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Full Length Research Article

THE IMPACT OF $CUCO_3$ NANO PARTICLES ON THE RHEOLOGY OF BIODIESEL EXTRACTED FROM CASTOR OIL

*[1]S.H. Gwadabe, [2]H.U. Jamo, [3]U.I. Ismail, [4]F.U. Musa, [5]A.R. Uba

[1]Kano Electricity and Distribution Company (KEDCO), No: 1 Niger Street, Post office Road, Fagge, Kano State
[2]Department of Physics, Aliko Dangote University of Science and Technology Wudil, P.M.B. 3244, Kano State
[3]Department of Physics, Sule Lamido University, P.M.B. 048 Kafin Hausa, Jigawa State
[4]Science and Technical Schools Board, BUK road, Kano state
[5]Rabiu Musa Kwankwaso CARS, Tudun Wada, Kano State

*Corresponding Author Email Address: gwadabes@gmail.com

ABSTRACT

Transesterification tend to be the most adopted method of producing biodiesel, but the outcome is associated with high viscosity especially at low temperature. Viscosity is the most important rheological property of biodiesel. This paper investigates the impact of Cupper II Carbonate ($CuCO_3$) nanoparticles on the rheology of biodiesel extracted from castor oil. The $CuCO_3$ nanoparticles has been subjected to Xray fluoroscopy (XRF) in order to determine its elemental composition. The crude castor oil was purified, trans-esterified and $CuCO_3$ nanoparticles were dispersed in the trans-esterified oil with concentration ranging from 0.1wt% to 1.0wt% in 0.1wt% interval. Fourier Transform Infrared spectra (FTIR) was used to examine the functional groups of the transesterified sample. The samples were subjected to viscosity measurement using digital viscometer at a temperature range of 20^0C to 100^0C at the interval of 20^0C. The XRF characterization shows that the $CuCO_3$ nanoparticles used is pure due to the fact that its percentage concentration tends to be 92.11%. FTIR analysis indicate that the ester (biodiesel) was achieved at 1744.4 peak. The viscosities of the samples decrease as the temperature increases and with the increase in the amount $CuCO_3$ concentration. The viscosity tends to be best at the application of 0.3wt%. This shows that $CuCO_3$ nanoparticles can be used as biodiesel additive using castor oil as feedstock.

Keywords: Castor oil, $CuCO_3$, FTIR, XRF, Viscosity

INTRODUCTION

A global energy crisis appears imminent due to the relentless growth in energy demand, driven by industrial expansion and population increases worldwide, with fossil fuels being the primary energy source (Muhammad *et al.,* 2023; Toshkent, 2023). The burning of fossil fuels has had a detrimental impact on the environment, releasing harmful gases that contribute to rising environmental temperatures, ultimately leading to devastating consequences such as global warming (Rehman *et al.,* 2021). This, in turn, has resulted in a range of negative effects, including decreased oxygen levels in oceans, melting of polar ice caps and glaciers, coral bleaching, and droughts (Upandhyay, 2020).

To mitigate the environmental impacts and economic burdens of fossil fuel use, a worldwide effort has been underway to develop and promote renewable and more economically viable energy sources, such as solar energy, hydroelectric power, wind power, and biofuels, as alternatives for domestic and industrial applications (Kudelin & Kutcherov, 2021; Ismail *et al.,* 2022)

Biodiesel is a biodegradable and non-toxic with low Sulphur emission fuel produced from renewable biological sources such as vegetable oils and animal fats. Biodiesel (fatty acids alkyl esters) can be seen as a promising alternative fuel to replace petroleum-based diesel as it is purely produced from renewable sources (Uba *et al.,* 2024). Vegetable oils such as soybean, sunflower, avocado, cotton seed, castor oil and many more are more suitable biodiesel feedstock compared to animal fats as they cannot solidify at room temperature (Alsairi *et al.,* 2023; Durumin-Iya *et al.,* 2024).

Castor oil is a vegetable oil extracted from castor beans, characterized by its colorless to pale yellow appearance, distinct flavor, and aroma. With a boiling point of 313°C (595°F) and a density of 0.961 g/cm3, castor oil is a unique blend of triglycerides, predominantly comprising ricinoleates (approximately 90% of fatty acids), as well as oleates and linoleates (Dias *et al.,* 2013). This versatile oil and its derivatives are extensively used in various industries, including the production of soaps, lubricants, brake fluids, paints, dyes, coatings, inks, plastics, waxes, polishes, nylon, pharmaceuticals, and perfumes (Singh & Jiswal, 2019).

