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EFFECT OF CARBON NANOTUBE DISPERSIONS TO THE PALM OIL DIESEL–BIODIESEL BLEND PROPERTIES

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ABSTRACT

This paper reports on the use of Carbon Nanotubes (CNT) as an additive to the palm oil diesel–biodiesel fuel blends and its effects to the fuel properties. The tested biodiesel fuels were prepared by dispersing CNT into the diesel-biodiesel fuel blends at five different concentrations of 0.005% vol, 0.010% vol, 0.015% vol, 0.020% vol, 0.025% vol respectively and have their properties tested and compared against the standard baseline pure palm oil biodiesel and diesel fuel. Three blending proportions of B100 (100% palm oil biodiesel by volume percentage), B20, and B10 were used for experimentations. Results shown that the thermal conductivity and flash point of the fuels dispersed with CNT have increased with higher dispersion concentration of CNT. The pour point data however, shown a decrement trend when dispersed with CNT at higher concentrations and suspension of CNT in blends has also increased the fuel's cetane number as well as fuel's Heating Value (HV). Dispersion of CNT as additive has improved the fuel properties and operational characteristics of palm oil biodiesel fuel and its blends.

***Keywords*:** Biodiesel fuels; Diesel fuels; Fuels blends; Carbon nanotubes; Biodiesel fuel properties.

INTRODUCTION

The current trend in world's energy demands and supplies has created a critical dent on the availability of global crude oil. As the source-demand gap is getting wider, our dependence to fossil fuel is now at marginal clearance as almost the entire transportation systems are heavily relying on it to produce power. Widely use of fossil based fuels has also promoted bad effects to the environment and caused deterioration in world climatic quality through the production of undesirable pollutions. Transportation systems are the world's biggest consumer of fossil fuel and if the diesel fuel can be totally replaced with any renewable sources such as biodiesel fuels and, in the meantime, required no significant modifications to the current compression ignition (CI) engines, world dependency to the crude oil source may be reduced.

Biodiesel fuels can be produced from various sources of vegetable oils through the chemical reaction called transesterification process (Halek et al., 2009; Hoekman et al., 2012; Bajpai et al., 2006). However, possibility of using any higher percentage of biodiesel fuel in diesel-biodiesel blends for satisfying the sustainability requirements, its compatibility with the currently available CI engines need to be addressed cohesively as the blends' properties and operational characteristics are not similar if compared to standard diesel fuels available in the market. This may lead to major modifications required to the current CI engines (Anand et al., 2011; Demirbas, 2008; Apltekin and Canakci, 2008). Higher percentage of biodiesel in the blend will also cause the engine's fuel consumption to increase significantly for the same amount of power generated as a result of low carbon content in biodiesel fuels. Biodiesels derived from various vegetable oils have in general 10% lower of HV compared to standard diesel fuels. Lower in carbon-oxygen ratio in biodiesel fuels has resulted in oxygen excess in fuel and this promote to a faster metal corrosion due to the oxidative behaviour possess by oxygen (Dantas et al., 2011; Knothe, 2007).

Combustion performance of the fuel will rely on the type of fuel used and how the carbon presents in the fuel. The presence of carbon in fine size and environment such as CNT will increase the ratio of carbon-oxygen in the biodiesel fuels thus improve the combustion performance of diesel-biodiesel blends. CNT is purely carbon substance constructed in cylindrical shape with nanometer size and its dispersion into the fuel will aid as combustion catalyst. Dispersion of CNT into diesel-biodiesel blends have also altered the thermal-physical properties of the fuel. Changes in key operational characteristics such as viscosity and density will greatly improve the parameters for engine performance (e.g.: fuel spray characteristics, injection timing, level of emissions, power produced, and the torque generated) (Halek et al., 2009; Kalam and Masjuki, 2008; Yamane et al., 2001; May et al., 2005; Knothe et al., 2003). Thus, this study give a great interest in the investigation of the variations of thermo-physical properties for the diesel-biodiesel fuel blends as to keep it as close as possible to commercially available diesel fuel. Properties like cetane number, heating value, flash point, and thermal conductivity are evaluated in this project and compared to those standard diesel fuels.

