
EFFECTS OF ADDITION OF CeO₂ NANO PARTICLES ON THE PHYSICAL PROPERTIES OF JATROPHA OIL

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Abstract

Biodiesel is gaining more and more importance as an attractive fuel due to the depleting fossil fuel resources. Chemically biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feed stock like vegetable oils and animal fats. This paper reports the results of experimental investigations on the influence of the addition of cerium oxide in the nanoparticle form on the rheological properties and the performance of biodiesel extracted from jatropha oil through trans-esterified process. The crude castor oil was purified, trans-esterified and nanoparticles were dispersed in the trans-esterified oil with concentration ranging from 0.25% to 1.0% in 0.25% interval. Fourier Transform Infrared spectra (FTIR) was used to examine the structures of the samples, The viscosity, pour point and the flash point were studied. It was found out among other things that small amount of 0.5% of CeO₂ nanoparticles in the oil could improve the physical properties of the fluid. It could be concluded that the optimum amount of CeO₂ nanoparticles to be used for nanofluid is 0.5%. Hence, the trans-esterified jatropha containing 0.5% CeO₂ nano particles has the potential to used as a lubricant oil.

Key words: Biodiesel, CeO₂, Jatropha, Nano Particles, Rheology

Introduction

Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly [1-17]. Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. Economic growth is always accompanied by commensurate increase in the transport. The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional one [18-20]. Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial [10]. One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine [11]. Biodiesel has many advantages include the following: its renewable, safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, non-flammable and nontoxic, reduces tailpipe emissions, visible smoke and noxious fumes and odors. The use of biodiesel has grown dramatically during the last few years. Feedstock costs account for a large percent of the direct biodiesel production costs, including capital cost and return [12- 16].

One way of reducing the biodiesel production costs is to use the less expensive feedstock containing

fatty acids such as inedible oils, animal fats, waste food oil and by products of the refining vegetables oils [13]. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel to the commercial filling stations. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative. With no competing food uses, this characteristic turns attention to *Jatropha curcas*, which grows in tropical and subtropical climates across the developing world [14].

The fact that *Jatropha* oil cannot be used for nutritional purposes without detoxification makes its use as energy or fuel source very attractive as biodiesel. In Madagascar, Cape Verde and Benin, *Jatropha* oil was used as mineral diesel substitute during the Second World War [15]. *Jatropha curcas* (Linnaeus) is a multipurpose bush/small tree belonging to the family of Euphorbiaceae. It is a plant with many attributes, multiple uses and considerable potential. The plant can be used to prevent and/or control erosion, to reclaim land, grown as a live fence, especially to contain or exclude farm animals and be planted as a commercial crop. It is a native of tropical America, but now thrives in many parts of the tropics and sub-tropics in Africa/Asia [16]. The seeds of *Jatropha* are good source of oil, which can be used as a diesel substitute after trans-esterification. They are used also in medicines, soap and cosmetics manufacture in various tropical countries [17]. The use of nano- particles in *Jatropha* biodiesel (nano fluid) is expected to improve the rheological properties of *Jatropha* biodiesel. Thus, the study of the rheological properties of a nano composite system may yield an invaluable tool in structure characterization and property prediction, but the connection of structures to flow is not completely understood. The aim of this research therefore is to study the effects of cerium oxide rheology of *jatropha* biodiesel.

MATERIALS AND METHODS

Materials

Chemicals

The materials and reagents used in carrying out the research are as follows: crude *Jatropha curcas* (Linnaeus), 8 % sodium hydroxide (NaOH), 64 % citric acid ($C_6H_8O_7$, purity: 99.7 %), Cerium Oxide reagent, activated carbon, acetone, and distilled water (H_2O).

Equipment

The equipments used in carrying out this study are: magnetic stirrer with thermostatically controlled rotary hot plate (IKA C-MAG HS10), Brookfield Digital viscometer {Brookfield,RVDV-I}, thermometer, measuring cylinder, Cheng Sang Vacuum oven (MA 0-30L), Digital weight balance (AND model GT2000 EC), beaker, 24 cm filter paper, funnel, Digital stop watch, sampling bottles, spatula.

