International Journal in Physical and Applied Sciences
Volume 06 Issue 06, June 2019 ISSN: 2394-5710 Impact Factor: 4.657
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

Influence of Na_2CO_3 Nanoparticles on the Physical Properties of Castor Oil.

H. U. Jamo
Department of Physics, Kano University of Science andTechnology Wudil, P.M.B. 3244 Kano

A. Aliyu
Department of Physics, Kano University of Science andTechnology Wudil, P.M.B. 3244 Kano

B. Yusuf
Department of Physics, Ahmadu Bello University, Zaria

Abstact
Effort has being on around the world to find alternative fluid for industrial application. Vegetable oil seems to be a perfect alternative but the use of most of the vegetable oil as feedstock posed a challenge to its use for industrial purpose. The recent trend is attempt to develop lubricantfluid from non-edible seed oil. This work investigates the influence of nanoparticles on the physical properties of castor oil. The crude castor oil was purified, trans-eterified 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 Na_2CO_3(0.25%) nanoparticles in theoil could improve the physical properties of the fluid. The nanofluid with 0.25% concentration of Na_2CO_3 appears to have optimum physical property.

Key words: Biodiesel,Na_2CO_3, Castor Oil, Nano Particles, Viscosity

Introduction

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 [1-20]. Biodiesel obtained from renewable castor can be used in diesel engines or blended at various proportions with petroleum diesel as fuel [2]. It consists of monoalkyl esters that are usually produced by transesterification of plant oil with methanol or ethanol. It has similar and sometimes better physical and chemical properties than petroleum diesel, such as higher flash point, ultra-lower sulphur concentration, better lubricating efficiency and few pollutants produced [3-6]. However, biodiesel is expensive due to the high price of plant oil and some processing technological issues, such as catalyst and equipment. Therefore, little commercial biodiesel is used in Nigeria. The raw materials exploited commercially by some developed countries are rapeseed, soybean, palm, sunflower, coconut and linseed oils [5,4]. The fraction of raw materials for world commercial biodiesel production is rapeseed oil 84%, sunflower oil 13%, palm oil 1%, soybean oil and others 2% [7].
Recently, many researchers focused their attention on fuel formulation technique for achieving better performance and emission characteristics. Among the recent fuel additives to biodiesel, the nanoparticles as additive in biodiesel has emerged as a new promising fuel additive for achieving utmost improvement in the performance and level best reduction of exhaust emission. Dreizin [8] observed that the nanoparticles dispersed test fuels shows better thermo physical properties due to its higher surface to volume ratio and acts as an oxygen buffer with

respect to NOx emission. Later, Kenneth et al. [9] observed that nanoparticles enhance the heat transfer rates due to its higher specific surface area. Idriss [10] experimentally studied the promotion of cerium oxide nanoparticles with ethanol and revealed that nanoparticles can be used as a fuelborne additive in hydrocarbon liquid fuels. Later Farfaletti et al. [11] employed ceria nanoparticles as additive in diesel emulsion fuel and found significant reduction of Particulate Matter, CO, and UBHC emission. Kao et al. [12] studied the working characteristics of a single cylinder diesel engine by using aluminium nanoparticles of 3 and 6% volume separately in diesel and found significant reduction of fuel consumption, smoke and NO emission. Arul Mozhi Selvan et al. [13] conducted experiments in computerized single cylinder, four stroke, DI variable compression ratio engine by using cerium oxide nanoparticles as additive in diesel and biodiesel-ethanol blends and observed substantial reduction of exhaust emission with marginal improvement in the brake thermal efficiency. Meantime Sajith et al. [14] conducted experiments in a naturally aspirated, four stroke, single cylinder, water cooled compression ignition engine to study the effect of cerium oxide nanoparticles dispersed at 20 to 80 ppm in Jatropha biodiesel for evaluating the engine performance and emission characteristics and resulted with significant reduction of NOx by 30% and unborn hydrocarbon (UBHC) by 40% for cerium oxide nanoparticles dispersed test fuel, besides percentage improvement of brake thermal efficiency by 1.5% (nano).