SAMPLE PREPARATION AND STABALIZATION

CNT dispersion into diesel-biodiesel blends

Both diesel and palm oil biodiesel fuels were acquired from the commercial suppliers and the type of CNT used is Multiwall CNT (MWCNT) with the outer diameter of 10 – 20 nm and the particle length in between 10 – 30 μm. Purity level of CNT used for this project is 95%. All samples were prepared in volumetric basis and the volume for each sample was taken as 100 ml. Corresponding mass for the CNT to be dispersed into the diesel-biodiesel blends were obtained through the mass-volume relationship, as shown the by general density relation of a substance in Eq. (1).

$$\rho = \frac{m}{V} \qquad (1)$$

where ρ = Density of the substance

m = Mass of the substance, and

V = Volume occupied by the substance

Corresponding CNT mass required for the dispersion into diesel-biodiesel blends for each concentration obtained from Eq. (1) and represented as in the Table 1.

Table 1. Corresponding CNT mass for the dispersion calculated from the volume basis.

Case	CNT volume (%) in diesel – biodiesel blends	Corresponding mass for dispersion (g)
1	0.005	0.013
2	0.010	0.026
3	0.015	0.039
4	0.020	0.052
5	0.025	0.065

Corresponding masses of CNT were measured using the available weight scale in the laboratory and later be dispersed into the diesel-biodiesel blends. A hot plate magnetic stirrer was used to provide the stirring effect to the fuel blends in order to prevent the CNT from early sedimentation during the blending process. Each sample blend was stirred for 20 minutes at the room temperature. Both diesel and palm oil fuels were measured their volume by using pippete.

Samples homogenization for dispersion stabilization

A stable and uniform dispersion over a long time for the CNT particles inside the fuel blends is critical as it will provide a good environment for the samples during the properties experimentation. Huge difference between densities of nanoparticles and the fuel blends is a major concern for unstable dispersion of the CNT. Due to the nano-scale size of CNT, the number of individual particles within the blend is high and this lead to the gap reduction among the particles and will influence the stability of particle dispersion within the fuel blends. Particle sedimentation will significantly influence the properties of the fuel and in the case of combustible substances like fuel, surfactant is unlikely to be added into the fuel blends to provide a stable dispersion. Surfactants were generally used as stability agents for the dispersion of nanoparticle into the water based nanofluids.

Scientz ultrasonic homogenizer was used in this project as particle homogenization device to the samples by supplying the sound wave that contained high energy to the CNT-fuel blend mixtures. High energy content from the sound wave will induce a huge pressure stream within the fuel blend and caused cavitation to form. Emergence of cavitation will help to reduce agglomeration of the nanoparticles thus prevent sedimentation from occurring as the pull-push effect among the particles is significantly reduced. Optimized time for samples' homogenization process is taken as 40 minutes for all the dispersion proportions (Azmi et al., 2012). Figure 1 shows the samples of B20 fuel blends after 40 minutes of homogenization process for various CNT proportions. It can be seen that homogenization effect has prepared stable dispersions of CNT in the diesel-biodiesel blends.

Effect of 40 minutes homogenization process where it can be clearly seen that CNT are uniformly dispersed within the fuel blend for all samples

Figure 1. Diesel-biodiesel blend samples with the homogenization effect.

In this project, a water bath system was also designed and manufactured in order to provide the elevated temperature environments during samples experimentations. The manufactured system has an active system to control the heating of 3.5 litre water reservoir and also equipped with the temperature sensitivity control of 0.1°C. It will maintain the samples' temperature at the specified temperature during the fuel properties testing and can be used to heat up the samples from the room temperature up to 80°C of temperature. Figure 2 shows the arrangement of the water bath system during the fuel properties experimentations. The water bath system was also installed with a stirrer that is used to ensure that temperature distribution within the heat reservoir for sample heating during experimentation will be uniformly distributed.

Figure 2. Water bath setup to test the fuel properties.

RESULTS AND DISCUSSION

This section presents the experimentation results generated from the controlled environments and experimental testing. Variations in diesel–biodiesel blends properties were reported as functions to the change in temperature settings of the samples as well as due to the increment of the CNT dispersion in fuel blends.