Copper (II) carbonate or cupric carbonate is a chemical compound with chemical formula $CuCO_3$ which at ambient temperatures exist as ionic solid (salt) consisting of copper (II) cations Cu^{2+} and carbonate anions CO^{2-} (Abdullah, *et al*., 2022).

Viscosity, a measure of a liquid's resistance to flow, is determined by assessing the time it takes for a specific volume of oil to flow through a standardized orifice. There are two primary types of viscosity: kinematic viscosity (cSt) and dynamic viscosity (mm2/s or mPa.s) (Zakari *et al.,* 2024). Viscosity is the most critical rheological property of biodiesel, as it significantly impacts the operational efficiency of fuel injection systems, particularly in low-temperature conditions (Jamo *et al.,* 2023). According to a study by Raja *et al.,* (2011), the viscosity of Jatropha biodiesel was found to decrease significantly from 57 to 4.73 cSt at 6:1 molar ratio of methanol to oil, 0.92% NaOH catalyst, 60ºC reaction temperature and 60 minutes of reaction time. Similarly, Ali *et al.,* (2013) reported a viscosity of 5.9 cSt for neem oil biodiesel. Djibri *et al.,* (2015) also measured the viscosity of neem oil, finding it to be 35.8 mm^2/s at a temperature of 40°C. Furthermore, Musa *et al.,* (2022) observed that the viscosity of transesterified neem oil decreased substantially from 96 mPa.s at 10°C to 24 mPa.s at 100°C.

The high values of viscosity associated with the transesterified vegetable oil tend to create operational problem in engine starting, unreliable ignition and deterioration in thermal efficiency. Several materials were used as biodiesel additive so as to reduce the amount of viscosity presence on the biodiesel and improved its quality (Zakari *et al.,*2024). Özgür *et al.,* (2015) found out that the

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viscosity of rapeseed oil biodiesel decreases with the addition of MgO and SiO_2 nanoparticles. Similarly, Jamo *et al.,* (2019) shows that the dynamics viscosity of castor oil decrease with increase in temperature and with the addition of Na_2CO_3 nanoparticles especially with 0.25wt%. But the use of $CUCO_3$ nano particles as additive on transesterified castor oil has not been reported in the literature. Therefore, the aim of this paper is to determine the impact of $CUCO_3$ nano particles on the rheology of biodiesel extracted from castor oil.

METHODOLOGY

Sample Preparation

Purification

A 200ml sample of castor oil was measured using a measuring cylinder and pre-heated to 70°C using a hot magnet stirrer equipped with a thermometer. Next, 1.5ml of citric acid was added to the heated oil and the mixture was continuously heated and stirred for 900 seconds at 70°C. Following this, 4ml of 8% NaOH solution (prepared by dissolving 8g of NaOH in 100ml of distilled water) was added to the oil and the mixture was heated and stirred for an additional 900 seconds at 70°C. The mixture was then transferred to a hot magnetic stirrer and heated to 70°C, after which 2g of silica hydrogel was added and the mixture was heated and stirred for 1800 seconds. The temperature was then increased to 85°C, and 4g of activated carbon was added to each 100ml of the oil sample. The mixture was heated and stirred for 180 seconds before being separated using filter paper (Ismail et al., 2022).

Transesterification

To produce biodiesel, 60g of crude castor oil was measured into a 250ml conical flask and heated to 60-65°C on a hot magnetic stirrer plate. In a separate step, 0.6g of NaOH was dissolved in 21ml of methanol and heated for 60 minutes on the hot magnetic stirrer plate, maintaining a temperature of 65°C. The NaOH-methanol solution was then combined with the heated castor oil and stirred uniformly. After cooling for approximately 40 minutes, the mixture separated into two distinct layers: biodiesel (upper layer) and triglycerol fatty acid (lower layer). The biodiesel was subsequently separated from its byproduct (Zakari *et al.,* 2024).

Transesterified Nano Fuid Preparation

The $CuCO_3$ nanoparticles of size 10-20nm with the volume concentrated of 0.1wt %, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt% 0.9 wt% and 1.0 wt% were dispersed into the 10g of transesterified castor oil and stirred for 2-3 hours using magnetic stirred which is then subjected to analysis (Musa *et al.,* 2022).

