then declined at 14:1. At 12:1, Carica papaya oil produced 97.10 ± 0.95% biodiesel with the nanocomposite compared with 92.04 ± 0.55% with KOH. For Citrullus lanatus, the corresponding yields were 83.40 ± 1.45% and 81.20 ± 0.55%. Excess alcohol beyond the optimum can complicate glycerol–ester separation and shift the apparent product distribution.

3.4 Effect of catalyst dose

Dose (g)	C. papaya + KOH (%)	C. lanatus + KOH (%)	C. papaya + nanocomposite (%)	C. lanatus + nanocomposite (%)
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	82.90 ± 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

Nanocomposite-catalyzed Carica papaya biodiesel reached 97.10 ± 1.05% at 4 g catalyst dose. The nanocomposite also produced high Citrullus lanatus yields around 3–4 g. Increasing catalyst beyond the optimum reduced yield, consistent with excessive solids promoting viscosity, gel formation or emulsion-related mass-transfer limitations.

3.5 Effect of reaction temperature and time

Biodiesel yield increased with temperature from 40 °C to a maximum at 80 °C and declined at 90 °C. At 80 °C, the nanocomposite-catalyzed Carica papaya system reached approximately 97.10%, while the nanocomposite-catalyzed Citrullus lanatus system reached approximately 83.40%. The homogeneous-catalyst systems were lower. Reaction-time experiments similarly showed increasing

ISSN:2584-2706 DOI: https://doi.org/10.5281/zenodo.21990862

conversion up to 120 min. At 120 min, the nanocomposite produced 97.10 ± 0.30% for Carica papaya and 83.40 ± 1.20% for Citrullus lanatus. Longer reaction times did not improve conversion and were associated with declining yield.

3.6 Overall catalyst performance

Across the investigated reaction variables, the alumina–chitosan nanocomposite generally outperformed KOH, with Carica papaya consistently producing the highest biodiesel yield. The porous morphology of the nanocomposite and the chemical interaction between alumina and chitosan may have increased the availability of catalytic sites. The use of a biologically derived chitosan precursor also provides a waste-valorization pathway that complements the renewable-fuel objective.

4. Conclusion

An alumina–chitosan nanocomposite synthesized using chitosan derived from Rhynchophorus phoenicis was successfully applied as a heterogeneous catalyst for biodiesel production from Carica papaya and Citrullus lanatus seed oils. FTIR, SEM and XRD confirmed modification of the chitosan after alumina incorporation. The optimum process conditions identified were a 12:1 alcohol-to-oil molar ratio, 4 g catalyst dose, 80 °C reaction temperature and 120 min reaction time. Under the investigated conditions, the nanocomposite generally achieved higher yields than KOH, and Carica papaya was the better-performing feedstock. The study demonstrates the potential of combining waste-derived chitosan with alumina to produce a heterogeneous catalyst for renewable biodiesel production.

5. Recommendations for Further Research

Further work should evaluate catalyst recovery and reuse over multiple cycles, quantify possible alumina or chitosan leaching, conduct detailed fatty-acid ester profiling, and assess engine performance and emissions. A techno-economic and life-cycle assessment would also be valuable for determining whether the catalyst and feedstocks can be scaled beyond laboratory production.

Declarations

Funding: No funding information was specified in the source thesis; the author should confirm this statement before submission.

Conflict of interest: The author should insert the appropriate conflict-of-interest declaration required by IJMSRT.

Data availability: Data supporting the article are derived from the author's doctoral research; the author should state the preferred availability arrangement at submission.

Author contributions: To be completed in accordance with the journal's authorship requirements.

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Editorial Note

This article has been extracted and reorganized from the uploaded PhD thesis as a focused journal manuscript. Before submission, verify the author affiliation/email, declarations, the journal's exact formatting requirements, and all bibliographic details against the complete thesis reference list. The thesis contains inconsistent use of “methanol” and “ethanol” in the methods/results narrative; this manuscript therefore uses the neutral term “alcohol” where necessary and preserves the reported 12:1 optimum rather than silently resolving the inconsistency.