Methodology

Sample Purification

The crude *Jatropha curcas* oil was purified through the following procedure; 200 ml of the neem oil was measured using measuring cylinder; the oil was pre-heated to 70 °C using hot magnet stirrer with thermometer. 1.5 ml citric acid was measured and added to the heated oil sample and continuously heated and stirred for 15 minutes at 70 °C. 4 ml of 8 % NaOH (by dissolving 8 g NaOH in 100 ml of distilled water) was then be added to the oil and continuously heated and stirred for 15 minutes at 70 °C. The mixture was then transferred to the vacuum oven where it was heated at 85 °C for 30 minutes. Then the mixture was taken back to hot magnetic stirrer and heated to 70 °C after which a 2 g of silicone reagent was added while it was being heated and stirred for 30 minutes. Then the temperature was increased to 85 °C and 4 g of activated carbon was added to



each 100 ml of the oil sample, heated and stirred for 30 minutes. Then the mixture was separated using filter paper.

Trans-esterification

60g of the *Jatropha curcas* oil was measured in 250ml of conical flask and was heated and stirred to a temperature of 60-65°C on a hot magnetic stirrer plate, 0.6g of NaOH was measured using the electronic weight machine and allowed to dissolve in 21ml of methanol and then allowed to heat for 60 minutes with the stirrer on the hot magnetic plate. After 60 minutes of uniform stirring and heating on the hot magnetic plate maintaining a temperature of 65°C, it was then poured into the separating funnel through a glass funnel. The mixture was allowed to cool for about 40 minutes. Afterwards, it was observed that it separated into two liquid layers. The upper layer is the biodiesel and the lower layer is triglycerol fatty acid. The biodiesel was then separated from its byproduct.

Nano-fluids Preparation

The cerium oxide Nano-particles powder was purchased from SkySpring Nanomaterials, Inc., U. S. A, the size of the nano-particles is 10-20nm and the surface was modified with Epoxy Group and its dispersible as mentioned by the company. Nano-fluids are prepared by two step process. The volume concentration of 0.25%, 0.5%, 0.75%, and 1% of powdered nano-particles and trans-esterified *Jatropha curcas* oil was made respectively. To make the nano-particles more stable and remain more dispersed, each sample was stirred for 3-4 hours using magnetic stirrer, then the samples were taken for analysis.

Viscosity

Viscosity was measured using Brookfield viscometer in a speed range of 50 rpm with spindle size of 2 since a small quantity of the sample is to be measured. The following are the detailed procedure for viscosity measurement; the sample was poured into a beaker, the spindle was fixed and the machine was started, the angular speed was selected on the viscometer and the viscosity was read and recorded the same procedure was repeated for the purified and trans-esterified oils.

Pour point

Using an improvised method, the experimental procedures of pour point measurement for both crude and purified oil are enumerated below;

The cylindrical test tube was filled with the crude *Jatropha curcas* oil to a specific level mark (5 ml). The test tube was clamped with a wooden clamp carrying the thermometer then placed in a bath of crushed ice (ice bath) and allowed to cool at a specified rate interval of 3 °C for flow characteristics the lowest temperature at which the movement of the oil is observed within 5 s is taken as pour point on the thermometer. ASTM 1999, D 97. The same procedure was repeated for the purified and trans-esterified oils.

Flash point

The flash point for both crude, purified and trans-esterified oil was also measured;

A 100 ml conical flask was filled to a specific mark level (10 ml) with *Jatropha curcas* neem oil and heated at 14 to 17 °C / min (25 to 30 °F / min) on the hot plate until the temperature is 56 °C (100 °F) below the expected flash point, the rate of temperature changes was then reduce to 5 to 6 °C /min (9 to 11 °F/ min) and the test flame was applied for every 2 °C (5 °F) until the oil burn for at least 5 s. The flash point was taken at the lowest temperature when an application of the flame test caused the vapor above the sample to ignite. ASTM 1999, D 92. The same procedure was repeated for the purified and trans-esterified oil.

