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Exploring the Efficacy of Calcined Eggshell as a Heterogeneous Catalyst in Enhancing Biodiesel Production Through Transesterification of Jatropha Oil

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Abstract

The conventional use of homogeneous base catalysts in biodiesel production via transesterification has limitations, prompting researchers to explore heterogeneous catalysts. This study examines the effectiveness of calcined eggshell as a heterogeneous catalyst in biodiesel production from Jatropha oil. The catalyst's chemical properties were analyzed using X-ray Fluorescence (XRF) ARL QUANT'X EDXRF Analyzer (S/N 9952120) of Umaru Musa Yaraduwa University Katsina cental laboratory, revealing a primarily CaO composition. Transesterification was performed using varying concentrations (0.1-0.6 wt%) of calcined eggshell, and Fourier Transform Infrared (FTIR) spectroscopy confirmed the presence of esters in the transesterified samples. The results show that 0.3 wt% calcined eggshell yielded the highest biodiesel production rate of 96.51%, demonstrating the significant role of calcined eggshell as a heterogeneous catalyst in biodiesel production from Jatropha oil.

Keywords: Calcination, Eggshell, FTIR, Jatropha oil, Transesterification

INTRODUCTION

Biodiesel is one of the promising renewable sources of energy that has significant advantages over its counterpart (fossil diesel) in terms of technological production, biodegradability, non-toxicity, release of less greenhouse gases, free from sulfur free from aromatics among others (Ismail *et al.,* 2022).

Biodiesel can be produced from renewable sources both edible vegetable oils (pea nut, clove, sesame, palm cannel etc) and non-edible vegetable oils (Jatropha, castor, calabash, neem etc) (Gebremanian & Marchetti, 2018). It can also be produced using animal fats and waste cooking oil, but the use of animal fats with high saturated fatty acids which normally exist in a solid form at room temperature may cause problems in the production process, which makes its processing cost to be significantly higher than that of vegetable oils (Jamo *et al.,* 2023). Thus, vegetable oils are more favorable and draw a higher attention than animal fats (Koh & Ghazi, 2011; Ismail *et al.,* 2022). Pure vegetable oil works well as a fuel for diesel engines itself, as Rudolf Diesel demonstrate in his engine at the 1900 world`s fair with peanut oil as the fuel (Muhammad *et al.,* 2023).

The transesterification process using homogeneous catalysts has gained popularity for biodiesel production due to its sustainability and reliability. However, this method has several drawbacks, including the formation of soap that deactivates the catalyst, challenging catalyst removal, and the generation of significant wastewater. Furthermore, the reaction's reversibility leads to reduced biodiesel yields. These limitations render the use of homogeneous base catalysts economically and environmentally unsustainable (Shan *et al.*, 2015; Tan *et al.*, 2017).

To overcome the limitations of homogeneous catalysts, heterogeneous catalysts are being explored as a viable alternative. Heterogeneous catalysts offer several benefits, including reduced environmental pollution, simplified product purification, and easy separation of the catalyst from the reaction mixture. Additionally, they have a high potential for reusability, which enhances the economic feasibility of the process (Karabas, 2013; Sudsakorn *et al.*, 2017; Sundaramahalingam *et al.*, 2021).

The Jatropha plant, also known as the Physic plant, is a drought-resistant species from the Euphorbiaceae family that thrives in uncultivated areas across Africa. Its fruit consists of a green outer layer, a fleshy middle layer, and a hard inner shell. Notably, Jatropha is considered a promising source of biodiesel due to its high oil yield (1000 barrels per year per square mile) that can be easily converted into biodiesel without refining. Additionally, its hydrocarbons have a higher carbon atom count (16-18) compared to conventional fossil fuels, making it an attractive alternative (Kumar & Sharma, 2008; Belewu *et al.*, 2010; Shaaban *et al.*, 2016; Jamo *et al.*, 2023).

Wadiyat *et al.*, (2016) created heterogeneous catalysts from three different calcium oxide (CaO) sources for biodiesel production. The CaO catalysts were synthesized from limestone, calcium hydroxide, and calcium carbonate through thermal processing at 900°C in a muffle furnace. The results revealed that the limestone-derived CaO catalyst exhibited superior characteristics compared to the other two sources. The biodiesel yields obtained were: 89.98% for the limestone catalyst, 85.15% for the calcium hydroxide catalyst, and 78.71% for the calcium carbonate catalyst.

