

Influence of the Addition of Al₂O₃ Nano Particles on Physical Properties of Transesterified Castor Oil

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Abstract

Biofuel has commanded a growing interest globally due to the limited fossil deposits and the volatile fuel prices. Energy support civilization, for development and mobility. But the continuous usage of fossil fuel, especially for transportation, has long been identified as a major contributor of air pollutants. The emissions of unburned hydrocarbons, carbon monoxide and nitrogen oxides are found to take years off people's lives. The recent trend is to attempt to develop biodiesel from non-edible seed oil. This work investigates the influence of nanoparticles on the physical properties of transesterified castor oil. The crude castor oil was purified, transesterified and nanoparticles were dispersed in the trans-esterified oil with concentration ranging from 0.2% to 1.0% in 0.2% intervals. Scanning electron microscopy analysis (SEM) was used to examine the surface morphology of the Al₂O₃ oxide as well as X-ray fluorescence (XRF) spectroscopy to investigate the percentage purity of the oxide. Fourier Transform Infrared spectra (FTIR) was used to examine the structures of the samples. The pour point, flash point and the fire were studied. It was found out among other things that a small amount of Al₂O₃ (0.4%) nanoparticles in the oil could improve the thermo physical properties of the fluid. The nano fluid with 0.4% concentration of Al₂O₃ appears to have optimum physical property. Increase in temperature results in decrease in viscosity of oil, an indication that its heat transfer process improved with increasing temperature.

Keywords: *Castor oil, morphology, nanoparticles, pour point and flash point.*

1. 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, most of all, these sources are finite and at current usage rates will be consumed shortly (Soudagar *et al.* 2021; Aluyor *et al.* 2018; Balat *et al.* 2018; Garba *et al.* 2013; Gopinath *et al.* 2018; Jamo (2019); M'Peko *et al.* 2013; Oluwole, (2010); Saengsawang (2020). 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 (Piera *et al.* 2018; Sadhik (2020); Saidur *et al.* 2018; Shameer *et al.* 2018; Singh *et al.* 2018). 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 (Wang *et al.* 2015 and Zhang 2018). Some of the advantages of biodiesel are: 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 odors. The use of biodiesel has grown dramatically during the last few years (Gugule *et al.* 2021 and Soudagar *et al.* 2021 Wang).

The use of nano- particles in castor biodiesel (nano fluid) is expected to improve the physical properties of castor biodiesel Zhang (2020). Commercially available diesel oil is a combination of fossil diesel and several additives, which are added in several amounts to perform specific functions. Among others, there are additives to (Aluyor *et; al.* 2018) reduce pernicious emissions; (Balat *et; al.*2016) improve fluid stability over a wider range of conditions; (Balat *et; al.*21619) improve the viscosity index, reducing the rate of viscosity change with temperature; (Garba *et; al.*2013) improve ignition by reducing its delay time, flash point, and so forth; and (Gopinath *et; al.*2019) reduce wear with agents that adsorb onto metal surfaces and sacrificially provide chemical-to-chemical contact rather than metal-to-metal contact under high-load conditions.

The aim of this research therefore is to study the effects of alluminum oxide nano particle on physical properties of castor biodiesel.

2.0 Materials and methodologies

2.1 Materials

2.1.1 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 %), Al_2O_3 nano-particles, activated carbon, acetone, and distilled water (H_2O).

2.1.2 Equipment

The equipment's 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.

2.2 Methodology

2.2.1 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°C using hot plate with magnetic 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 .4g of 8% NaOH (by dissolving 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

2.2.2 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°C - 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.

2.2.3 Nano-fluids Preparation

The Al₂O₃ Nano-particles powder was purchased from Sky Spring 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 0.2%, 0.4%, 0.6%, 0.8% and 1.0% of powdered nano-particles and purified castor oil was made respectively. To make the Al₂O₃ 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.

3.0 Results and Discussions

Figure 1 below shows the scanning electron microscope of the Al₂O₃ nano particle. It can be seen from the picture that the morphology of the oxide is white, oval in shape with a porous structure.

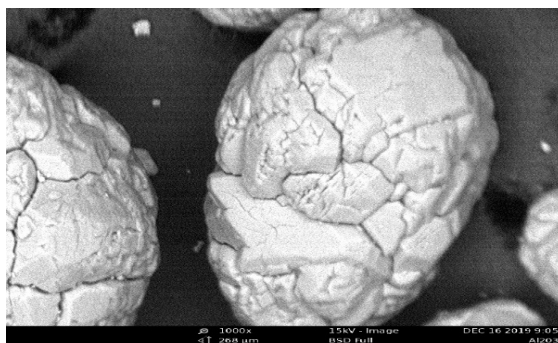


Figure 1: SEM of Al₂O₃ Magnification X 1000

The XRF of the Al₂O₃ was observed at Umaru Musa Yaraduwa University Katsina, in order to find out the percentage concentration of the oxide composed in the sample of nano particle used to carry out the research and the result is summarized in table 1 below. It could be seen that from the table Al₂O₃ (94.844) has the highest percentage in the sample followed by Cl (1.085).

