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THE EFFECTS OF NANOPARTICLES AS ADDITIVES TO THE FUEL CHARACTERISTICS PROPERTIES OF THE PALM METHYL ESTER BIODIESEL (PMEB) OIL

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Abstract: This paper presents the effect of nanoparticles as additives on PMEB's fuel properties. There are three types of nano additives used: Aluminium oxide (Al_2O_3), titanium dioxide (TiO_2), and silicon dioxide (SiO_2). In addition, the proportions of each nano additive are 50, 100, and 150 ppm and were tested on 20% of PMEB fuel. Several fuel properties tests, density, viscosity, SEM, XRD, and bomb-calorimeter, were investigated. This study found viscosity and density properties on the B20$SiO_2$150 nano blend with maximum values of 3.7792 mm^2/s and 820.36 kg/m^3 compared to the readings on B20, respectively. While in terms of heating value, the maximum value when compared to the B20 fuel is B20$Al_2O_3$150 (45122 J/g). Furthermore, the properties analysis testing revealed the interrelation of nanoparticle additives enriched B20 fuel properties as it is more effective in improving the biodiesel fuel blend characteristics and reducing the catastrophic gas emissions due to their combustion rate.

Keywords: Palm methyl ester, nanoparticles, fuel properties test, SEM, XRD.

Introduction

In the history of development economics, the shipping industry has been known to be a critical factor in 90% of global trade until now (Hassiba Menamara, Jan Hoffman, 2019; Wang *et al*., 2021). The main global trade includes international trade, bulk shipment of raw materials, and importing and exporting moderately priced food and manufactured goods (MIKC, 2015). In addition, since shipping activities play a vital role in the metabolism of world trading, high data on vessel emission pollution has been produced, which causes environmental degradation and contributes to climate change in the world (Sayyed *et al*., 2022). Due to strict regulations on environmental emissions by International Maritime Organisations (IMO) and the United Nations (UN) organisations, 17 Sustainable Development Goals (SDGs) were proposed by the year 2030. The main agendas that arise from this critical factor are climate action named Goal 13 and affordable and clean energy, Goal 7 (Cichos & Salvia, 2018; McInnes, 2018), which need to be applied to shipping liners worldwide.

IMO (IMO, 2022) also suggests controlling the emission through Goal 13 which focuses on climate action. This is due to increasing carbon dioxide (CO_2) and greenhouse gas emissions (GHG) from human activities, which have a significant influence on the seas (IMO, 2022). Other than that, a joint project of the Global Maritime Energy Efficiency Partnership (GloMEEP) was also improvised under IMO, the United Nations Development Programme (UNDP), and Global Environment Facility (GEF) is concentrating on building maritime energy efficiency globally, regionally, and also nationally (McInnes, 2018). Ultimately, these sustainable goals are being achieved through improvement in the fuel characteristics that are used by ships.

This study aims to investigate the palm methyl ester biodiesel (PMEB) fuel, which is one of the plant-based biofuels that most ships use nowadays. This is towards preserving energy while lowering GHG emissions for the environment. Since a high percentage of data emissions contribute to the highly polluted environment from ships, the International Maritime Organisation (IMO) suggests the emission standard needs to be increased and stricter towards these concerns.

Since there is an increasing concern that conventional diesel is depleting over time, researchers, especially from marine technologies, are prompt to contrive current diesel fuel into biodiesel fuel to comply with the suggested standard by IMO without modifying the marine engine (Sohaimi *et al.,* 2016; Noor *et al.*, 2020). According to Krishnasamy and Bukkarapu (2021), biodiesel fuel can be found from various feedstock sources, depending on their cost and local availability. Table 1 represents the list of biodiesel production originating from different countries (Krishnasamy & Bukkarapu, 2021).