Qadriyya *et al.*, (2019) investigated the use of synthetic and eggshell catalysts for biodiesel production. They achieved a biodiesel yield of 35.20% using microwave power of 300 W, 1% synthetic catalyst, and a reaction time of 2 minutes. However, the highest biodiesel yield of 65.36% was obtained when using 1% eggshell catalyst, microwave power of 300 W, and a reaction time of 10 minutes with Calophyllum inophyllum L oil.

Adepoju *et al.*, (2021) investigated the use of catalysts derived from chicken foot bone powder (CFBP), catfish bone (CCB), and a mixed catalyst (CMCP) for biodiesel production. The results showed that these catalysts achieved high CaO-based yields of 93.52%, 91.24%, and 99.84%, respectively. The optimal conditions for biodiesel production were determined using a central composite rotatable design, resulting in a minimum acid value of 1.27 mg KOH/g oil. The maximum biodiesel yields of 93.54%, 91.87%, and 96.88% were obtained at specific reaction times, catalyst amounts, temperatures, and molar ratios. The mixed catalyst (CMCP) demonstrated superior recyclability and reusability compared to single catalysts over five cycles. The produced biodiesel met the recommended standards, and the study concluded that all tested catalysts were suitable for biodiesel production, with the mixed catalyst (CMCP) showing the best results.

In research conducted by Ismail *et al.*, (2022) using Jatropha oil and eggshell as heterogeneous catalyst, 94.3% of biodiesel was obtained at the application of 0.2wt% eggshell as catalyst using 1:6 oil to methanol ratio in 1hr at 60-65°C.

Despite the role of jatropha as feedstock for biodiesel and eggshell as heterogeneous catalyst, there is no single literature that show research conducted on the determination of catalytic performance of calcinated eggshell on jatropha oil. Due to this it can be concluded that there is a missing gap in the literature that has to be filled. Therefore, this paper wishes to explore the efficacy of calcined eggshell as a heterogeneous catalyst in enhancing biodiesel production through transesterification of jatropha oil.

METHODOLOGY

Sample Collection and Preparation

Eggshells were collected from restaurants and cleaned with tap water to remove any contaminants. They were then air-dried overnight at a temperature range of 29-37°C for two days. Following drying, the eggshells were ground into a fine powder using a mortar and pestle, and subsequently calcined in a furnace at 900°C for 1.5 hours to produce a calcined eggshell catalyst (Ismail *et al.*, 2022).

X-ray Fluoroscopy of Eggshell

The calcined eggshell was analyzed using X-ray fluorescence (XRF) characterization with an ARL QUANT'X EDXRF Analyzer (S/N 9952120). The XRF process involves bombarding the sample with X-rays, which ejects inner orbital electrons, exciting the atoms and producing high-energy radiation. The emitted radiation is then detected and integrated to produce characteristic spectral lines with varying intensities. These intensities are subsequently converted into elemental concentrations, providing a quantitative analysis of the sample's composition (Zakari *et al.*, 2024).

Transesterification of Jatropha Oil without Calcinated Eggshell

Initially, 60g of Jatropha oil was heated to 60-65°C in a 250ml conical flask using a hot magnetic stirrer plate. Meanwhile, 0.6g of NaOH was dissolved in 21ml of methanol and added to the oil mixture. The reaction mixture was then heated and stirred for 60 minutes at 65°C. After cooling for 40 minutes, the mixture separated into two distinct layers in a separating funnel. The upper layer consisted of biodiesel, while the lower layer comprised triglyceride fatty acid (Durumin-Iya *et al.*, 2024).

Transesterification of Jatropha Oil Using Calcinated Eggshell

The process involved heating 60g of Jatropha oil to 60-65°C in a 250ml conical flask using a hot plate with magnetic stirrer. Various concentrations ranging from 0.1wt% to 0.6wt% of calcined eggshell were dissolved in 21ml of methanol and added to the heated oil. The mixtures were then heated for 60 minutes and poured into separating funnels. After cooling for 40 minutes, the samples separated into two layers: biodiesel (upper layer) and triglycerol fatty acid (lower layer). This procedure was repeated for each catalyst concentration (Uba *et al.*, 2024).

Infrared Spectral Analysis of Transesterified Jatropha Oil

FTIR spectral analysis was conducted using a SHIMADZU FTIR-8400S Spectroscopy machine to identify the functional groups present in the sample. The sample was prepared as a thin film between two potassium bromide discs, allowing it to spread evenly. The FTIR machine generated radiation that passed through the sample, interferometer, and detector, producing a signal that was amplified and converted to a digital signal. The digital signal was then transferred to a computer, where Fourier transform was performed to analyze the spectral data (Ismail *et al.,* 2022).