Table 1: The percentage concentration of the element

Element	Al ₂ O ₃	Cl	SiO ₂	MgO	Na ₂ O	S	CaO	Fe ₂ O ₃	Ni ₂ O	Ga ₂ O ₃	LOI
Con (%)	94.84	1.08	0.957	0.61	0.41	0.106	0.0637	0.0376	0.0125	0.0112	1.85
	4	5	4	2	5	1	2	6	1	9	5

The result of pour point is presented in Table 2. It could be seen from the Table the pour point decreases with purification and transesterification. The pour point for crude oil is 12 °C, on purification the values drops to 9 °C, then after transesterification 6 °C, when 0.4 % of Al₂O₃ nano particles was added, 4°C was record. The addition of the additives to the biodiesel decreases the viscosity, density and flash point, though, the oxygen content of the blend is increased. In most of the recent studies Wang (2019), the oxygenated additives are used due to their low cost and the availability of synthesis devices. At higher engine loads, the oxygenated additives reduce the CO emission due to rise in temperature of the combustion chamber. Furthermore, the additives have an inherent property of cooling, resulting in the reduction of cylinder temperature. Pour point occurs during further cooling as a result

of crystal growth and agglomeration involving not only the saturated, but also unsaturated components. The higher the proportion of saturated components therefore leads to higher pour point. Generally, additives are developed to distort the crystal shape and to some extent alter their size, or directly inhibit their growth habit, thereby reducing pour point temperatures.

Table 2: Pour point, Flash Point and Fire Point Result of Castor

S/N	Sample	Pour Point (°C)	Flash Point (°C)	Fire Point (°C)
1	Crude Castor Oil	12	120	133
2	Purified Castor Oil	9	123	145
3	Trans – esterified	6	130	152
4	Trans - esterified (0.2w% Al ₂ O ₃)	5	139	157
5	Trans - esterified (0.4w% Al ₂ O ₃)	4	132	163
6	Trans - esterified (0.6w% Al ₂ O ₃)	6	132	160
7	Trans - esterified (0.8w% Al ₂ O ₃)	7	131	158
8	Trans - esterified (1.0w% Al ₂ O ₃)	8	129	156
9	Biodiesel standard	-15 to 10	100 to 170	>130
10	Diesel standard	-15 to 5	60 to 80	60 to 80

Flash (Table 2) point is an important temperature specified for safety during transport, storage and handling Yusuf (2019) and Mahlia (2020). The flash point and fire point of castor biodiesel was found to be 132°C and 163°C respectively. Fuels with flash point 50°C above 66°C are considered to be safe fuel (Zhang *et al.* 2018). This is attributed to the tensio-active agent as small molecules, the polar group in its structure which were made deep in the nucleus of fatty acid methyl ester with its generation eutectic effect, and non-polar group was distributed in plane of crystal, affects the interfacial property of wax crystalline substance, thus changes wax crystal particle. In addition, dimer acid amide has amorphism, snappiness and good low-temperature performance, be not easy crystallization at low temperatures, its non-polar group was made active eutectic brilliant in wax, is easily combined with paraffin phase, its polar group can cover the brilliant surface of wax, change the direction of growth of wax crystalline substance, prevent the formation of wax tridimensional network, finally play the effect improving status of low-temperature fluidity of biodiesel.

From the Table 2 the fire point increases as the crude oil was purified and transesterified respectively. The flash point of the crude, purified, transesterified and transesterified nanofluid (0.6% Al₂O₃ nanoparticles) oils are 133°C, 145 °C, 152°C and 163°C respectively, the higher temperatures of the transesterified (0.4% Al₂O₃ nanoparticles) 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 0.4% Al₂O₃ nanoparticles.

Al₂O₃ nanoparticles additives mainly reduce the concentration of organic carbon but not so much the concentration of elemental or black carbon. Elemental carbon is the major constituent when biodiesel fuels are burned with hydrocarbons and inorganic species. The Al₂O₃ additives form new particles if concentration of the additive is too high. It was found that the addition of Al₂O₃ to the biodiesel decreased the peak number concentrations and the light-off temperature but increased the oxidation rate. The result was found to be within the specified limit of ASTM 960-52.