Cetane number

Variations on the blends' calculated cetane number with regard to CNT dispersions were evaluated using American Society for Testing and Materials (ASTM) standard 4737 (ASTM 4737). Shasx 200 Octane Meter was used to measure the cetane index of the samples. Cetane number is an index to indicate the fuel's combustion quality during the injection process. The higher the cetane index of a fuel, the shorter the fuel's ignition delay. Higher cetane indexes are more desirable as shorter ignition delay will combust fuel more completely and reduce the proportions of unburned constituents as well as improved the level of emissions release to the environment. Effect of CNT dispersion to the diesel-biodiesel blends on fuels' cetane index is shown as in Figure 3.

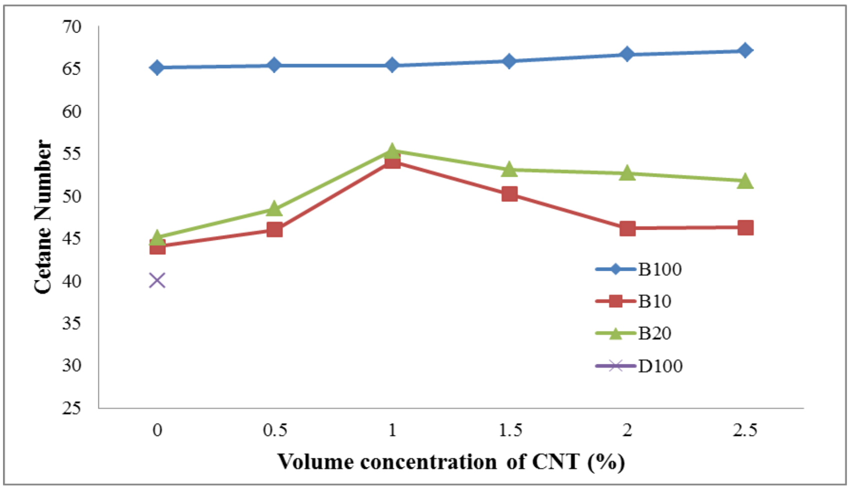


Figure 3. Variation in cetane numbers of the various fuel blends with respect to various proportions of CNT dispersions.

From the experimental results, it is shown that cetane index increases with the increment of both biodiesel proportions in the blend as well as with the higher percentage of CNT dispersion proportions. Biodiesel fuel has comparatively lower cetane index as a result of the presence of aromatic compounds and high sulphur content in the fuel (Verduzco et al., 2011). In general, biodiesel fuels have 10% – 12% higher in oxygen content compared to pure diesel fuel and this has contributed to the higher cetane index for diesel fuels (Verduzco et al., 2011; Kish et al., 2010; Ramos et al., 2009). However, dispersion of CNT at higher concentration (0.025% vol.) has also produce a dominating effect in increasing the fuel's cetane index. Higher proportion of biodiesel in the blend will increase the carbon chain length in the fuel. Palmitic (C16:0) in the biodiesel fuel has 16 Carbons and it's in saturated condition, meaning that no double bonding can exist in the esters. That has resulted in the longest ester compared to other saturated one and this is believed to have increased the fuel's cetane index (Kish et al., 2010).

Dispersion of CNT in higher concentration has also indirectly influence the cetane index of the fuel. Density and viscosity of the fuel will respond proportionally to the amount of CNT dispersed into the blend and theoretically, change in fuel's density has an effect on the cetane index (Kish et al., 2010). However, changes in the viscosity of the fuel have to be addressed meticulously as it will improve other fuel properties such as spray characteristics and emissions level.

For B10 and B20 blends, value for cetane indexes shown decrement patterns beyond 0.010% of CNT concentration. This may be resulted from the low proportions of biodiesel in the blend and higher concentrations of CNT have changed the environment of CNT in the fuel. Both blends have comparatively lower viscosity compared to B100 and dispersion of CNT at greater than 0.010% of concentration will improve the dispersion stability within the fuel even though after the samples have been homogenized.