One of the recently popularity gaining methods to vary the physicochemical properties and combustion characteristics of a hydrocarbon fuel is the use of additives, which are found to be especially effective in nanoparticle form, due to the enhancement of the surface area to volume ratio. In an experimental research, the influence of the addition of cerium oxide in the nanoparticle form on the major physicochemical properties and the performance of biodiesel were studied. The physicochemical properties of the base fuel and the modified fuel formed by dispersing the catalyst nanoparticles by ultrasonic agitation are measured using ASTM standard test methods [16]. The effects of the additive nanoparticles on the individual fuel properties, the engine performance, and emissions are studied, and the dosing level of the additive is optimized [17]. Comparisons of the performance of the fuel with and without the additive are also presented. The cold temperature properties of biodiesel do not show significant variation, due to the addition of cerium oxide nanoparticles. Engine tests with the modified biodiesel at different dosing levels (20–80 ppm) of the additive showed an improvement in the efficiency of the engine. The flash point and the viscosity of biodiesel were found to increase with the inclusion of the cerium oxide nanoparticles. The emission levels of hydrocarbon and NOx are appreciably reduced with the addition of cerium oxide nanoparticles [18]. The aim of this study is to investigate the influence of Na_2CO_3 nanoparticles on the physicalproperties of castor oil. The crude castor oil will be purified, trans-esterified and nanoparticles will be dispersed in the purifiedoil with concentration ranging from 0.25% to 1.0% in 0.25% interval. Fourier Transform Infrared spectra (FTIR) will be used to examine the structures of the samples, The physical properties such as viscosity,pour point and flash point were studied.

MATERIALS AND METHODS

Materials

Chemicals

The materials and reagents used in carrying out the research are as follows: crude castor oil, 8 % sodium hydroxide (NaOH), 64 % citric acid ($C_6H_8O_7$, purity: 99.7 %), Na_2CO_3 reagent, activated carbon, acetone, and distilled water (H_2O).

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.

Methodology

Sample Purification

The crude castor oil was purified through the following procedure;200 ml of the castor oil was measured using measuring cylinder; the oil was pre-heated to 70 ^oC 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 ^oC.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 ^oC.The mixture was then transferred to the vacuum oven where it was heated at 85 ^oC for 30 minutes.Then the mixture was taken back to hot magnetic stirrer and heated to 70 ^oC after which a 2 g 0f silicone reagent was added while it was being heated and stirred for 30 minutes.Then the temperature was increased to 85 ^oC and 4 g of activated carbon was added to each 100 ml of the oil sample, heated and stirred for 30 munites.Then the mixture was separated using filter paper.

Trans-esterification

60g of the crude castor 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 minute 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 minute. 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 it byproduct.

Nano-fluids Preparation

The Na_2CO_3 Nano-particles powder was purchased from SkySpringNanomaterials, 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 purified castor oil was made respectively. To make the Na_2CO_3 nano-particles more stable and remain more dispersed, each sample was stirredfor 3-4 hours using magneticstirrer, then the samples were taken for analysis.

Samples measurement

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 castor oil.

Pour point

Using an improvised method, the experimental procedures of pour point measurement for crude, purified and trans-esterified oils are enumerated below;the cylindrical test tube was filled with the crude castor 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 ºC 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-esterifiedcastor oils.

Flash point

The flash point for crude, purified and trans-esterified oils was also measured;A 100 ml conical flask was filled to a specific mark level (10 ml) with crude castor oil and heated at 14 t0 17 ºC / min (25 to 30 ºF / min) on the hot plate until the temperature is 56 ºC (100 ºF) below the expected flash point, the rate of temperature changes was then reduce to 5 to 6 ºC /min (9 to 11 ºF/ min) and the test flame was applied for every 2 ºC (5 ºF) 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 trans-esterified castor oils.

