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Full Length Research Article

EFFECT OF ADDITION OF TITANIUM OXIDE NANOPARTICLES ON THE VISCOSITY OF OLIVE OIL

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ABSTRACT
Biodiesel has drawn more and more attention in recent years because it is renewable and has less detrimental effects on environment as compared with conventional diesel derived from petroleum. Biodiesel obtained from renewable olive can be used in diesel engines or blended at various proportions with petroleum diesel as fuel. This work investigates the influence of titanium oxides nanoparticles on the viscosity of olive oil. The crude olive oil was purified, transesterified and titanium oxides nanoparticles were dispersed in the transesterified olive oil with concentration ranging from 0.2% to 1.0% in 0.2% interval. Fourier Transform Infrared spectra (FTIR) was used to examine the structures of the samples. The viscosity, of the crude, purified and transesterified olive oil were studied. It was found out among other things that small amount of titanium oxides (0.4%) nanoparticles in the oil could improve the physical properties of the fluid. This is due to the fact that high reactive surface area responsible for more complete combustion due to reduction in ignition delays. It was also found out that the use of nanoparticle not only helps in effective mixing of components, but also provides close contact between them, which facilitates the diffusion of reactants to the surface and increase their reactivity. The nanofluid with 0.4% concentration of titanium oxides appears to have optimum physical property. The measured values of viscosity coincide with the standard values.

Keywords: Nanoparticles, Olive oil, Purification, Transesterification, Titanium oxide, Viscosity,

INTRODUCTION
The depletion of hydrocarbon fuel reserves, the increase in environmental pollution, and unstable energy prices have triggered a search for clean and sustainable energy resources (Sekoai *et al.,* 2019; Attia *et al.*, 2022; Nawaz *et al.,* 2022; Rezania *et al.,* 2022; Annamalai *et al.,* 2016; Sayyed 2022; Wang *et al.,* 2009; Jamo *et al.,* 2019a; Jamo *et al.,* 2019b; Jamo *et al.,* 2019c; Jamo *et al.,* 2019d; Mendecka *et al.,* 2020; Kroehong *et al.,* 2016; Abdullah *et al.,* 2022; Qi et al., 2009; Sulaiman et al., 2019). Biofuel development initiatives are widely being implemented in many countries in order to mitigate these challenges (Mahlia *et al.,* 2022). 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 ones (Aghababaie *et al.,* 2017). 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 (Dantas *et al.,* 2020). One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Abdullah *et al.,* 2022). The use of biodiesel has grown dramatically during the last few years. Feedstock costs account for a large percentage of the direct biodiesel production costs, including capital cost and return (Natarajan *et al.,* 2014). Furthermore, the use of nanoparticles as an additive is expected to enhance the properties of biodiesel. Several researchers (Gohain *et al.,* 2020) have found that nanoparticle inclusion shows better properties over micron size particles such as availability of high reactive surface area responsible for more complete combustion due to reduction in ignition delays. Annamalai *et al.,* (2016) indicates that the use of nanoparticle not only helps in effective mixing of components, but also provides close contact between them, which facilitates the diffusion of reactants to the surface and increase their reactivity. The facts revealed from various studies mentioned above shows that blending of diesel fuel with micro/nanoparticle have significant effect on fuel properties and combustion characteristics. Jones *et al.,* (2011) investigated the combustion behavior of nanoscale metal and metal oxide particles of aluminum (n-Al and n- Al_2O_3) in ethanol, from their experimental work they concluded that during combustion of a stable suspension of n-Al in ethanol, the amount of heat released increases almost linearly with n-Al concentration, but that trend was observed only when n-Al concentration was kept above 3%. The addition of n-Al_2O_3 particles in ethanol does not contribute any heat in the total heat of combustion as they do not participate reactively in the combustion process. Furthermore, other burning parameters such as mass burning rates and ignition delay are also influenced by the amount of heat released. D'Silva *et al.,* (2015) in his experiment observed that diesel blended with magnesia additives shows appreciable reduction in flash point, viscosity, freezing point and pollutant emissions. A group of researchers (Saxena et al., 2017; Jamo *et al.,* 2019d; Mendecka *et al.,* 2020) also investigated the combustion behavior of different nanoadditives with liquid fuels have the near common consensus that these secondary energy carriers definitely enhance the ignition and combustion characteristics. However, the effects of titanium oxide nanoparticles on rheological properties of olive oil has not been reported. The use of titanium oxide nanoparticles is expected to boost the viscosity of olive oil. Hence this research wishes to study the effects of titanium oxide nanoparticles on viscosity of olive oil.