Heating value

HV of the fuel and its blends for various CNT concentrations were evaluated using the ASTM D240-02 standard. HV is a representation of the amount of energy per unit mass contained in the fuel. Evaluation on HV values for the blends will determine the compatibility of the blends to be used in the existing CI engines without significant modifications required to the engine. It's expected that the diesel-biodiesel blends will produce a comparable performance to the standard diesel fuel in terms of power output as well as the fuel consumption. Anton Paar Oxygen Bomb Calorimeter was used to measure the fuels' HV and results from the experimental works are presented as in Figure. 4.

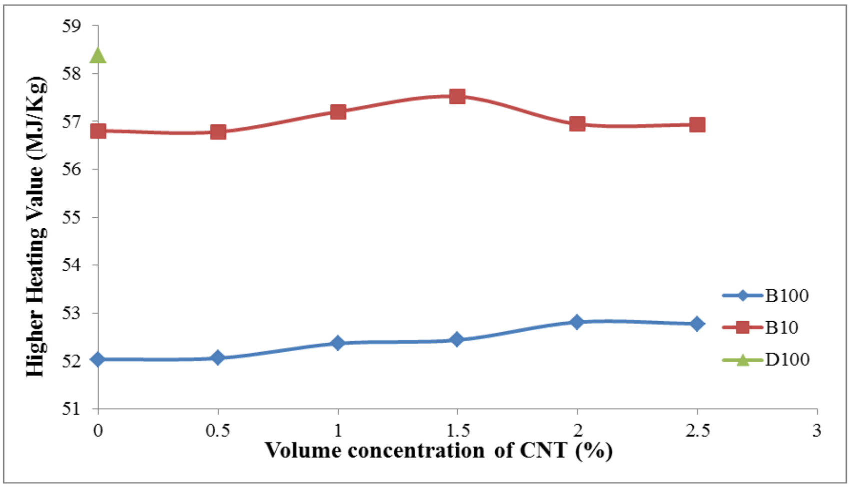
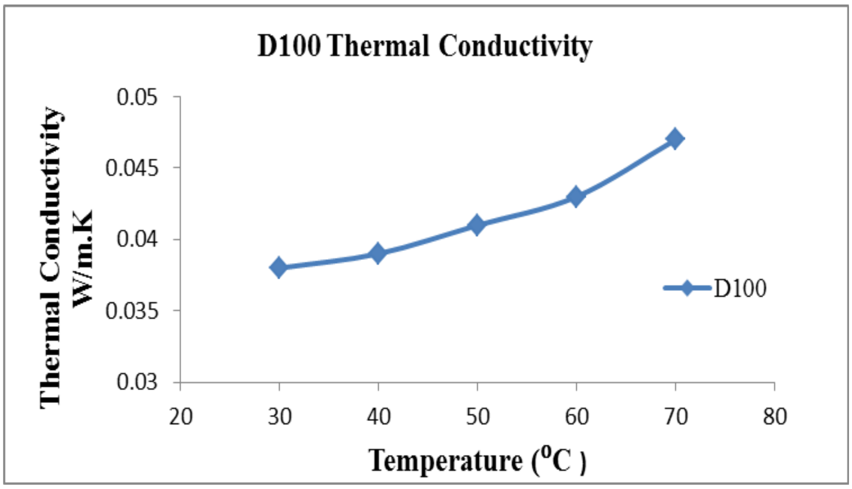


Figure 4. Variation of heating values of the various fuel blends with respect to various proportions of CNT dispersions.

