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EFFECTS OF SiO_2 NANO PARTICLES ON PHYSICAL PROPERTIES OF TRANSESTERIFIED RAPESEED OIL

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Abstract

Ever since the research community highlighted the emission and sustainability aspects of pure diesel in the transportation sector, then began the search of next prospective fuel source that would address the shortcomings of diesel fuel. In the present research the effects of SiO_2 nanoparticles on physical properties of transesterified rapeseed oil was investigated. The crude rapeseed oil was purified, transesterified and nanoparticles were dispersed in the transesterified oil with concentration ranging from 0.2% to 1.0% in 0.2% interval. The physical properties such as refractive index, specific gravity, pour point, fire point, flash point Etc, were studied. It was found out among other things that small amount of 0.4% of SiO_2 nanoparticles in the oil could improve the physical properties of the fluid. It could be concluded that the optimum amount of SiO_2 nanoparticles to be used for nanofliud is 0.4%. Hence, the trans-esterified rapeseed containing 0.4% SiO_2 nano particles has the potential to be used as lubricant oil.

Keywords; Flash point, Nanoparticles, Pour Poimt, SiO_2, Transesterified

Introduction

Recently, the world is facing an acute energy crisis due to the fact that high energy demands from the fossil fuels such as coal, petroleum and natural gas at present and compete with the feedstocks requirement for chemical industries. The demand of these non-renewable sources of energy is increasing rapidly which are getting consumed by us at an extraordinary rate. Attention continues to be focused on biomass-derived fuels or known as biofuels for energy production. One of the liquid biofuels considered for this application is biodiesel. Biodiesel is defined as mono alkyl esters of long chain fatty acids derived from natural renewable materials, such as vegetable oils of fats and they are mainly employed as fuel for vehicles engines [1-13]. The advantages of the biodiesel compared with the conventional fossil diesels are their renewability, biodegradability, non-toxicity and low exhaust emissions due to the free of sulphur and aromatics in biodiesel [14-21]. Biofuels production is expected to offer new opportunities to diversify income and fuel supply sources, to promote employment in rural areas, to develop long term replacement of fossil fuels, and to reduce GHG emissions, boosting the decarbonisation of transportation fuels and increasing the security of energy supply.

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, 22-23]. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel to the commercials filling stations. Fortunately, some vegetable oils, mostly produced by seed-bearing trees and

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shrubs can provide an alternative. With no competing food uses, this characteristic turns attention to rapeseed, cultivated mainly for its oil-rich seed, which naturally contains appreciable amounts of toxic erucic acid. Canola are a group of rapeseed cultivars which were bred to have very low levels of erucic acid. Rapeseed is the third-largest source of vegetable oil. The seeds of rapeseed are good source of oil, which can be used as a diesel substitute after transesterification. The use of nanoparticles in transesterified rapeseed biodiesel (nano fluid) is expected to improve the physical properties of rapeseed. Thus, the aim of this research therefore is to study the effects of cerium oxide rheology of rapeseed transesterified biodiesel.

Methodology

Sample Purification

The rapeseed oil was purified through the following procedure; 200 ml of the rapeseed oil was measured using measuring cylinder; the oil was pre-heated to 70 ^oC 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 ^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 rapeseed oil was measured in 250ml of conical flask and was heated and stirred to a temperature of 60-65℃ 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℃, 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 its by product.

Nano-fluids Preparation

The SiO_2 Nano-particles powder was purchased from Sky Spring Nanomaterials, Inc., U. S. A, 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 nanoparticles and purified rapeseed oil was made respectively. 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. Physical properties such as refractive index, specific gravity, pour point, fire point, flash point Etc, were calculated.