Although previous study of literature was done on palm biodiesel and nanoparticles at individual capacities, a lack of studies found in the literature regarding analysing the effect of Al_2O_3, TiO_2, and SiO_2 nanoparticles at various concentrations (50 ppm, 100 ppm, and 150 ppm) of PMEB fuel blend. Moreover, this study also presents the effect of fuel properties tests on marine diesel engines. With this novelty, the experimental work was performed to study the impact of pure diesel (B0), palm methyl ester biodiesel (PMEB), and PMEB in conjunction with Al_2O_3, TiO_2, and SiO_2 nanoparticles that give out the potential fuel blends in maximising the marine diesel engine performance while considering lower emissions emits.

Materials and Methods

Biodiesel–nanoparticles Fuel Production

In the present investigations, commercial fuel manufacturers produced diesel oil (B0) and pure palm oil (B100) locally. In this laboratory, palm methyl ester biodiesel (B20) was produced

Table 1: Feedstock used to produce biodiesel based on their countries (Atabani *et al*., 2012; Krishnasamy & Bukkarapu, 2021)

Country	Feedstocks
Argentina	Soybean oil
Brazil	Soybean oil
Canada	Rapeseed/mustard/animal fat/yellow grease/soybean oil/tallow
China	Used cooking oil
France	Sunflower oil/rapeseed oil
Germany	Rapeseed oil
Greece	Cottonseed oil
India	Karanja/jatropha/rapeseed/soybean/peanut/sunflower oil
Indonesia	Palm oil/coconut/jatropha
Ireland	Animal fats/frying oil
Italy	Sunflower/rapeseed oil
Japan	Used cooking oil
Malaysia	Palm oil
Mexico	Waste oil/animal fats

by blending process where 80% of B0 was mixed with 20% of B100 with 1% of Span 80 surfactant, respectively.

Then, nine sample biodiesel fuels with three different nanoparticles (aluminium oxide, Titanium dioxide, and Silicon dioxide) as additives were tested with different concentrations (50, 100, and 150 ppm). This biodiesel-nanoparticles fuel blends are characterised as B20$Al_2O_3$50, B20$Al_2O_3$100, B20$Al_2O_3$150, B20$TiO_2$50, B20$TiO_2$100, B20$TiO_2$150, B20$SiO_2$50, B20$SiO_2$100, and B20$SiO_2$150. Figure 1 shows the workflow diagram for the preparation of biodiesel nanoparticles.

Fuel Properties Series Test

The fundamental physiochemical parameters of PMEB fuel and its blends with pure diesel are tested in the laboratory following the ASTM standards. ASTM test method is an international testing method that is used worldwide to produce detailed technical data standards. A portable viscometer (density and viscosity), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and bomb-calorimeter testers are used to determine the density, viscosity, heating value and phase view of the B20 and B20 and nanoparticles blends, respectively.

Beforehand, a dispersion stability test using ultraviolet-visible (UV-Vis) spectroscopy (GENESYS 50) analysis was conducted for all fuel samples. An ultrasonic shaker was used to shake well and retained for another 30 minutes at 30-35°C in an ultrasonic bath for a consistent suspension of fuel blends. The fuels were observed for 15 days. The spectra were plotted using automated UV-Vis software and replotted through Microsoft Office Excel using the obtained raw data spectrum. Then, all of the fuel samples were compared to observe the effectiveness of the sample in synthesising nanoparticles and biodiesel.