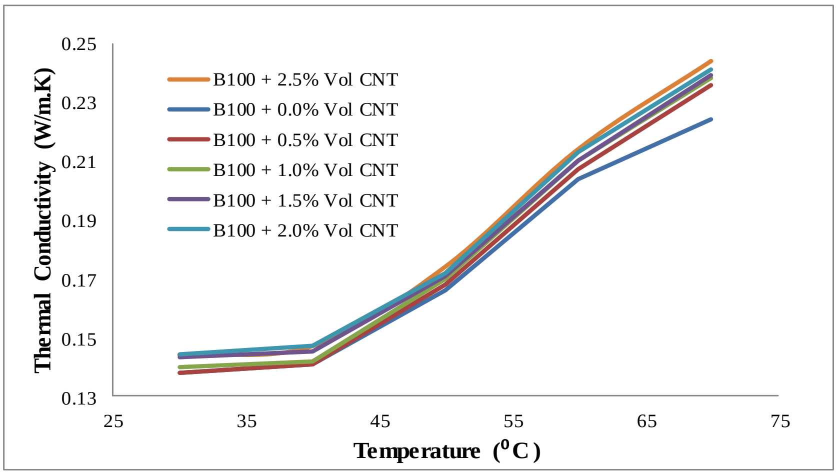
Interpretation to the results were straightforward that D100 has the highest calorific value (at 58.5 MJ/kg) compared to diesel-biodiesel blends at any proportions and the B100 has significant 12.2% reduction (at 52.0 MJ/kg) of the combustion capability relative to D100. This is in good agreement with most literatures that pure biodiesel fuels have somewhat 10% lower in calorific value due to its high oxygen content in the fuel. This is a clear evident that fuel consumption for the engines operating on B100 will be high as more fuel has to be injected into cylinder during the combustion process (as a result of lower energy content per unit mass) (Alptekin et al. 2008). Dispersing the B100 with maximum CNT concentration has only increased the calorific value of the fuel by 1.4% (to be 52.7 MJ/kg) and this did not help much in enhancing the fuel's carbon content. Instead, higher concentration of CNT dispersed in the fuel will improve the fuel's viscosity and thus altered the fuels' spray characteristics and pollutions formation. With high concentration of CNT is suspended in the fuel, its dispersion stability to remain uniformly homogenized throughout the fuel is very difficult to achieve. As for the B10, the pattern looked promising as the calorific values increased to the maximum value with the increment of dispersion concentrations before gradually decreased as the concentration increased further. The value peaked at 0.005% of CNT concentration, largely due to the presence of fine size carbon throughout the fuel before decreased to almost the same calorific value when there was no carbon dispersed (0% of concentration). This may be resulted from the excess carbon present in the fuel at higher dispersion concentrations and caused the ratio of carbon to oxygen to be saturated. Adding carbon beyond this saturation point will not enhance the combustion capability of the fuel further.

Thermal conductivity

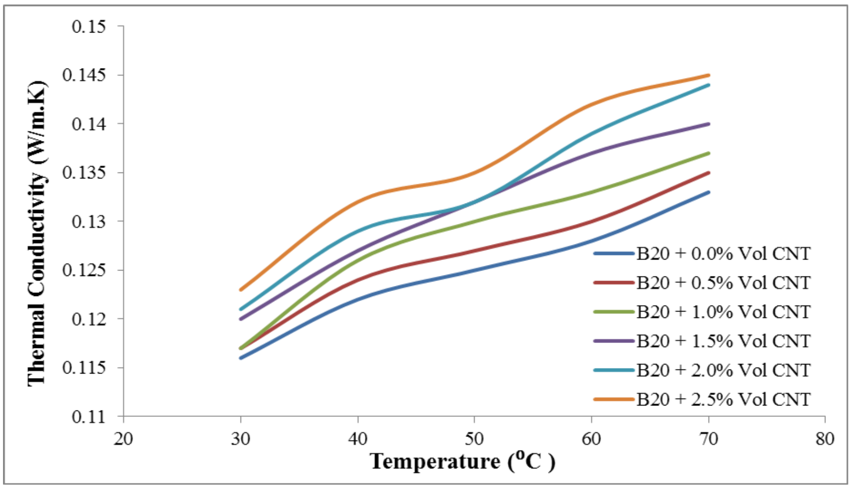
Thermal conductivity may not directly influence the fuel's operational characteristics, however, its importance emerged to be significant when the fuel line system is exposed to somewhat extremely low operational environments. Fuel's ability to absorb heat that is supplied from the fuel heating system in order to remain in liquid phase is highly determined by its thermal conductivity behaviour. Thus, fuels are always desirable to have higher thermal conductivity during its operation. For experimentation with thermal conductivity, all samples were continuously heated in the range of 30°C–70°C of temperature (taken as normal operating temperature of the fuel) during the testing. Thermal conductivity for all samples was recorded at every 10°C of temperature interval and results obtained are represented as in Figure 5(a) – (d). For all samples, thermal conductivity increased as a function to the temperature and this is true until 70 °C of temperature.