Characterization

XRF of $CuCO_3$

The elemental composition of $CUCO_3$ was analyzed using X-ray fluoroscopy on an ARL QUANT'X EDXRF Analyzer (S/N 9952120). The process involved directing incoming X-rays from the XRF machine onto a 1g sample of $CUCO_3$, causing the electrons in the inner orbitals of the atoms to be ejected. This led to the excitation of the atoms, resulting in the emission of high-energy radiation, including photons, protons, and electrons. The emitted radiation was then detected and integrated to produce varying intensity levels, which were subsequently converted into elemental concentrations. Finally, the concentrations were displayed on the monitor, providing a detailed elemental analysis of the $CUCO_3$ sample (Haschke, 2014).

Infrared Spectral Analysis of Transesterified Castor Oil

Fourier Transform Infrared (FTIR) spectral analysis was conducted at the Umaru Musa Yaradua University Katsina central laboratory using SHIMADZU FTIR-8400S to identify the functional groups present in the sample. During the analysis, a thin film of the sample was prepared by placing a drop of the liquid sample between two potassium bromide discs, which were made from single crystals. The sample was then spread evenly into a thin film. The FTIR machine's source generated radiation that passed through the sample and interferometer, ultimately reaching the detector. The detected signal was amplified and converted into a digital signal using an amplifier and analog-to-digital converter, respectively. Finally, the digital signal was transferred to a computer, where a Fourier transform was performed to analyze the spectral data (*Ismail et al.,* 2022).

Measurement of Viscosity

The viscosity of various castor oil samples was measured using a Brookfield viscometer DV-II+PRO (S/N 621-216) at the Umaru Musa Yaradua University, Katsina central laboratory. The viscometer was operated at a speed range of 50 rpm with a spindle size of 2. The measurement procedure involved pouring the crude castor oil into a beaker, selecting the angular speed on the viscometer, and recording the displayed viscosity value. This process was repeated for purified, transesterified castor oil, and transesterified castor oil with added CuCO3 nanoparticles at concentrations of 0.1wt%, 0.2wt%, 0.3wt%, 0.4wt%, 0.5wt%, 0.6wt%, 0.7wt%, 0.8wt%, 0.9wt%, and 1.0wt% (Nura *et al.,* 2023).

RESULTS AND DISCUSSION

XRF OF $CuCO_3$

Table 1: The percentage concentration of the element

Element	**$CuCO_3$**	**O**	**SiO**	**Al_3**	**SO_3**	**Fe_2O_3**	**CaO**	**Cl**	**LOI**
Conc. %	92.11	2.19	1.91	0.74	0.69	0.45	0.22	0.19	1.50

Base on Table 1, $CuCO_3$ result has the highest percentage concentration of 92.11%, followed by O with 2.19%, then SiO with 1.91%, then Al_3 with 0.74%, then SO_3 with 0.69% followed by Fe_2O_3 with 0.45% then CaO with 0.22% followed by Cl with 0.19% and finally LOI of 1.50%. It can be seen that $CuCO_3$ Nanoparticle used to carry out this work has a purity of 92.11%. This is Similar to the result obtained by Saxena *et al.,* (2019).

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FT-IR Spectra
Figure 1 shows the FTIR spectrum for transmittance (%) against the wave number (cm^{-1}) based on the amount of light absorbed by specific molecules present in the transesterified castor oil.

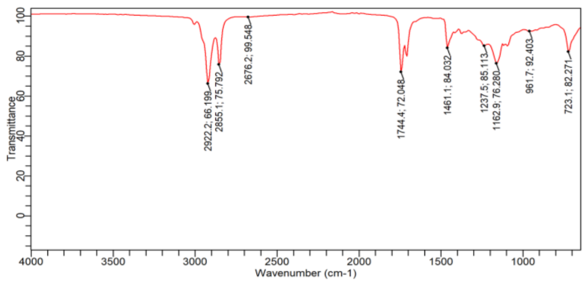

Figure 1: FT-IR Spectra of trans-esterified castor oil

The FTIR spectral analysis revealed specific band vibrations corresponding to various functional groups. The band values between 650-1400 cm^{-1} indicated the presence of C-O bonds, while values between 1500-1800 cm^{-1} represented C=O bonds. Additionally, the range of 2700-3000 cm^{-1} corresponded to C-H stretching, and 3000-3700 cm^{-1} indicated OH bonds. Notably, the C-O and C=O bonds indicated the presence of ester or ether groups in the sample, as reported by Ismail *et al.,* (2022). Specifically, the peak at 1744.4 cm^{-1} in Figure 1 confirmed the presence of an ester group, which is consistent with the findings of Durumin-Iya *et al.,* (2024).

Viscosity of the samples
Figure 2 is the graph of viscosity against temperature of crude, purified and transesterified castor oil.