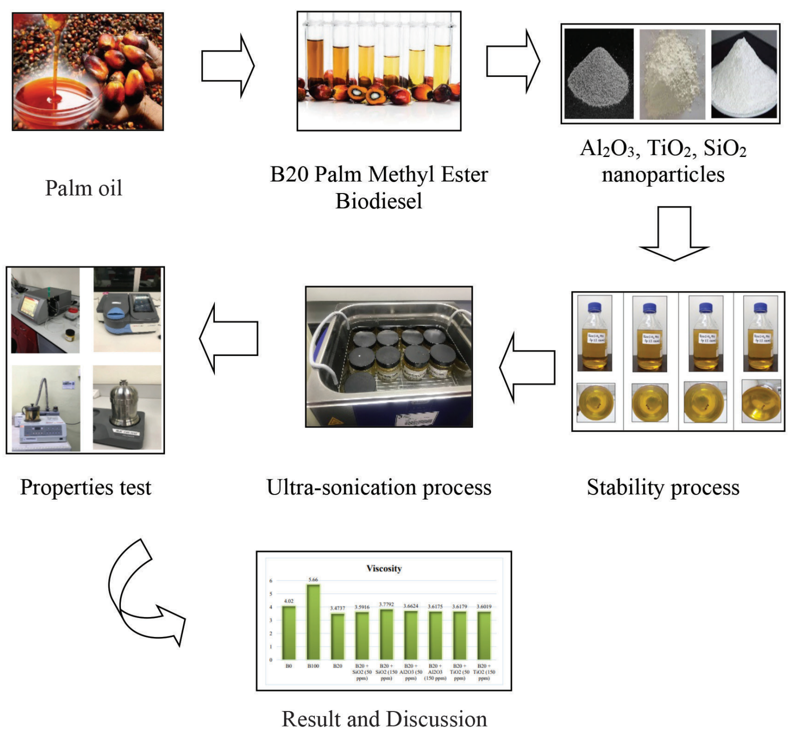


Figure 1: The workflow diagram preparation of biodiesel-nanoparticles

Portable Viscometer (Density and Viscosity)

The categorisation of Al_2O_3, TiO_2 and SiO_2 nanoparticles was carried out by portable viscometer analysis. The portable viscometer (Anton Paar SVM 30001) was used to measure the lubricants and heavy fuel and to classify the density and viscosity of fuel blends. Due to the uncertainty of time, it may affect the findings of the measured value throughout the experiment, ± 5 s is used as a tolerance (Emma *et al.,* 2022). Table 2 shows the test method and equipment used for the property test.

SEM and XRD Analysis

According to Tarannum *et al.* (2019), scanning electron microscopy (SEM) analysis was done to study the irregular, triangular, hexagonal, isotropic, polyhedral, flower, pentagonal, anisotropic, and rod structures (Tarannum *et al.,* 2019). The size and range of the nanoparticles have a major impact on the degree of aggregation and dispersion in the final fuel blend (Narayanasamy & Jeyakumar, 2019). The surface morphology of Al_2O_3, TiO_2, and SiO_2 nanoparticles was studied using SEM (JEOL 6369 LA) which provides data at the nanoscale level and creates detailed images of 3D surfaces with diameters ranging from 1 to 100 nm and categorised according to their different forms and sizes (Khan *et al.,* 2019). The resolution and magnification of the SEM used were 2-5 µm and 15 K, respectively.

Next, X-ray diffraction (XRD) testing was performed to determine the crystalline structure together with the presence of oxygen in the Al_2O_3, TiO_2, and SiO_2 nanoparticles (Soudagar *et al*., 2020). XRD (MiniFlex II diffractometer) equipment is used to display an X-ray diffraction analysis procedure that shows the face-centred cubic crystalline structure of the nanoparticles. This testing was done before the engine testing experiment. This is because the correlation between each significant data plays an important role in defining the outcome of the investigations (Noor *et al.,* 2019).

Bomb Calorimeter

The bomb calorimeter (Model IKA Calorimeter C6000) determines the heat of combustion isoperibol calorific value of the PMEB fuel blend with nanoparticle additives. This properties test is a constant volume type calorimeter that can measure the heat of a particular reaction of the fuel mixtures following the ASTM D240 procedures state for the instruments. By using the bomb calorimeter, 1 g of each of the samples was taken in the crucible and was electrically ignited to burn with the presence of pure oxygen. During the combustion, heat was released, and a temperature rise was measured. The PMEB fuel with 50, 100, and 150 ppm of nanoparticles fuel blends was used as a fuel to estimate the effective heat capacity of water (Calorimeter, 2007). The details of heating value, density and viscosity for all sample fuel blends are shown in Table 3.