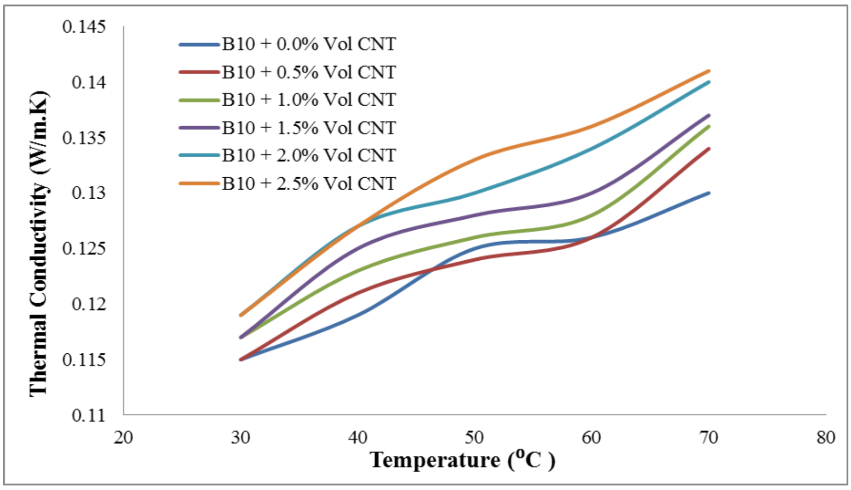
(a) D100 thermal conductivity as a function of temperature and CNT dispersion.



(b) B100 thermal conductivity as a function of elevation and CNT dispersion.



(c) B20 thermal conductivity as a function of temperature elevation and CNT dispersion.



(d) B10 thermal conductivity as a function of temperature and CNT dispersion.

Figure 5(a) – (d). Variation of thermal conductivity of fuel blends with respect to temperature and various proportions of CNT dispersions.

Compared to the blends, pure fuels (either D100 or B100) have comparatively higher thermal conductivity. This may be resulted from the inter-molecules interactions among the blend components thus improved the fuel's thermal conductivity. With the presence of single molecules (either in D100 or B100), it looked like to have positive influence on fuel's heat transfer capability. It is clear that the increased thermal conductivity with the increased temperature is attributed to the significant increment of Brownian motion of the fuel particles. The motion has led to the formation of strong convective current and has resulted in higher thermal conductivity.

In general, dispersion of CNT at increased proportions has increased the fuels' thermal conductivity. This is true for all samples. This may be resulted from the effect of nanoparticles size. Suspension of CNT into the fuel has provided greater surface area and created larger contact patch among molecules and in return produce higher thermal conductivity (Mohamad et al., 2012).

Flash point and pour point

Flash point reflects on safety issue in fuel handling process where it is used to measure the fuel's storability and transportability. Higher flash point is desirable for a fuel as that will give a less likehood of that fuel to form combustible vapour. The effect of CNT dispersion to the samples' flash point is shown as in the Figure 6.