Result and Discussions

Figure 2 shows the effects of temperature onviscosity of crude, pure and trans-esterified. As shown in the figure, the viscosities, as expected, decrease with increasing temperature and there are similar trends for all fuels and the blends in the studied temperature range [12] .The biodiesel obtained from the castor oil (Figure 2) presents a lower viscosity than the purified and the crude castor oil because of the transesterification process. At least with respect to base catalysis, two factors may be responsible for the observed yields attained with castor oil. In the first place, the free fatty acids present in the castor oil used may have led to the neutralization of part of the catalyst present, thus reducing the formation of methoxides and producing soaps within the reaction medium. Not only would mass transfer during the reaction be reduced by the formation of soaps, but also their presence during the product recovery step would exacerbate the problem of phase separation.8 Second, the hydroxyl group at C-12 of ricinoleic acid may be converted, in basic medium, to an alkoxide. The generation of this anionic species may compete with the formation of methoxide species and consequently reduce the yield of ester.10 It is important to mention that this alkoxide probably is not effective for the transesterification reaction, using conventional catalysts.
The viscosity behavior is one of the important issues in the study of finished products. In other words, it is constituted by the changes in the form and in the flow of a material. The real fluids, liquids and gases, present a certain resistance to the flow or deformation, resulting from the viscosity of the material. For gases, the viscosity is related to the transfer of impulse because of the molecular agitation. The viscosity of the liquids is more related to the cohesion forces among the molecules.

,

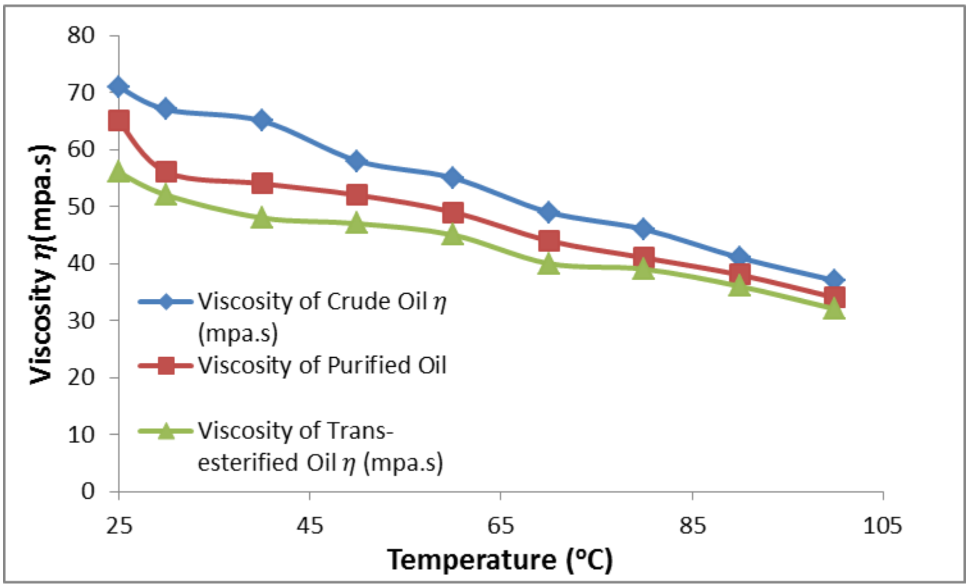

Figure 1: Viscosity Versus Temperature of Castor Oil

Figure 2 shows the plot of viscosity versus temperature, the viscosity decreases with the increase in temperature and also with increase in nano particles concentration. The viscosity decreases as the temperature increases from 10^{O}C to 70^{O}C. One can see that the viscosity increases with increasing Na_2CO_3 until 2.5% concentration. As the temperature increases above 70^{O}C the viscosity increases. This is as a result of the fact that as the amount of nanoparticles increases in the fluid, more nanoparticles are driven to the liquid surface and try to get closer to each other. As a result, a strong, cohesive force exerted between the molecules and resulting higher surface tension of nanofluids.