MATERIALS AND METHODS

Chemicals
The materials and reagents used in carrying out the research are as follows: crude olive oil, 8 % sodium hydroxide (NaOH), 64 % citric acid (C6H8O7, purity: 99.7 %), titanium oxide reagent, activated carbon, acetone, and distilled water (H2O).

Equipment
The equipment 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.

Fourier-transform Infrared Spectroscopy (FTIR)
The Fourier transform infrared (FTIR) spectroscopy machine was used for the identification of the functional group. Liquids samples in the form of thin film were placed between two potassium bromide discs made from single crystals for FT-IR analysis. A drop of the liquid is placed on one of the discs and the other is placed on top, this spreads the sample into a thin film. The machine used was SHIMADZU FTIR-8400S Spectrophotometer at National Research Institute for Chemical Technology (NARICT) Zaria.

Sample Purification
The olive oil was purified through the following procedure; 200 ml of the olive oil was measured using measuring cylinder; the oil was pre-heated to 70 ^{o}C using hot magnet stirrer with thermometer. Then 1.5 ml citric acid was measured and added to the heated oil sample and continuously heated and stirred for 15 minutes at 70 ^{o}C. 4 ml of 8 % NaOH (by dissolving 8 g NaOH in 100 ml of distilled water) was then added to the oil and continuously heated and stirred for 15 minutes at 70 ^{o}C. The mixture was then transferred to the vacuum oven where it was heated at 85 ^{o}C for 30 minutes. Then the mixture was taken back to hot magnetic stirrer and heated to 70 ^{o}C after which a 2g of silicone reagent was added while it was being heated and stirred for 30 minutes. Then the temperature was increased to 85 ^{o}C and 4 g of activated carbon was added to each 100 ml of the oil sample, heated and stirred for 30 minutes. The activated carbon was derived from charcoal. The carbon was purchased from local supplier and is commonly used to filter contaminants. Then the mixture was separated using filter paper.

Trans-esterification
60g of the olive 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 weighing machine and allowed to dissolve in 21ml of methanol and then added to the oil and continue heating 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 triglycrol fatty acid. The biodiesel was then separated from its by product.

Nano-fluids Preparation
The titanium oxide nanoparticles powder was purchased from Sky Spring Nanomaterials, Inc., U. S. A, modified with Epoxy Group and its dispersible as mentioned by the company. Nano-fluids are prepared by two step process. The volume concentrations of 0.2%, 0.4%, 0.6%, 0.8% and 1% of powdered nanoparticles and purified oil were made respectively. The volume of the purified oil is kept constant. To make the nanoparticles more stable and remain more dispersed, each sample was stirred for 3-4 hours using magnetic stirrer, then the samples were taken for analysis.

Samples Viscosity Measurement
Viscosity was measured using Brookfield viscometer at 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 all the purified olive oil samples.

RESULTS AND DISCUSSION

Effect of Temperature on Viscosity of Olive Oil
Figures 1 and 2 shows the graph of viscosity versus temperature of the crude, purified, transesterified oil and nano-transesterified olive oil. The viscosity decreases with purification and transesterification. Similarly, the addition of titanium oxide further decreases the viscosity of the fuel. At the addition of 0.4% titanium oxides nanoparticles, least viscosity values were achieved. Viscosity is the main property that plays an important role in the combustion of fuel. The direct injection in the open combustion chamber through the nozzle and pattern of fuel spray decides the ease of combustion and thermal efficiency of the engine. Too low viscosity can lead to excessive internal pump leakage whereas system pressure reaches an unacceptable level and will affect injection during the spray atomization. The effect of viscosity is critical at low speed or light load conditions.