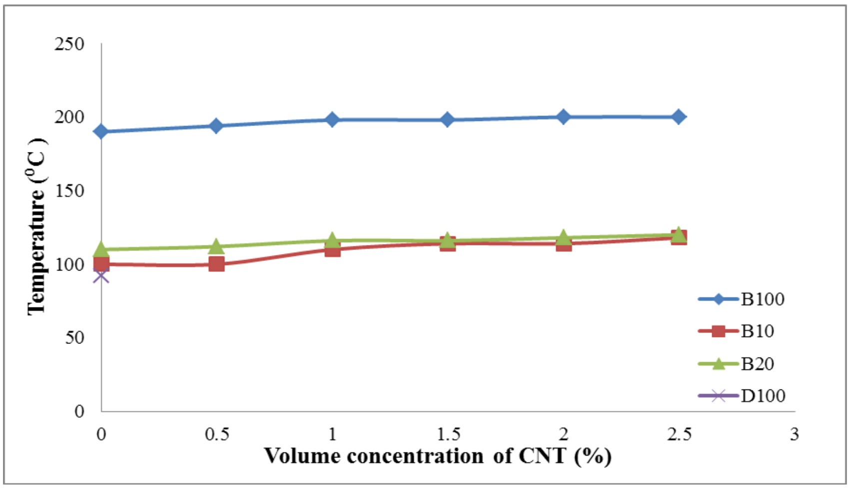
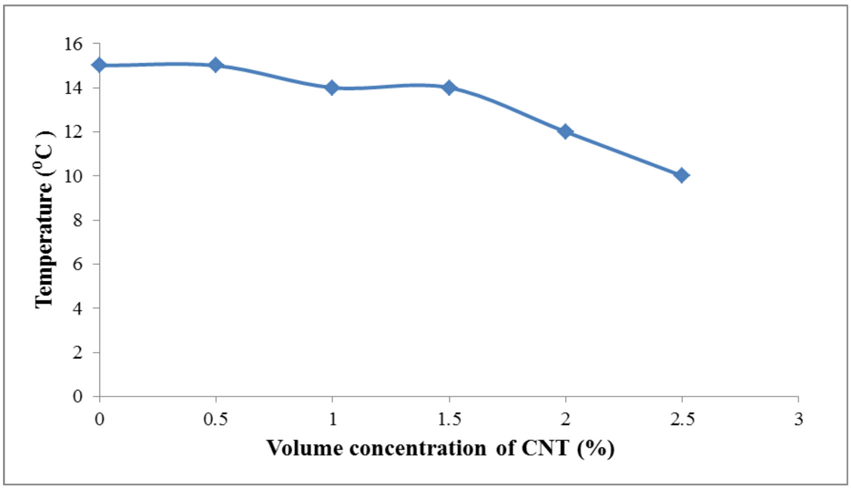


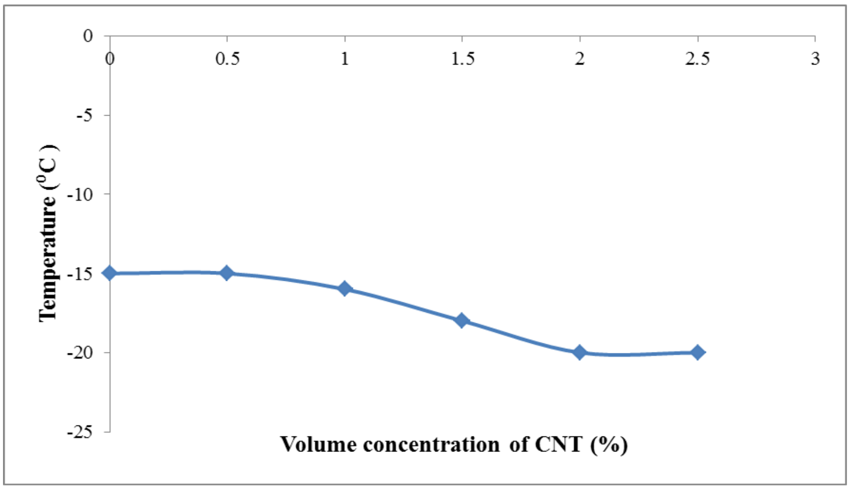
Figure 6. Variation in pour point temperature of the fuel blends with respect to various proportions of CNT dispersions.

From the experimentation, D100 has the lowest flash point temperature (at about 92°C) due to its light viscosity as compared to other fuel samples. The lower the viscosity, the lesser the amount of energy required for the substance to change phase under the heat influence. It is clear that B100, resulted from its high viscosity has the highest flash point temperature (at about 190°C). Dispersion of CNT of all concentrations has minimum influence to the fuel's flash point temperature as can be deduced from Figure 6. Gradual increment of flash point with regard to the increased of dispersion concentrations is due to the attraction van der walls force among the fuel molecules and CNT particles, and resulted in slightly elevated surface tension of the fuel. With higher surface tension, a protective film is formed to prevent the fuel from producing the combustible vapour.