Result and Discussion

All materials that show flow behavior are referred to as fluid. In all fluid, there are frictional forces between the molecules which display a certain flow resistance and normally measured as viscosity. Viscosity is a transport property which referred to the resistance of materials to flow. The graph of viscosity versus temperature of crude, pure and trans-esterified oils are given in Figure 1. As the temperature of oil is increased, its viscosity decreases and it is therefore able to flow more readily. The viscosity of the trans-esterified oil is lower than that of the purified and crude oils. Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The viscosity of the crude oil is higher than that of purified oil while that trans-esterified is least.

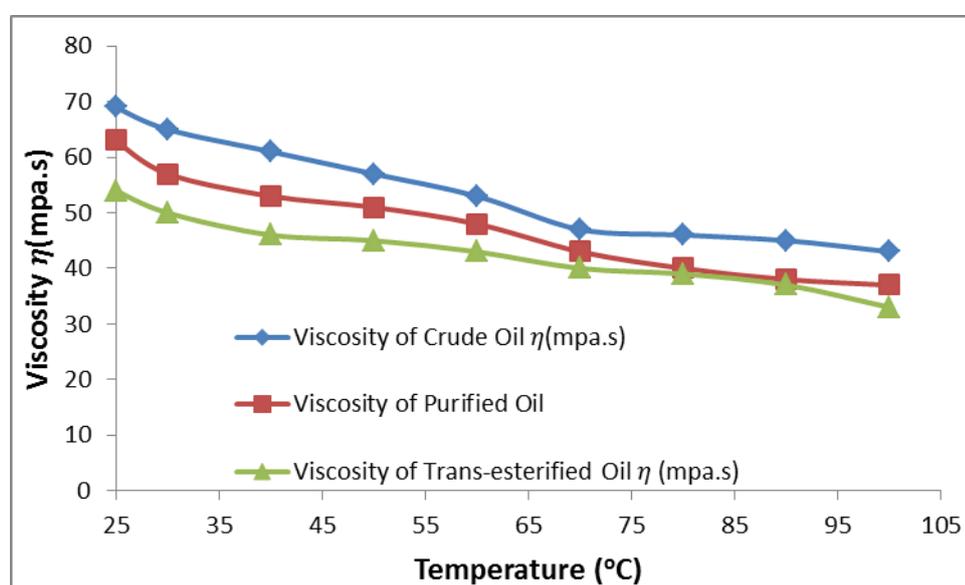


Figure 1: Viscosity Versus Temperature of Jatropa Oil

It is apparent from Figure 2 that viscosity decreases as the temperature increases. The Viscosity defined as resistance liquid to flow. Viscosity increased with molecular weight but decreased with increasing unsaturated level and temperature [22]. At room temperature kinematic viscosity of the sample higher than at a relatively high temperature. The viscosity of Jatropa oil seed must be reduced for biodiesel application since the dynamic viscosity of biodiesel were very low compared to vegetable oils. High viscosity of the jatropa oil seed are not suitable if its use directly as engine fuel, often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubricating oil as a result of contamination by the vegetable oils. Different method such as preheating, blending, assisted methanol transesterification and supercritical methanol transesterification are being used to reduce the viscosity and make them suitable for engine applications.

This research adopted Transesterification of jatropa in order to make it suitable for use as a lubricant in transformers. It could be seen from the graph that the addition of nano 0.5wt% CeO_2 particles in the transesterified oil causes the viscosity to decrease. It is established that addition of nanoparticles in the lubricant more than 0.5wt%, may enhance the viscosity of lubricant [22]. The viscosity of lubricant plays a significant role in the bearing system. When a bearing rotates at high speed, the heat generated due to large shear rates in the lubricant film raises its temperature, which

lowers the viscosity of the lubricant. When a bearing rotates at the high eccentricity ratio, the reduction in load capacity due to decrease in viscosity is 40% less when compared with the load capacity obtained in isoviscous lubricants [23]. But the presence of nanoparticles (0.75wt% - 1wt%) will enhance the viscosity of lubricant and in turn load capacity of the bearing and this reduction in load capacity can be compensated to some extent, by the addition of nanoparticles.