Petroleum based Diesel fuels have different chemical structures than vegetable oils. Diesel fuel contains only carbon and hydrogen atoms, which are arranged in straight chain or branched chain structures as well as aromatic configurations. Vegetable oils contain up to three fatty acids linked to a glycerin molecule with ester linkages and is called triglycerides. The fatty acids vary in their carbon chain length and in numbers of double bonds. There was little difference between the gross heat content of any of the vegetable oils [11]. Heat contents were 88% of that of no. 2 Diesel. Transesterification is the process of using an alcohol (e.g. methanol) in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, and nano particles to break chemically the molecule of the raw renewable oil into methyl or ethyl esters of the renewable oil, with glycerin as a byproduct. The transesterification reactions of the vegetable oils in the supercitical methanol proceeds under the same reaction mechanism as that of using liquid methanol in the catalytic transesterification method. The reaction proceeds without any catalyst as follows:

Triglycerides + Methanol Glycerin = Methyl esters
In this reaction, a some amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters, as the proposed product [6]. The variables affecting the methyl ester yield during the transesterification reaction, such as molar ratio of alcohol to vegetable oil nano particles and reaction temperature, were investigated. Figure 2 shows the plot of viscosity versus temperature, the viscosity decreases with the increase in temperature and also with increase in nano particles concentration. The viscosity decreases as the

temperature increases from 10^{O}C to 70^{O}C. One can see that the viscosity increases with increasing Na_2CO_3 until 2.5% concentration. As the temperature increases above 70^{O}C the viscosity increases. This is as a result of the fact that as the amount of nanoparticles increases in the fluid, more nanoparticles are driven to the liquid surface and try to get closer to each other. As a result, a strong, cohesive force exerted between the molecules and resulting higher surface tension of nanofluids.

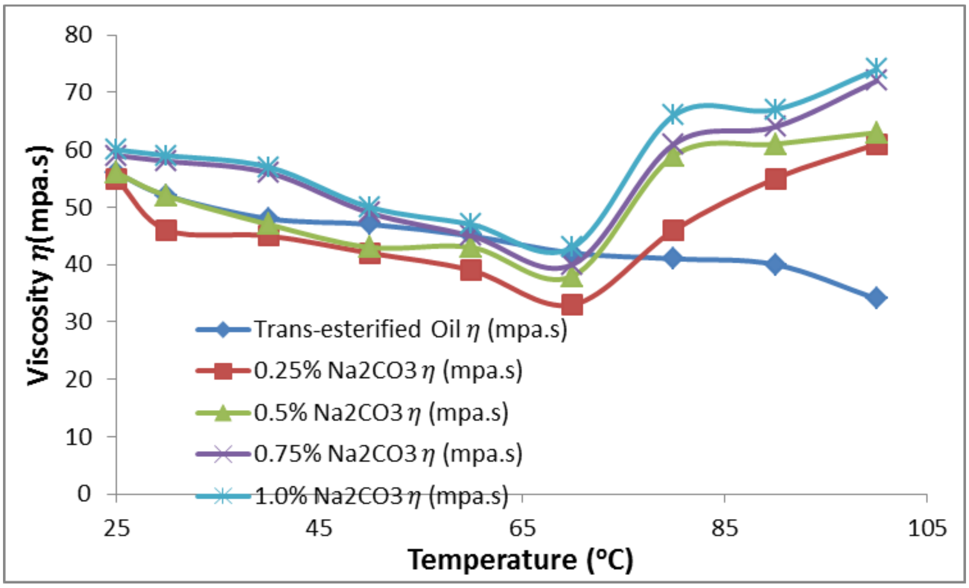

Figure 2: Viscosity versus Temperature of Na_2CO_3 Nano -Castor fluid

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. Its was found that found that the pour point of the crude is 11℃ while that of the purified oil is 9℃, for Trans – sterified is 5℃ and for Trans - esterified Trans - esterified (0.25w% Na_2CO_3) is 3℃. This implies that the Trans - esterified (0.25w% Na_2CO_3) is 2℃ 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 whether condition.