The viscosity of biodiesel is typically higher than that of petrodiesel often by factor of two, the viscosity increases as the percentage of biodiesel increases. Viscosity is greatly affected by temperature, many of the problems resulting from high viscosity are most noticeable under low ambient temperature and cold start engine condition (Annamalai *et al.,* 2016; Sayyed 2022). Viscosity increases with chain length of either the fatty acid or alcohol moiety in a fatty ester or in an aliphatic hydrocarbon. The increment in viscosity over a certain number of carbons is smaller in aliphatic hydrocarbons than in fatty compounds (Abdullah *et al.,* 2022; Qi et al., 2009). It could be seen from Figure 1 that the viscosity keep decreasing as the temperature increases. While in Figure 2 the viscosity decreases as the temperature and the addition of titanium oxide nanoparticle increases to particular point. As the addition reaches 0.4% the viscosity increases, this is as result of agglomeration of the nanoparticles.

Viscosity increases with the addition of nanoparticles above 0.4% at the temperature of 70 ^{o}C, and also the chain length of either the fatty acid or alcohol moiety in a fatty ester or in an aliphatic hydrocarbon. The increase in viscosity over a certain number of carbons is smaller in aliphatic hydrocarbons than in fatty compounds. The viscosity of unsaturated fatty compounds strongly depends on the nature and number of double bonds with double bond position affecting viscosity less. Terminal double bonds in

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aliphatic hydrocarbons have a comparatively small viscosity-reducing effect. Branching in the alcohol moiety does not significantly affect viscosity compared to straight-chain analogues. Free fatty acids or compounds with hydroxy groups possess significantly higher viscosity. The viscosity range of fatty compounds is greater than that of various hydrocarbons comprising petrodiesel. The effect of nanoparticles, a sulfur-containing compound found in petrodiesel fuel, on viscosity of toluene is less than that of fatty esters or long-chain aliphatic hydrocarbons.

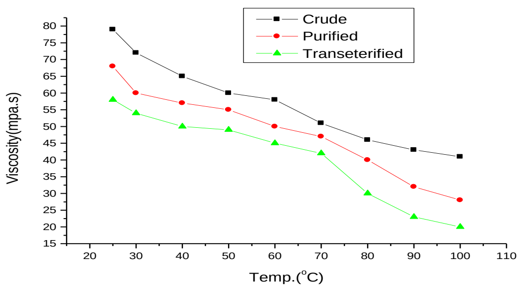

Figure 1: Viscosity versus Temperature of Olive Oil

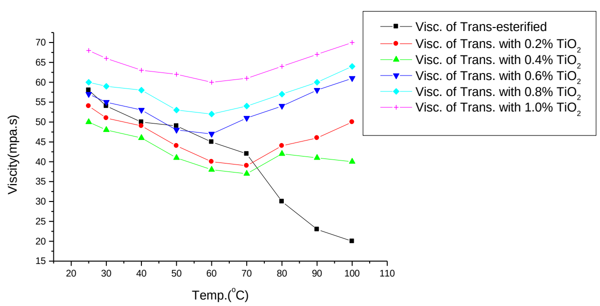

Figure 2 Viscosity versus Temperature of TiO_2 Nano -Olive fluid

FTIR Spectra of Purified Olive Oil

The displayed FTIR Spectra result in both Figure 3 and 4 shows the bands that exist in natural esters. The bands with peaks at 2924.18cm^{-1} and 2854.74cm^{-1} describe methylene C-H censoring. Stretch and methylene C=H censoring. Stretch respectively. While the band with peak at 1103.32cm^{-1} describes cyclic ethers, large rings, C-O stretch which originates from C-O-C (esters). This particular band describes esters. Lastly, in Figure 4, relatively strong band with peak at 1458.23 cm^{-1} (methylene C-H bend) and a relatively weak band with peak at 1365.65 cm^{-1} (methyl –CH3) plus a band with peak around 720 cm^{-1} in all describe methylene rocking vibration. Similar results was reported by Jamo *et al.,* 2019.