Percentage of Biodiesel Yield

The percentage of biodiesel yield during the transesterification processes was determined using the relation below (Torres *et al.,* 2016; Durumin-Iya *et al.,* 2024).

$$Percentage\ of\ biodiesel\ yield = \frac{Mass\ of\ biodiesel\ produced}{Mass\ of\ oil\ used}\ X\ 100\% \qquad (1)$$

RESULTS AND DISCUSSION

XRF Analysis of Calcinated Eggshell

Table 1 reveals the XRF analysis which indicates the compounds composition of calcinated eggshell in terms of percentage.

Table 1: XRF result of eggshell.

S/N	Compounds	Percentage concentration (%)
1	CaO	96.115
2	SiO_2	1.210
3	P_2O_5	1.101
4	MgO	0.120
5	SO_3	0.050
6	Al_2O_3	0.034
7	$M_{n_2O_3}$	0.023
8	$F_{e_2O_3}$	0.017
9	SrO	0.015
10	K_2O	0.012
11	Others	0.301
12	Lost of ignition	1.002

Table 1 reveals the chemical composition of calcined eggshell, with CaO being the predominant compound at 96.115%. The remaining constituents are present in significantly lower concentrations, with K_2O having the lowest percentage at 0.012%. This indicates that calcined eggshell is primarily composed of calcium oxide. These findings are consistent with previous studies by Ayodeji *et al.*, (2018), Yasar (2019), Ismail *et al.*, (2022), and Durumin-Iya *et al.*, (2024), which also reported similar chemical compositions for calcined eggshell."

Percentage of Biodiesel Yield

Table 2 indicates the amount of biodiesel obtained while transesterifying Jatropha oil with and without the use of calcinated eggshell as heterogeneous catalyst using equation 1.

Table 2: Percentage of Biodiesel Produced

S/N	Catalyst used (wt%)	Biodiesel produced (%)
1.	0.00	65.01
2.	0.10	75.51
3.	0.20	86.01
4.	0.30	96.51
5.	0.40	85.33
6.	0.50	73.25
7.	0.60	62.11

It can be seen from Table 2 that, the biodiesel produced tend to increase at regular interval after the application of calcinated eggshell as catalysts from 0.00wt% to 0.3wt% i.e from 65.01% to 96.51% at the interval of 10.5%, but on the application of 0.4wt% to 0.6wt% the biodiesel yields tends to decrease drastically at irregular intervals. This critically shows that 0.3wt% of calcinated eggshell tend to be the best amount to be used as heterogeneous catalyst on jatropha oil due to the facts that amount over that tends to decrease the yield of production. In research conducted by Adepoju *et al.,* (2021); Ismail *et al.,* (2022) and Durumin-Iya *et al.,* (2024) similar results were obtained.

The results of Table 2 can be represented diagrammatically on Figure 1 as biodiesel produced (%) against catalysts used (wt%).

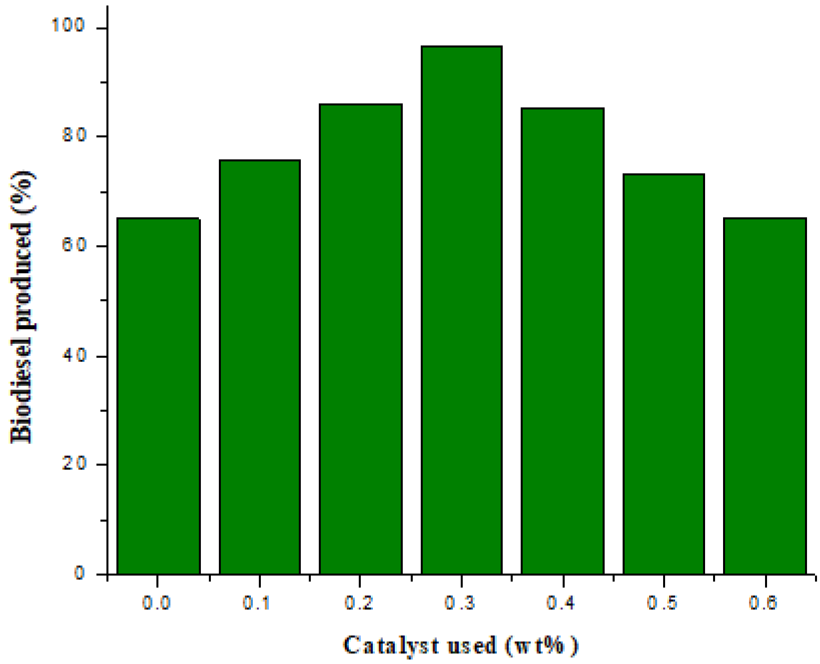

Figure 1: Biodiesel Produced against Catalyst Used.