Results and Discussion

Dispersion Stability

The dispersion stability of PMEB biodiesel nanoparticles depends upon the soluble capability of the Al_2O_3, TiO_2, and SiO_2 nanoparticles. Nanoparticles improve fuel quality according to performance and emission characteristics (Perumal & Ilangkumaran, 2018). Hence, to observe the nanoparticle's dispersion stability, UV spectroscopy dispersion (UV-Vis) was used to identify any single-

Table 2: The test method and equipment of the property test

Property Test	Equipment	Test Method
Density	SVM 3001	ASTM D7042
Viscosity	SVM 3001	ASTM D7042
Heating value	Bomb calorimeter	ASTM D240

Table 3: The physiochemical properties test of PMEB fuel with nanoparticles

Properties	B0	B100	B20	$B20Al_2O_3$		$B20TiO_2$		$B20SiO_2$	
				50 ppm	150 ppm	50 ppm	150 ppm	50 ppm	150 ppm
Density @15°C (kg/m^3)	811.89	834.91	815.62	818.28	818.11	818	817.96	817.74	820.36
Viscosity (mm^2/s)	3.4725	3.916	3.4737	3.6224	3.6175	3.6179	3.6019	3.5916	3.7792
Heating Value (J/kg)	45886	42130	44747	44958	45122	-	45110	-	45090

cell configuration composition that provides information about the sample.

It was seen that there are major changes in Al_2O_3 and TiO_2 while minor changes in SiO_2 fuels blend regarding their fuel colour and particle dispersion. Figure 2 shows the dispersion stability result of three nanoparticle blends with B20 PMEB biodiesel with different concentrations. Fuel blends of $B20TiO_2100$ and $B20TiO_2150$ show the highest absorbance while fuel blends for $B20SiO_2150$ have the lowest absorbance compared to other nanoparticles-biodiesel fuel blends.

Consequently, the differences between the absorbance result within the biodiesel-nanoparticles fuel blends were directly proportional when van der Waals attractive forces outweighed electrostatic repulsive force as the nanoparticles were clumped together (Krishnakumar & Elansezhian, 2022). The results will primarily attributed to changes in viscosity, increased density and improved heating value (Gad & Jayaraj, 2020) while minimising issues with overloading and sedimentation in the engine fuel system.

Density and Viscosity

The fuel properties, such as the density and viscosity of biodiesel nanoparticles, were determined. It is found that the addition of nanoparticles increased the properties of the B20 fuel blend, as shown in Figure 3 and Figure 4. The lowest density of biodiesel-nanoparticles of (817.74 kg/m^3) was recorded by $B20SiO_250$ and the highest density of (820.36 kg/m^3) by $B20SiO_2150$. Density for all nano additives fuel blends decreases compared to B100 while slightly increasing (1%) compared to