Flash point; the flash point test is sensitive in the study of lubricating fluid, because its gives the 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% Na_2CO_3) oils are 127℃, 131 ℃, 142℃ and 145℃ respectively, the higher temperatures of the Trans - esterified (0.25w% Na_2CO_3) oil indicates its usefulness for lubrication and it may be as a result of removing the flammables materials from the crude oil, as well as the addition of 0.25w% Na_2CO_3nano particles.

The FTIR analysis is employed in order to identify the presence of Na_2CO_3 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 neem 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 2854 cm^{-1} describes C-H stretching. The bands with peaks at 1674 cm^{-1} and 1033 cm^{-1} are vibration of C=O and C-O. These are typical bands that describe esters. The bands with peaks at 1427 cm^{-1} and 840 cm^{-1} are due to methylene scissoring and rocking.
The addition of Na_2CO_3 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% and 0.5%, a band was observed around 840 cm^{-1} and 848$cm^{-1}$is believed to be shrouded ester C-O band.

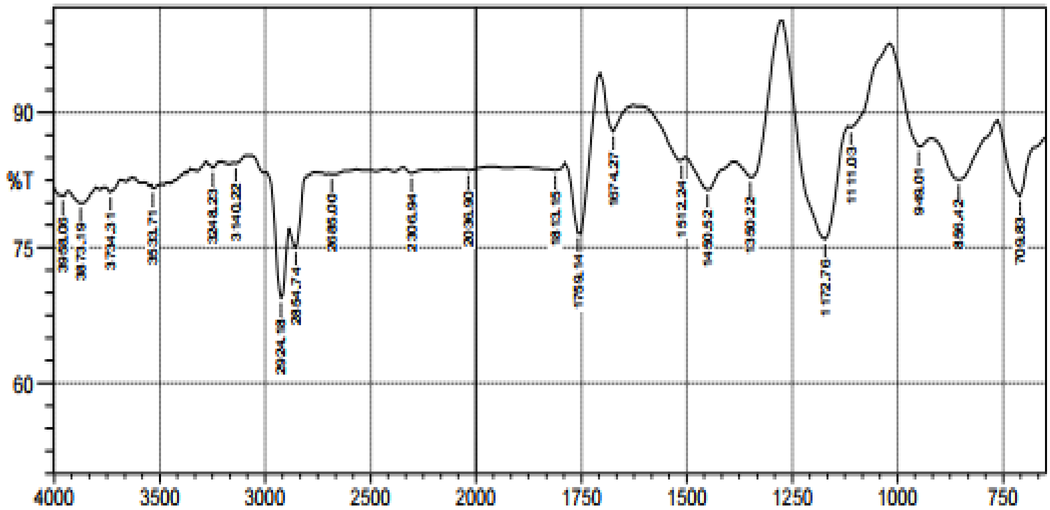

Figure 3: FT-IR Spectra of crude castor oil

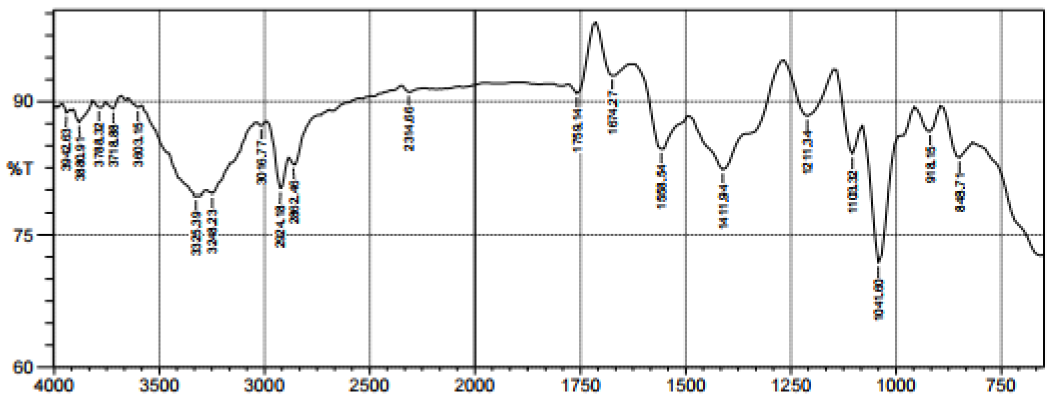

Figure 4: FT-IR Spectra of purified castor oil

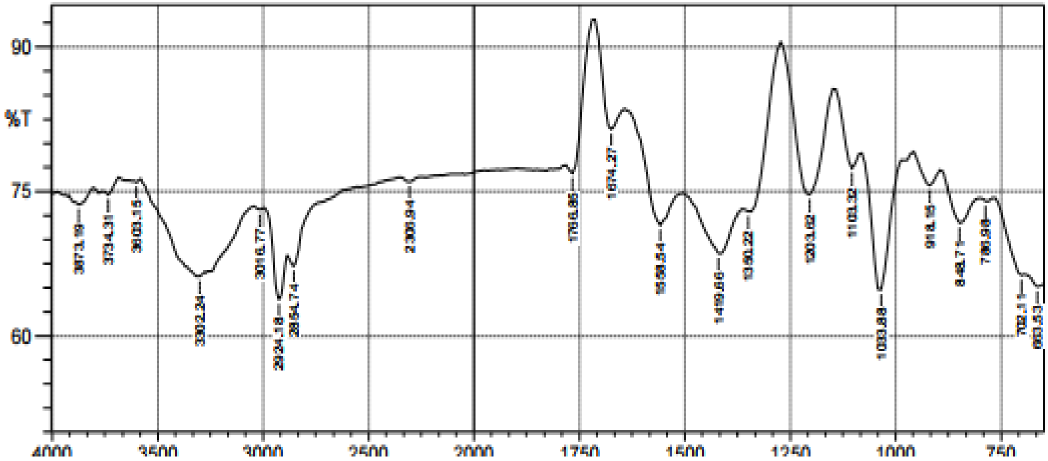

Figure 5: FT-IR Spectra of trans-esterified castor oil

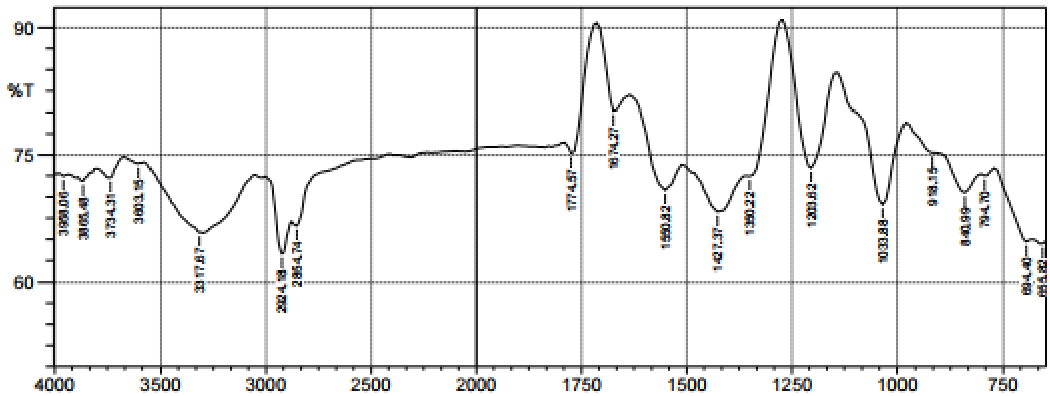

Figure 6: FT-IR Spectra of 0.25% nanoparticles concentration in castor oil

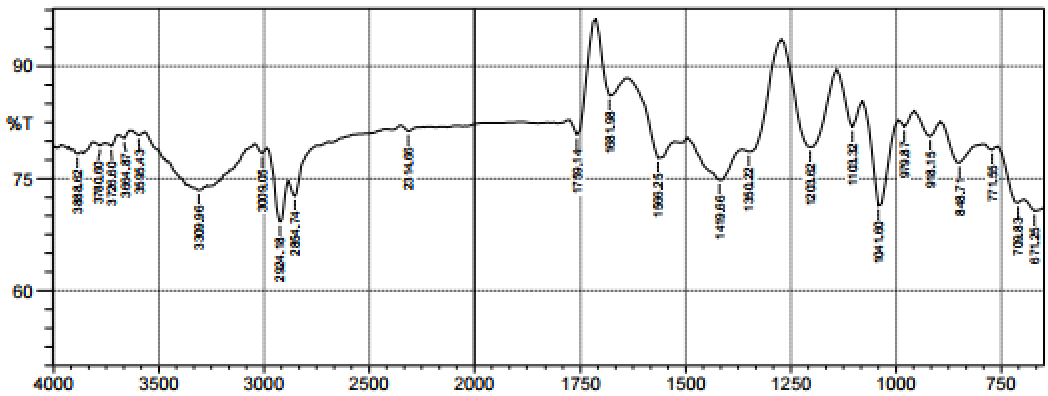

Figure 7: FT-IR Spectra of 0.5% nanoparticles concentration in castor oil

CONCLUSIONS

Viscosity of the nanofluid was measured using BrookfieldViscometers. The experimental results shows that the samples has viscosity lower than conventional insulating fluid. Just like most insulating fluids, the dynamics viscosity decrease with increase in temperature. The addition of nanoparticles(0.25w% Na_2CO_3) resulted in decrease in viscosity. The viscosity change may have contributed to the observed increase in with temperature. The Trans - esterified nanofluid with (0.25w% Na_2CO_3) appears to be more suitable for insulation as the sample was observed to have lowest pour point of 2℃and higher flash point of 145℃. This is due to the removal of gums in form of phospholipids from the crude oil. Hence, therefore, the result of the study shows that the trans-esterified nano fliud castor oil with 0.25% oil is potential candidate for the production of lubricating fluid.

Acknowledgement

The authors would like to acknowledge the financial support of Tertiary Education Trust Fund (TETFund) for sponsoring this research and Directorate for Research and Development KUST Wudil, for facilitating the process of accessing the research grant.