Refractive index

Apparatus: Open rectangular transparent container, light source, an opaque strip 3-4 cm long, and sheet paper as shown in Figure 1

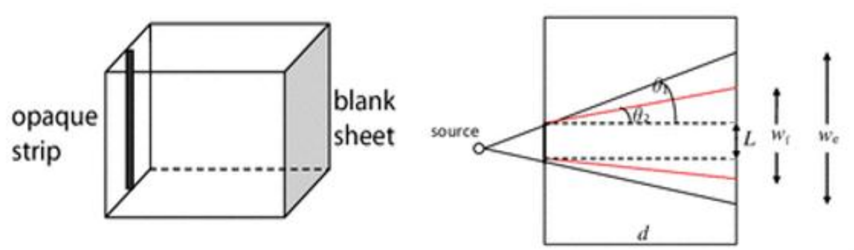

Figure 1 Transparent box and Ray sketch

The strip was fixed on the middle of one wall of the container, and the sheet of paper was placed on the opposite wall as shown in the Figure 1. The light source was placed at a convenient distance near the strip. With the empty container was placed on the edge of the shadow of the strip and was marked on the paper. The container was filled with oil and marked again the width of the shadow reduced compare to the previous width because of refraction.

Let L = the width of the strip

W_e = the shadow when the box is empty

W_f = the shadow when the box is full with oil

Then the geometry shown on the side view of Figure 1. The angle $\vartheta 1$ is angle substended by empty box, $\vartheta 2$ is angle subtended by box full with oil, then using Snell's law, the refractive index of the oil can be calculated as:

$n = \frac{\sin\vartheta 2}{\sin\vartheta 1}$ ………………… (1)

And the approximately $\sin\vartheta \approx \tan\vartheta$, justified the dimensions of the apparatus, we have.

$n = \frac{W1-L}{Wf-L}$ ……………………(2)

Note: that adjusting the strength of the source, the width of the container (affecting the absorption of light), and distance of the source from the opaque strip will result in optimally sharp shadows.

Specific gravity (S.G)

Specific gravity (S.G) is the ratio of the weight of the liquid to the weight the equal volume of water OR

The ratio mass of liquid to the mass of equal volume of water

OR

The ratio of density of oil to the density of water at the same temperature.

Specific Heat Capacity

To calculate the specific heat capacity of the oil, the following apparatus was use:

- Thermometer
- Calorimeter
- Solid of unknown specific gravity which can be calculated as follows.

Let: Mass of the solid = M_s= 100g = 0.1kg

Initial temperature of the solid = $\vartheta 3 = 100°c = 373K$

Mass water =M_w =75g =0.075g

Specific heat capacity of water C_w =4200j/kg k

Initial temperature of water = $\vartheta 1$ =23ºC (293k)

Mass calorimeter = M_c =42g =0.042kg

Specific heat capacity of copper calorimeter C_c = 390J/kgK.

Procedure:

The solid was weighted to its mass, heated in boiling water at a temperature ϑ m3 for 10 min and then quickly transferred to a calorimeter containing the water, then the water is stirred and the temperature is $\vartheta 2$. as in the Figure 2 below.

Figure 2: Heating mass to temp. of 100 ºC Figure 3: Hot mass in oil

Assuming no heat loss from the calorimeter when the hot solid dropped in to it.

Then:

Heat given out by solid on cooling from $\vartheta 3$ to $\vartheta 2$ = heat gained by water warming from $\vartheta 1$ to $\vartheta 2$ + heat received by calorimeter warming from $\vartheta 1$ to $\vartheta 2$.

$$M_sC_s(\vartheta3-\vartheta1) = M_wC_w(\vartheta2-\vartheta1) + M_cC_c(\vartheta2-\vartheta1)$$
$$= (M_wC_w + M_cC_c)(\vartheta2-\vartheta1)$$
$$Cs = \frac{(MwCw + McCc)(\vartheta2-\vartheta1)}{Ms(\vartheta3-\vartheta1)}$$
$$= \frac{(0.075\times4200+0.042\times390)(350-294.5)}{0.1(373-305)}$$
$$= 511.689$$
$$\approx 512\ J\ Kg^{-1}K^{-1}$$

The specific capacity of the solid to be use is found to be 512 J $Kg^{-1}K^{-1}$.