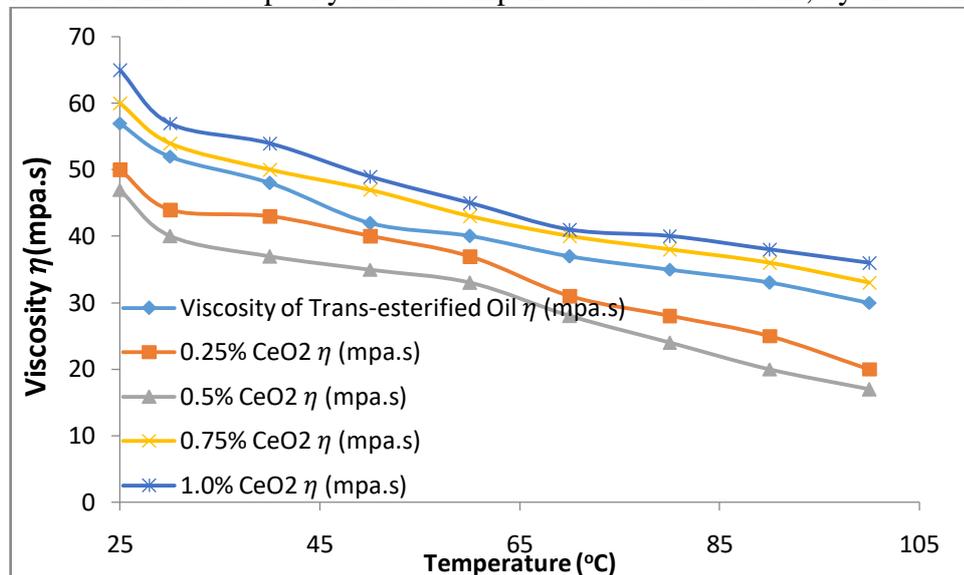


Figure 2: Viscosity versus Temperature of CeO₂ Nano -Jatropha fluid

Pour point; the pour point of lubricating fluid gives an indication of the temperature below which it may not be possible to pour or remove the oil from its container. It was found that the pour point of the crude is 9°C while that of the purified oil is 7°C, for Trans – sterified is 4°C and for Trans - esterified Trans - esterified (0.25w% CeO₂) is 2°C. This implies that the Trans - esterified (0.25w% CeO₂) oil has lower pour point due to the removal of gums in form of phospholipids from the crude oil, it well known that lubricating fluid with low pour point is better especially in a cool weather condition.

Flash point; The flash point test is sensitive in the study of lubricating fluid, because it gives an indication of the flammability of an oil. They may also be used to provide a quantitative indication of contamination with more flammable materials. The flash point of the crude, purified, Trans – esterified and Trans - esterified (0.25w% CeO₂) oils are 122°C, 129°C, 133°C and 140°C respectively, the higher temperatures of the Trans - esterified (0.25w% CeO₂) oil indicates its usefulness for lubrication and it may be as a result of removing the flammable materials from the crude oil, as well as the addition of 0.25w% CeO₂ nano particles.

The FTIR analysis is employed in order to identify the presence of CeO₂ nanoparticles in the based trans-esterified castor oil, the FTIR spectra of all the samples were obtained using SHIMADZU FTIR-8400S Spectrophotometer at National Research Institute For Chemical Technology (NARICT) Zaria. It is an established fact that the fundamental vibrations of solids particle (fingerprint) are localized in the low frequency region (<1200 cm⁻¹) of the midrange (400-4000cm⁻¹) of the infrared spectrum. So the FTIR spectra of purified jatropha and nano-fluid are presented below.

The FTIR spectra shown in Figures 3- 6, displayed the typical bands that exist in natural esters. The band with a peak at 2924 cm⁻¹ describes C-H stretching. The bands with peaks at 1759 cm⁻¹ and 1188 cm⁻¹ are vibration of C=O and C-O. These are typical bands that describe esters. The bands with peaks at 1450 cm⁻¹ and 709 cm⁻¹ are due to methylene scissoring and rocking.