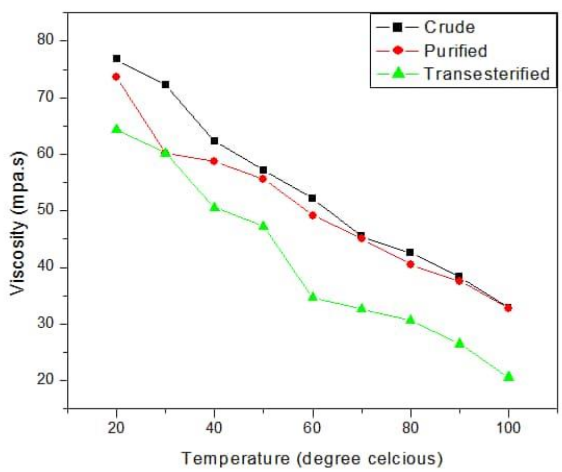

Figure 2: Graph of viscosity against temperature of crude, Purified and Transesterified Castor oil.

It can be seen that the viscosity of the crude castor oil decreases from 76.8 mpa.s to 32.9 mpa.s as the temperature increases from 20°C to 100°C. It can equally be seen that as the crude castor oil purified, the viscosity further decreases from 73.7 mpa.s to 32.7 mpa.s as the temperature increases from 20°C to 100°C. This is as a result of the reduction of the molecular agglomeration of the oil. In a similar development, the viscosity of trans-esterification castor oil decreases from 64.3 mpa.s to 20.6 mpa.s as the temperature increases from 20°C to 100°C this was attributed due the reaction between the castor oil and the methanol in the presence of sodium hydroxide. This was similar to the result obtained by Jamo *et al.,* (2023) and Zakari *et al.,* (2024).

Figure 3 reveals the viscosity against temperature for transesterified castor oil with addition of $CuCO_3$ with concentration of 0.1wt% to 1wt% for an interval of 0.1wt%.

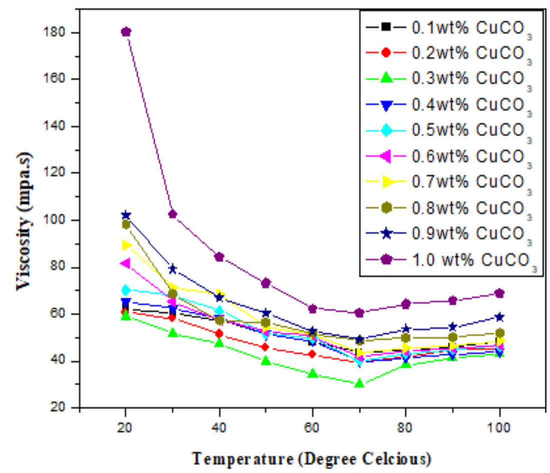

Figure 3: Graph of viscosity against temperature of Transesterified Nano fluid

It was clear from Figure 3 that when 0.1% of $CuCO_3$ was added the viscosity decreases from 62.4 mpa.s to 43.8 mpa.s with increase in temperature and rises to 48.1 mpa.s when the temperature was above 70°C, similarly with addition of 0.2% of $CuCO_3$, the viscosity further decreases from 60.7 mpa.s to 39.7 mpa.s as the temperature increases, and also rises to 45.1 mpa.s when the temperature was above 70°C, when the viscosity of the concentration increases to 0.3% of $CuCO_3$ it produces a better result. Furthermore, 0.4% of $CuCO_3$ to 1.0% of $CuCO_3$ indicates that the viscosity increases as the Nano-fluid increases, meanwhile the viscosity decreases as the temperatures increases. Likewise, the viscosity increases when the temperature rises over 70 degrees celsius. These results were in agreement with the results obtained by Durumin-Iya *et al.,* (2024).

In addition, it can be deduced from figure 3 that viscosities of the samples decrease with increase in temperature and the percentage concentration shows a significant effect in the enhancement of the viscosity of the fluid.

Conclusion
The FTIR spectral analysis confirmed the successful production of biodiesel via trans-esterification while XRF analysis shows that pure $CuCO_3$ nanoparticles was used as additive as it dominates the compound concentration with 92.11%. The rheological study conducted through viscosity measurements of various samples (crude castor oil, purified castor oil, transesterified castor oil and transesterified castor nano fluid) revealed a temperature-dependent decrease in viscosity, as well as a concentration-dependent decrease with the addition of $CuCO_3$. Notably, the optimal $CuCO_3$ concentration for minimizing viscosity was found to be at the addition of 0.3wt%.

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