FT-IR Spectra

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 Al₂O₃ nanoparticles is expected to change the FTIR spectra of the fluid. 0.4%, a band was observed around 840 cm⁻¹ and 848cm⁻¹ is believed to be shrouded ester C-O band.

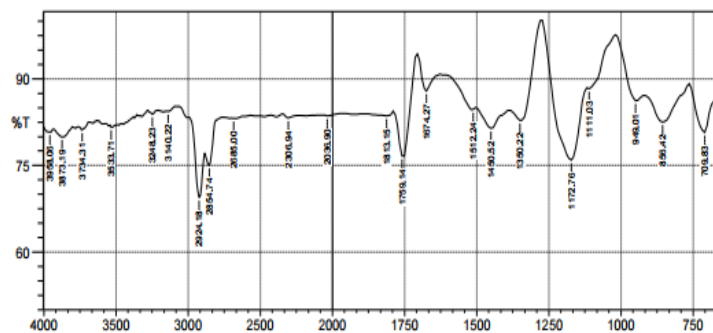


Figure 2: FT-IR Spectra of crude castor oil

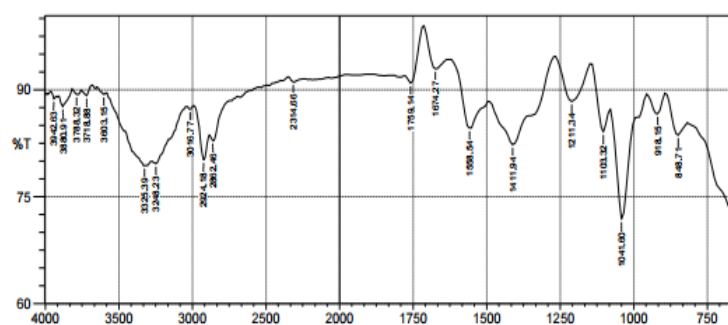


Figure 3: FT-IR Spectra of purified castor oil

The FTIR spectra in Fig.4. Displayed the typical bands that exist in natural esters this confirmed that the sample is an ester which is the biodiesel. The band with a peak at 2928 cm^{-1} describes C-H stretching. The bands with peaks at 1740 cm^{-1} and 1164 cm^{-1} are vibration of C=O and C-O. These are typical bands that describe esters. The bands with peaks at 1465 cm^{-1} and 720 cm^{-1} are due to methylene scissoring and rocking (Xie *et al.* 2020 Zhang *et al.* 2019).

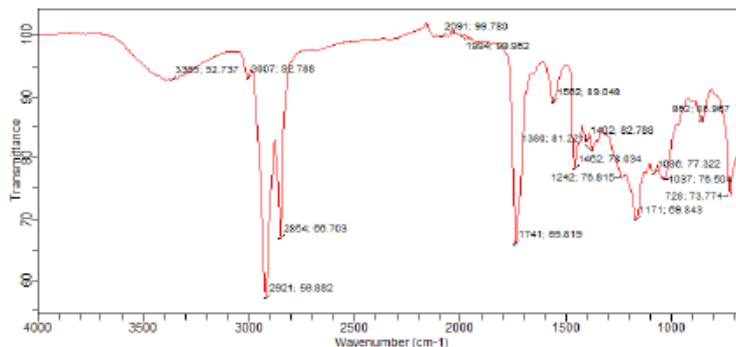


Figure 4: FT-IR Spectra of trans-esterified castor oil

The FTIR spectra in Fig.4, displayed the typical bands that exist in the Trans-esterifies castor oil. The band with a peak at 2920 cm^{-1} describes C-H stretching. The bands with peaks at 1774 cm^{-1} and 1265 cm^{-1} are vibration of C=O and C-O. These are typical bands that describe esters. The bands with peaks at 1724 cm^{-1} and 960 cm^{-1} are due to methylene scissoring and rocking (Wang *et al.* 2019).



Conclusions

The experimental results show that the samples have good physical properties than conventional insulating fluid. Just like most insulating fluids, the pour point, flash point and fire point decrease with increase in temperature and with increase in addition of nano particles. The addition of nanoparticles (0.4% Al_2O_3) resulted in enhancing physical properties. The change in the properties may have contributed to the observed increase in with temperature and the increase in additives. Furthermore, the tensio-active agent as small molecules, the polar group in its structure which were made deep in the nucleus of fatty acid methyl ester with its generation eutectic effect, and non-polar group was distributed in plane of crystal, affects the interfacial property of wax crystalline substance, thus changes wax crystal particle. The Transesterified nanofluid with (0.4% Al_2O) appears to be more suitable for insulation as the sample was observed to have lowest pour point of 5°C and higher flash point of 163°C.

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