The addition of CeO₂ nanoparticles is expected to change the FTIR spectra of the fluid. Meanwhile

no visible change was observed when the concentration of the nanoparticle in the fluid was 0.25%. After increasing the concentration of the nanoparticles to 0.5%, a band was observed around 3950 cm^{-1} . The nanoparticle band around 1111 is believed to be shrouded ester C-O band.

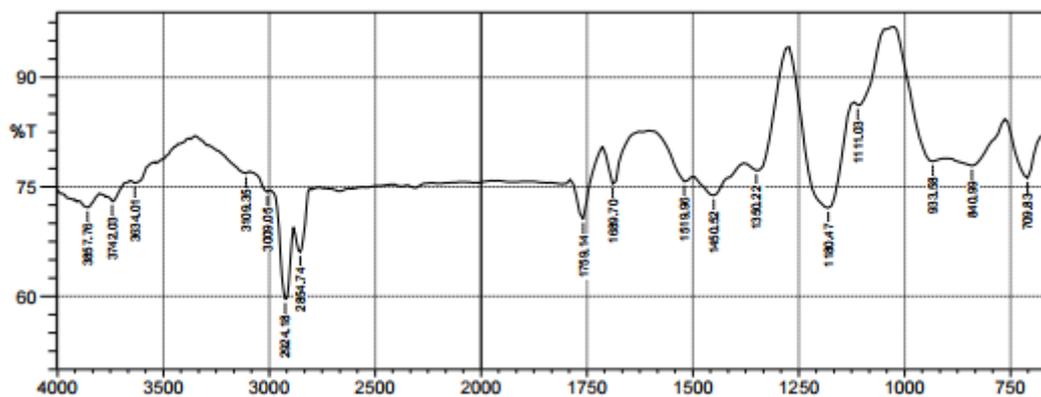


Figure 3: FT-IR Spectra of crude jatropha oil

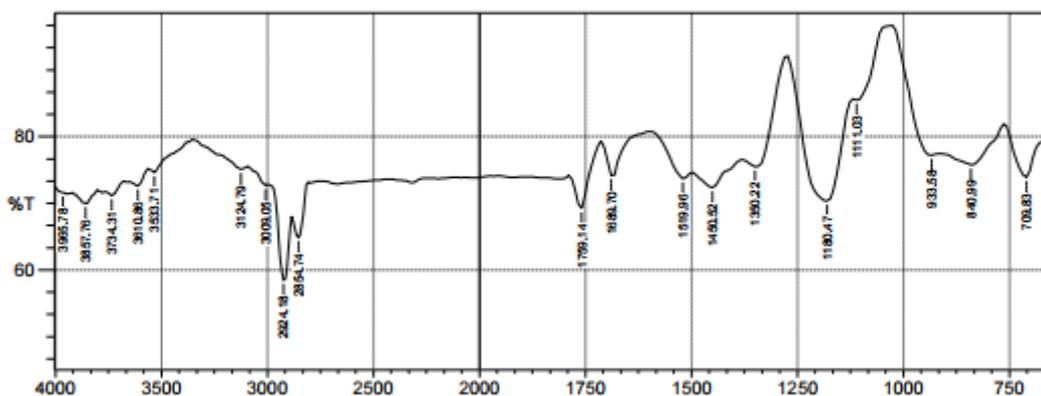


Figure 4: FT-IR Spectra of purified jatropha oil

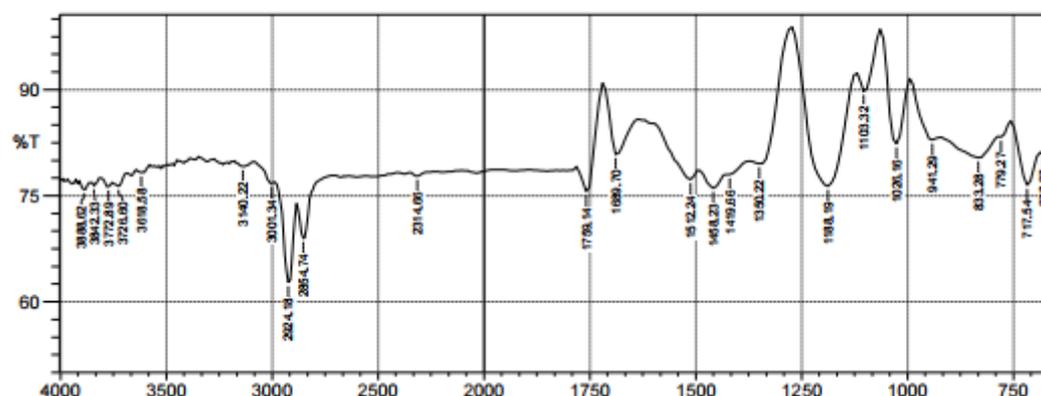


Figure 5: FT-IR Spectra of trans-esterified jatropha oil

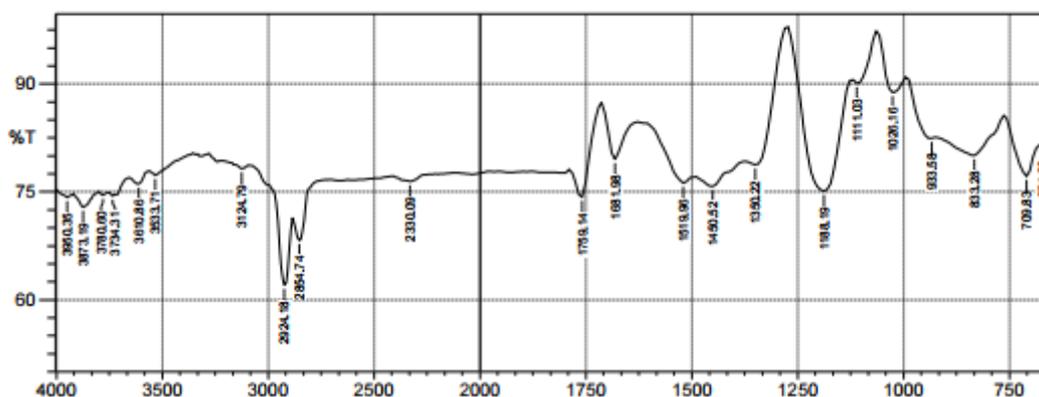