References

[1] Prabu, A., 2017. Nanoparticles as additive in biodiesel on the working characteristics of a DI diesel engine. Ain shams Engineering journal.
[2] Sierra, M.J., Tamayo, K., Herrera, A.P., Ojeda, K.A. and Sanchez, E.L., 2018. Environmental Assessment of Biodiesel Improved with Nanoparticles.
[3] Özgür, T., Özcanli, M. and Aydin, K., 2015. Investigation of nanoparticle additives to biodiesel for improvement of the performance and exhaust emissions in a compression ignition engine. International journal of green energy, 12(1), pp.51-56.
[4] Knothe, G., 2006. Analyzing biodiesel: standards and other methods. Journal of the American Oil Chemists' Society, 83(10), pp.823-833.
[5] Campos, D.C., Dall'Oglio, E.L., de Sousa Jr, P.T., Vasconcelos, L.G. and Kuhnen, C.A., 2014. Investigation of dielectric properties of the reaction mixture during the acid-catalyzed transesterification of Brazil nut oil for biodiesel production. Fuel, 117, pp.957-965.
[6] M'Peko, J.C., Reis, D.L., De Souza, J.E. and Caires, A.R., 2013. Evaluation of the dielectric properties of biodiesel fuels produced from different vegetable oil feedstocks through electrochemical impedance spectroscopy. International Journal of Hydrogen Energy, 38(22), pp.9355-9359.
[7] Kim, H. and Choi, B., 2010. The effect of biodiesel and bioethanol blended diesel fuel on nanoparticles and exhaust emissions from CRDI diesel engine. Renewable energy, 35(1), pp.157-163.
[8] Dreizin, E.L., 2000. Phase changes in metal combustion. Progress in Energy and Combustion Science, 26(1), pp.57-78.
[9] Kenneth KK, Risha GA, Evans BJ, Boyer E. Potential usage of energetic nanosized powders for combustion and rocket propulsion. Mater Res Soc Symp MRS Proc 2003;800:3–14.
[10] Idriss H. Ethanol reactions over the surface of noble metal/cerium oxide catalysts. Platin Met Rev 2004;48:105–15
[11] Farfaletti A, Astorg C, Martini G, Manfredi U, Mueller A, Rey M, et al. Effect of water/fuel emulsions and a cerium-based combustion improver additive on HD and LD diesel exhaust emissions. Environ Sci Technol 2005;39:6792–9.
[12] Kao MJ, Ting Chen-Ching, Lin Bai-Fu, Tsung Tsing Tshih. Aqueous aluminium nanofluid combustion in diesel fuel. J Test Eval 2008;36(2):1–5.
[13] Arul Mozhi Selavn V, Anand RB, Udayakumar M. Effects of cerium oxide nanoparticle

addition in diesel and diesel-biodiesel-ethanol blends on the performance and emission characteristics of a CI engine. J Eng Appl Sci 2009;4:1–6.
[14] Sajith V, Sobhan CB, Peterson GP. Experimental investigations on the effects of cerium oxide nanoparticle fuel additives on biodiesel. Adv Mech Eng; 2010. p.1–6 [ID 581407].
[15] Sadhik Basha J, Anand RB. An experimental investigation in a diesel engine using carbon nanotubes blended water–diesel emulsion fuel. J Power Energy 2010;225:279–88.
[16] Campanella, A., Rustoy, E., Baldessari, A. and Baltanás, M.A., 2010. Lubricants from chemically modified vegetable oils. Bioresource Technology, 101(1), pp.245-254.
[17] Aluyor, E.O. and Ori-Jesu, M., 2008. The use of antioxidants in vegetable oils–A review. African Journal of Biotechnology, 7(25).
[18] Garba, Z.N., Gimba, C.E. and Emmanuel, P., 2013. Production and characterisation of biobased transformer oil from Jatropha Curcas Seed. Journal of Physical Science, 24(2), p.49.
[19] Shameer, P.M. and Ramesh, K., 2018. Assessment on the consequences of injection timing and injection pressure on combustion characteristics of sustainable biodiesel fuelled engine. Renewable and Sustainable Energy Reviews, 81, pp.45-61.
[20] Annamalai, M., Dhinesh, B., Nanthagopal, K., SivaramaKrishnan, P., Lalvani, J.I.J., Parthasarathy, M. and Annamalai, K., 2016. An assessment on performance, combustion and emission behavior of a diesel engine powered by ceria nanoparticle blended emulsified biofuel. Energy conversion and management, 123, pp.372-380.
[21] Conceiçao, M. M., Candeia, R. A., Dantas, H. J., Soledade, L. E., Fernandes, V. J., & Souza, A. G. (2005). Rheological behavior of castor oil biodiesel. Energy & Fuels, 19(5), 2185-2188.
[22] Meneghetti, S. M. P., Meneghetti, M. R., Wolf, C. R., Silva, E. C., Lima, G. E., de Lira Silva, L., ... & de Oliveira, L. G. (2006). Biodiesel from castor oil: a comparison of ethanolysis versus methanolysis. Energy & Fuels, 20(5), 2262-2265.