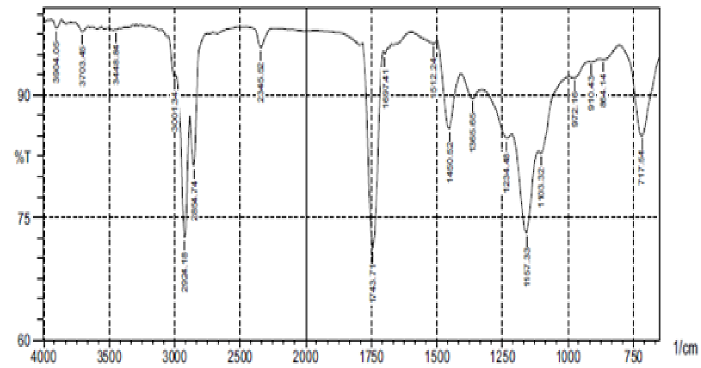

Figure 3 FTIR Spectra of Purified Olive Oil

FTIR Spectra of Transesterified Olive Oil

A similar result analyses holds for the FTIR spectra of the trans-esterified as show in Figure 4 except with significant changes which makes no difference in the end result analyses. A relatively strong band with peak at 1450.52 cm^{-1} (methylene C-H bend) and a relatively weak band with peak at 1365.65 cm^{-1} (methyl –CH3) plus a band with peak around 720 cm^{-1} in all, still describe methylene rocking vibration.

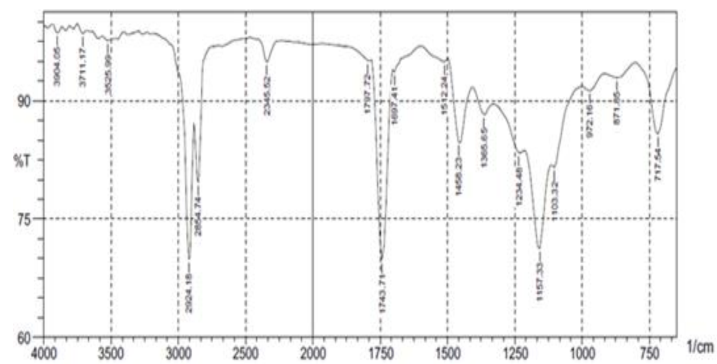

Figure 4: FTIR Spectra of Trans-esterified Olive

CONCLUSION

The rheological properties of transesterified olive oil was studied as function of temperature and the addition of nanoparticles. The relationship between viscosity and the addition of titanium oxides nanoparticles in the transesterified olive oil shows that the viscosity decreases as the addition of nanoparticles increases. The addition of 0.4% titanium oxides nanoparticles in the transesterified olive oil exhibit higher properties. Addition of nanoparticles above 0.4% brings about high viscosity values. The viscosity of unsaturated fatty compounds strongly depends on the nature and number of double bonds with double bond position having (affecting viscosity) this can be removed lesser effect on viscosity. Terminal double bonds in aliphatic hydrocarbons have a comparatively small viscosity-reducing effect. Branching in the alcohol moiety does not significantly affect viscosity compared to straight-chain analogues. Free fatty acids or compounds with hydroxy groups possess significantly higher viscosity. The viscosity range of fatty compounds is greater than that of various hydrocarbons comprising petrodiesel. The higher viscosity of biodiesel refers to a main reason which is the higher molecular weight of the biodiesel than diesel. The measured values of viscosity coincide with the standard values.

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