Figure 6: FT-IR Spectra of 0.25wt% nanoparticles concentration in jatropha oil

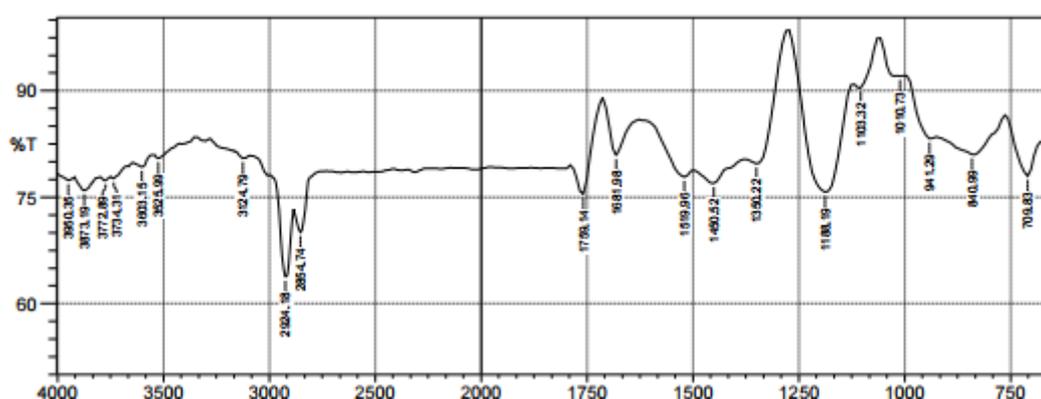


Figure 7: FT-IR Spectra of 0.5wt% nanoparticles concentration in castor oil

Conclusion

The nanofluid with 0.5% of CeO₂ appears to be more suitable for insulation as the sample was observed to have lowest viscosity. Increasing the concentration of CeO₂ nanoparticle above 0.5% was observed to have initiated an increase in viscosity. This may make the fluid with higher nanoparticles suitable as a base fluid for conducting drilling fluid. To fully characterize the fluid for specific industrial application, more tests need to be performed on other relevant parameters.

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