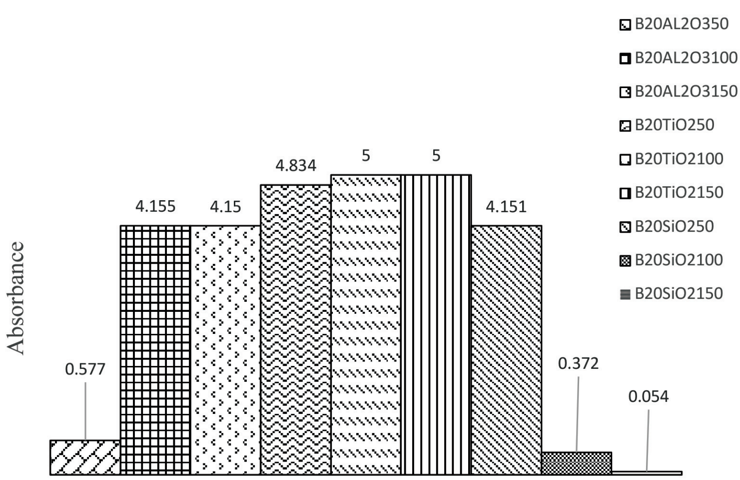


Figure 2: Dispersion stability in biodiesel-nanoparticles blends

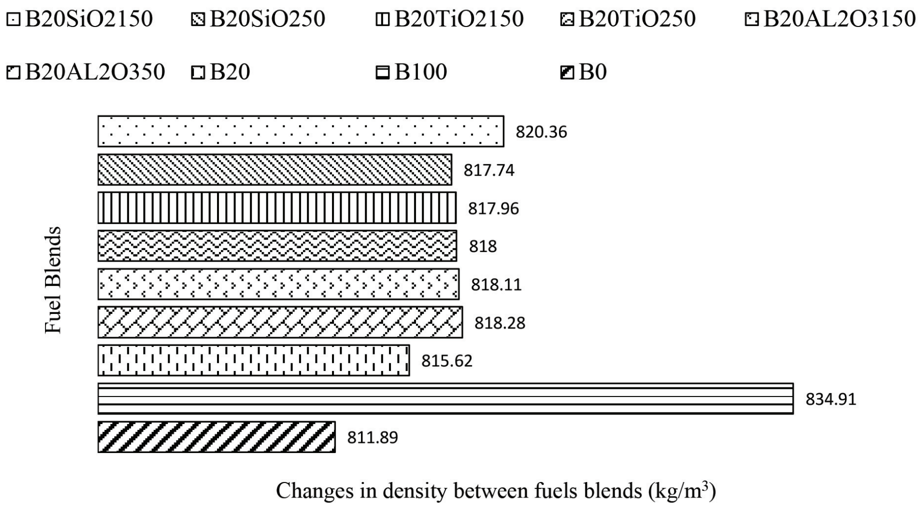


Figure 3: Changes in density between fuel blends

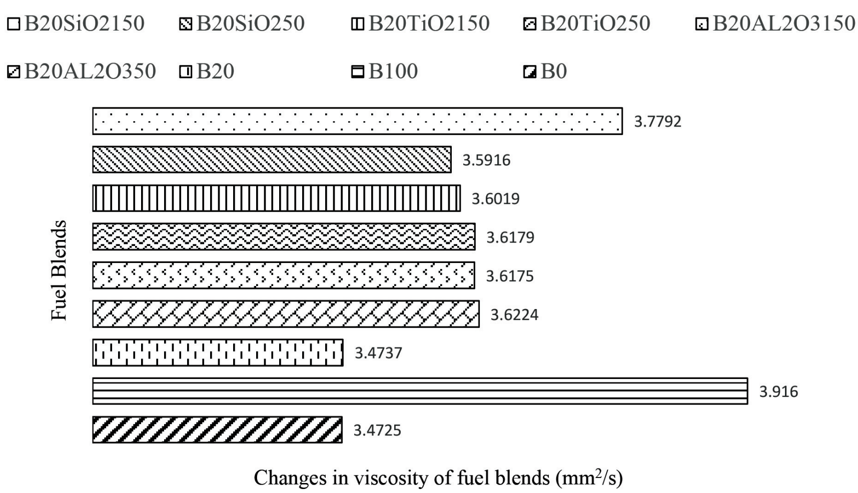


Figure 4: Changes in viscosity of fuel blends

B20 and B0. This same goes for the result of viscosity, where about 4.2% higher than B20. The kinematic viscosity of the biodiesel nanoparticles was the lowest (3.5916 mm^2/s) for B20$SiO_2$50 and the maximum (3.7792 mm^2/s) for B20$SiO_2$150. The changes in kinematic viscosity between the fuel blends are presented in Figure 4. The changes in viscosity gradually reduced when concentrations of nanoparticles were added, compared to B20 biodiesel, when the temperature was increased. It is due to differences in the performance of individual nanoparticles. This helps increase the surface area enhances the conversion of palm oil to biodiesel and improves the quality of engine emission and combustion (De & Boxi, 2020).