The specific heat capacity of oil can be calculated as

$$M_sC_s(\vartheta3-\vartheta2) = M_{oil}C_{oil}(\vartheta2-\vartheta1) + M_cC_c(\vartheta2-\vartheta1)$$
$$C_{oil} = \frac{MsCs(\vartheta3-\vartheta2) - McCc(\vartheta2-\vartheta1)}{Moil(\vartheta2-\vartheta1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Pour point

The cylindrical test tube was filled with the crude palm 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 rapeseed oil.

Flash point

The flash point for both crude and purified rapeseed oil was also measured; A 100 ml conical flask was filled to a specific mark level (10 ml) with palm oil and heated at 14 to 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 purified and transesterified rapeseed.

Results and Discussions

The refractive index of the samples is presented in the Tables 1 and 2 below. The refractive index decreases with purification (1.4463) and transesterification with the values of 1.4539 of the refractive index was achieved. This is as a result of reduction in the concentration of organic carbon but not so much the concentration of elemental or black. It was observed that the addition of nanoparticles to the biodiesel decreased the peak number concentrations and the light-off temperature but increased the oxidation rate [19]. In a similar research carried out by Jamo *et. al*., [3], they asserted that the physical properties of a purified oil castor oil is less than that of crude and the transesterified has the least values of physical properties which is within the standard limit of biodiesel.

With the addition of 0.4% of SiO_2 nanoparticles the values of refractive index increases to 1.4544 of the refractive index. The refractive is a useful physical property in forensic glass characterization. It can be measured to a high degree of accuracy and precision, which is essentially independent of fragment size [20]. Therefore, impurities of a substance will increase the refractive index of that substance. An increase in the refractive index of a substance means that light will travel more slowly through the substance, more impurities in a substance means there are more opportunities for light to be refracted or bent. 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.

Table 1: Refractive Index Rapeseed Oil

S/ N	Sample	Refractive Index
1	Crude Rapeseed oil	1.4852
2	Purified Rapeseed oil	1.4463
3	Transesterified Rapeseed oil	1.4539
4	Biodiesel standard	1.4548
5	Diesel standard	1.4650

Table 2: Refractive Index SiO_2 Nano fluid

S/N	SiO_2 (%)	Refractive index of SiO_2
1	0.2	1.4500
2	0.4	1.4544
3	0.6	1.4702
4	0.8	1.4839
5	1.0	1.4923

The specific gravity is presented in the Tables 3 and 4. The crude rapeseed oil has the values of specific gravity to be 0.943 but after purification the values decreases to 0.938. On transesterification the values of the specific gravity further increases to 0.907. The specific gravity, is the ratio of the density of a substance to the density of a given reference material. The specific gravity of the nanofluids was achieved with a value of 0.910 with the addition of 0.4% nanoparticles.

Table 3: Specific Gravity

S/N	Sample	Specific gravity
1	Crude Rapeseed oil	0.943
2	Purified Rapeseed oil	0.938
3	Transesterified Rapeseed oil	0.907
4	Biodiesel standard	0.903 to 0.921
5	Diesel standard	0.82 to 0.95

Table 4: Specific Gravity of SiO_2 Nano fluid

S/N	SiO_2 (%)	SiO_2 Nano fluid
1	0.2	0.909
2	0.4	0.910
3	0.6	0.931
4	0.8	0.947
5	1.0	0.956

The specific heat capacity of the samples is shown in Tables 5 and 6. The result of specific heat capacity of the crude, purified and transesterified oils were achieved with values of 14402.2 J/kgK, 14391.8 J/kgK and 14348.3 J/kgK respectively. The result of specific heat capacity of the of the transesterifed oil further decreases on the addition of 0.4% nanoparticles 14222.1 J/kgK. Addition of nanoparticles above 0.4% causes the specific heat capacity of the of the transesterifedto increase this could be as a result of agglomeration of the nanoparticles.