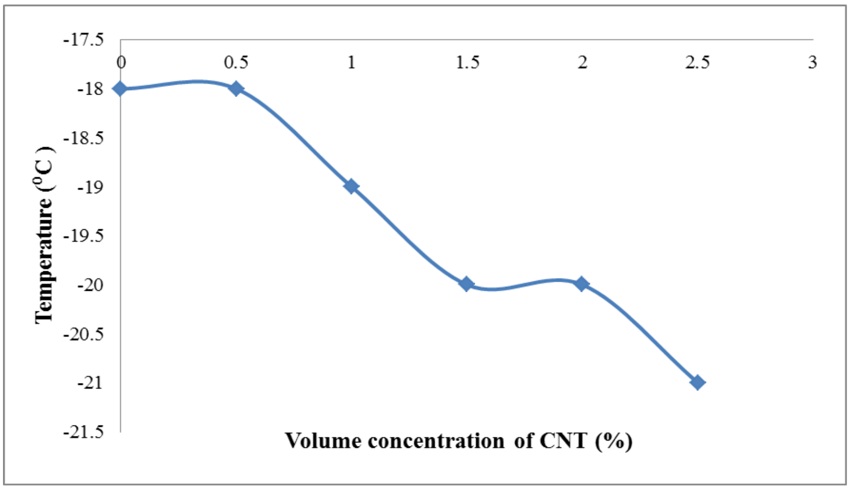
As for the pour point, it is a measure of the fuel's flow ability under the low temperature conditions. Internal combustion engines operating in cold environments needs uninterrupted continuous fuel supply in order to run smoothly. Wax and gum formation at low temperatures cannot be avoided thus the temperature at which fuel agglomeration starts to form must be determined as to ensure the safe operational margin during harsh environment operation. Figure 7(a) – (c) represents the pour point trend for all samples with respect to the increment of CNT dispersion concentrations. D100 has the lowest pour point temperature at –27°C. B100 (at 0% CNT dispersion) has the highest pour point at 15°C and this resulted from the difference in viscosity between the two fuels. Whereas, for the diesel-biodiesel blends, range of pour point temperature lay somewhat in between these two limits. Interestingly, dispersing the CNT into the fuel has improved the pour point score for the samples significantly. This may be resulted from the increase of fuel's thermal conductivity in which has the effect of lowering the pour point of nanofluid (Tijerina et al. 2012). Apart from the effect exerted by CNT itself, it can also be concluded that the pour point is very much influenced by the presence of diesel fuel in the blend as compared from Figure 7. It is a clear evident that for B100, the pour point score is still above the 0°C of temperature (Figure 7(a)) even though the dispersion of CNT is maximum in the fuel. However, this has improved significantly with the presence of diesel component in the blend where the pour point for both B10, and B20 blends have fallen to –15°C, and –18°C of temperature, respectively. This has to be addressed with meticulous attention shall a proposal for the B100 to be used commercially is presented. As for the effect of CNT on the pour point, it is believed that dispersion of CNT in the fuels functions to reduce the size and shape of wax crystals in the blends by prohibiting it from growing through a barrier to stop agglomeration at low temperature conditions (Bohsui et al. 2008).



(a) B100 pour point as a function of CNT dispersion concentration.



(b) B20 pour point as a function of CNT dispersion concentration.



(c) B10 pour point as a function of CNT dispersion concentration.

Figure 7(a) – 7(c). Variation of pour point of the fuel blends with respect to proportions of CNT dispersions.

CONCLUSION

Experimental testing and evaluation of the fuel properties after CNT were dispersed into the diesel-biodiesel fuel blends have found that:

i) The increment in blends' cetane number for a certain limit of CNT dispersion concentration.
ii) Gradual enhancement on the blends heating value due to the improvement of carbon-oxygen ratio inside the fuels.
iii) Significant effect on fuel's thermal conductivity after the CNT dispersion and looked promising as the dispersion increases further. However, this has to be addressed further as too much CNT dispersed into the fuel would alter its standard operational characteristics.
iv) No significant improvement on the blends' flash point with carbon presence. However, for the pour point, CNT particles have somewhat promising effect towards using the blends in extremely low temperature operations.

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