Figure 1 indicates that the percentage of biodiesel produced increased as the amount of catalyst used increased from 0.00wt% to 0.30wt% and decreases with increase in the amount of calcinated eggshell used above 0.3wt%. This has justified the positive impact of calcinated eggshell as heterogeneous catalysts in producing biodiesel at the application of 0.3wt% using jatropha oil as feedstock.

FTIR Spectra of Transesterified Jatropha Oil

Figure 2 displays the FTIR spectrum, which graphs transmittance percentage against wavenumber, revealing the absorption patterns of specific molecules in the transesterified Jatropha oil. This spectrum provides insight into the molecular composition of the oil, showcasing the characteristic absorption peaks of various functional groups present in the sample.

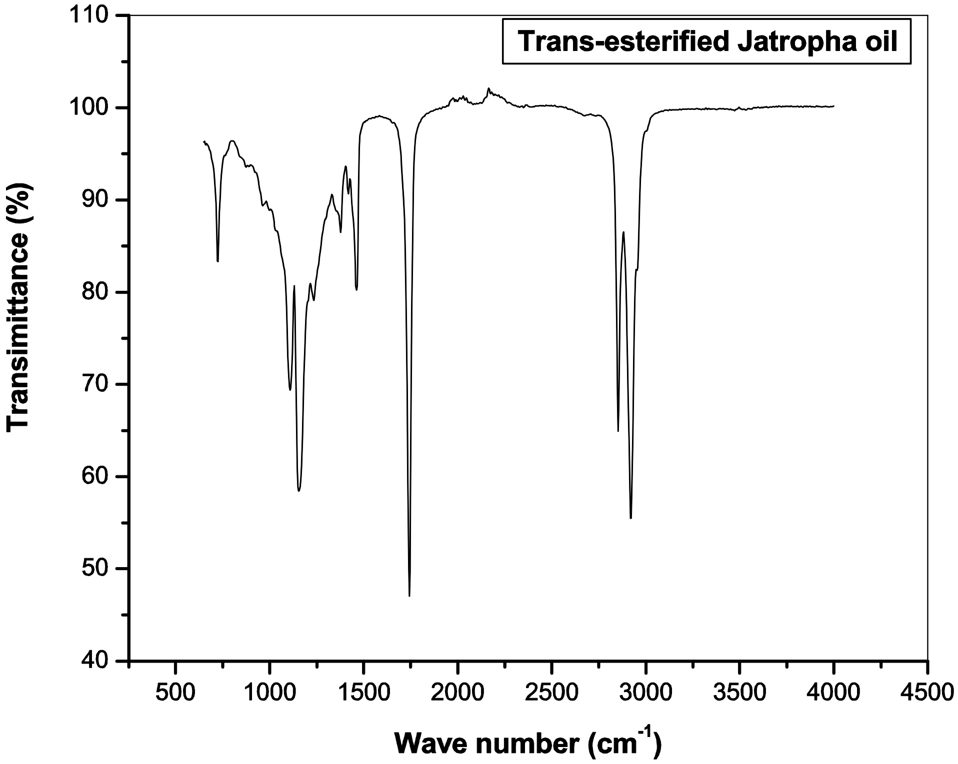

Figure 2: FT-IR Spectra of Trans-esterified Jatropha oil

Figure 2 reveals the FTIR spectrum, where specific wavenumber ranges correspond to particular chemical bonds. The peaks between 650-1400 cm^{-1} indicate C-O bonds, while those between 1500-1800 cm^{-1} signify C=O bonds, characteristic of esters. The ranges 2700-3000 cm^{-1} and 3000-3700 cm^{-1} correspond to C-H stretching and OH bonds, respectively. Notably, the peak at 1755 cm^{-1} confirms the presence of esters, specifically biodiesel, which aligns with the findings of Ismail *et al.,* (2022), validating the successful production of biodiesel.

CONCLUSION

Calcined eggshell can be effectively utilized as a heterogeneous catalyst in biodiesel production via the transesterification process, using jatropha oil as the feedstock. This is evident from the fact that a yield of 96.51% biodiesel was achieved by applying 0.3wt% calcined eggshell, with an oil-to-methanol ratio of 1:6, within a reaction time of 1 hour at a temperature range of 60-65°C."

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