Table 5: Result of Specific Heat Capacity SiO_2 Nano fluid

S/N	Sample	S.H.C (J/Kg/K)
1	Crude oil	14402.2
2	Purified	14391.8
3	Transesterified	14348.3
4	Biodiesel standard	14214.0
5	Diesel standard	14300.0

Table 6: Result of Specific Heat Capacity of ZnO Nano fluid (J/kgk)

S/N	SiO_2 (%)	SiO_2 Nano fluid (J/kgK)
1	0.2	14291.4
2	0.4	14222.1
3	0.6	14341.4
4	0.8	14414.6
5	1.0	14516.2

Pour point

Pour point (Table 7) decreases as the crude oil was purified, similarly, it decreases further as the oil was transesterified. The least pour point was achieved at temperature of 4 ^{O}C with the addition of 0.4w% SiO_2 nanoparticles with. 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 cloud point and 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. Many additives contain proprietary components, and copolymers of ethylene and vinyl acetate or other olefin-ester copolymers.

Table: 7 Pour Point, Flash Point and Fire Point

S/No	Sample	Pour Point (^{O}C)	Flash Point(^{O}C)	Fire Point (^{O}C)
1	Crude rapeseed Oil	10	139	138
2	Purified rapeseed Oil	8	144	143
3	Trans – esterified rapeseed Oil	7	147	148
5	Trans - esterified (0.2w% SiO_2)	6	150	154
7	Trans - esterified (0.4w% SiO_2)	4	156	157
9	Trans - esterified (0.6w% SiO_2)	5	151	153
10	Trans - esterified (0.8w% SiO_2)	8	148	149
11	Trans - esterified (1.0w% SiO_{2v})	9	143	139
12	Biodiesel standard	-15 to 10	100 to 170	>130
13	Diesel standard	-15 to 5	60 to 80	60 to 80

Flash Point

From the Table 7 the flash point decreases as the crude oil was purified and transesterified respectively. The flash point of the crude, purified, transesterified (0.4w% SiO_2 nanoparticles) oils are 139℃, 144 ℃, 147℃ and 156℃ respectively, the higher temperatures of the transesterified (0.4% SiO_2) 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% SiO_2 nanoparticles.

Fire Point

Fire point of the rapeseed oil increases after transesterification as shown in Table 7. The volatile characteristics had improved and it is also safe to handle. The pour point of crude rapeseed oil was 138 ^{O}C after purification 143 ^{O}C then after transesterification 148 ^{O}C when 0.4% SiO_2 nanoparticles was added the fire point the fire point was recorded at temperature of 157 ^{O}C.

Conclusion

The refractive index of the crude oil (1.4852) decreases with purification (1.4463) and further decreases with transesterification (1.4539). With the addition of 0.4% of SiO_2 nanoparticles the values of refractive index increases to 1.4544 of the refractive index. The crude rapeseed oil has the values of specific gravity to be 0.943 but after purification the values decreases to 0.938. On transesterification the values of the specific gravity further increases to 0.907. The result of specific heat capacity of the crude, purified and transesterified oils were achieved with values of 14402.2 J/kgK 14391.8 J/kgK and 14348.3 J/kgK respectively. The specific heat capacity of the of the transesterified oil further decreases on the addition of 0.4% nanoparticles 14222.1 J/kgK. Addition of nanoparticles above 0.4% causes the specific heat capacity of the of the transesterified to increase this could be as a result of agglomeration of the nanoparticles. Pour point decreases as the crude oil was purified, similarly, it decreases further as the oil was transesterified. The least pour point was achieved at temperature of 4 ^{O}C with the addition of 0.4w% SiO_2 nanoparticles with. Pour point occurs during further cooling as a result of crystal growth and agglomeration involving not only the saturated, but also unsaturated components. The flash point results revealed that the higher temperatures of the transesterified (0.4% SiO_2) oil the more it usefulness for lubrication and this could be as a result of removing the flammables materials from the crude oil, as well as the addition of 0.4% SiO_2 nanoparticles. It could therefore, be concluded that transesterified with 0.4% SiO_2 nanoparticles appear to be more suitable for lubrication.

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