Heating Value

In this work, a bomb calorimeter was explored to determine the heating value of biodiesel nanoparticles (B20$Al_2O_3$50, B20$Al_2O_3$150, B20$TiO_2$150, B20$SiO_2$150). Heating value is one of the critical factor parameters in defining the intensity of heat release rate that presents the energy efficiency of engine performance. The heating value obtained for all biodiesel-nanoparticle fuel blends was higher than B20s. This result shows the B20$Al_2O_3$150 heating value has the highest heating value among other biodiesel-nanoparticle additives blends of 45,122 J/g. Such high heating values mean that these materials have the potential to be used as energy sources (Ahmad *et al.*, 2019). Moreover, given the high heating value from biodiesel-nanoparticles compared to B20, it will reflect in brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) of marine diesel engines. This highlighted how incorporating nanoparticles enhanced the heating value of biodiesel-nanoparticle blends and guaranteed a benefit in reducing BSFC due to the minimum quantity of fuel oil injected to achieve maximum power output (Ağbulut *et al.*, 2020). Concerning issues on depleting oil sources such as crude oil, it can be encountered by reusable waste oil with nanoparticles as it has the potential to maximise the engine performance and combustion while lowering the engine emissions due to improved surface area and reactivity (Sukjit & Maneedaeng, 2022). Figure 5 shows the changes in heating value between the fuels blend.

SEM and XRD

Understanding the distinctive characteristics of nanoparticles requires their characterisation, and scanning electron microscopy (SEM) testing has proven to be a useful method for clarifying these nanoparticles' structural and morphological characteristics. SEM image magnification of 4 K and 6 K for Al_2O_3, TiO_2, and SiO_2 nanoparticles are represented in Figure 6 (a) (b), Figure 7 (a) (b), and Figure 8 (a) (b), respectively. The SEM images revealed that Al_2O_3 nanoparticles have a more hexagonal crystalline-like structure and are larger in diameter than TiO_2 and SiO_2, which are finer. The SEM image also showed that SiO_2 nanoparticles agglomerated more easily than Al_2O_3 and TiO_2 nanoparticles.

The use of X-ray diffraction (XRD) analysis has greatly expanded the study of nanoparticle properties and provided previously inaccessible information about the structural characteristics of nanoparticles. XRD further validated the element presence of the three nano additives as shown in Figure 6 (c), 7 (c), and 8 (c). The intensity between peaks for Al_2O_3 nano additives were shown at 19.75°, 32.78°, 37.13°, 45.42°, 61.5°, and 66.84° and agreeing to reflection planes of (111), (220), (311), (400), (511), and (440) correspondingly. For TiO_2, the peaks were noted at 25.27°, 27.4°, 36°, 37.79°, 38.57°, 47.94°, 53.95°, 54.98°, 62.66°, 68.99°, 70.35°, and 74.89° correspondingly at planes (101), (110), (103), (004), (200), (105), (211), (220), (213), (116), (215), and (301) were indexed to pure cubic fluorite structure of TiO_2 (Narayanasamy & Jeyakumar, 2019). While for

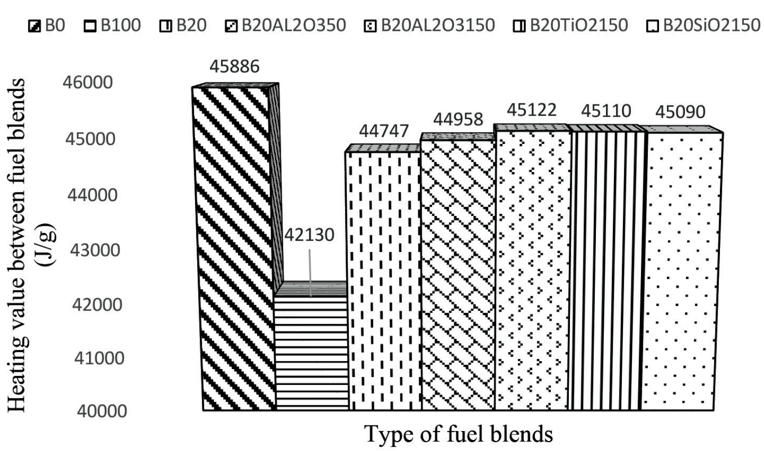
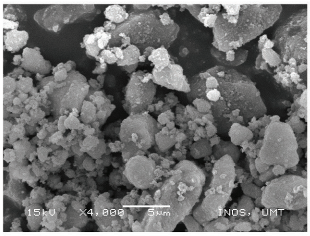
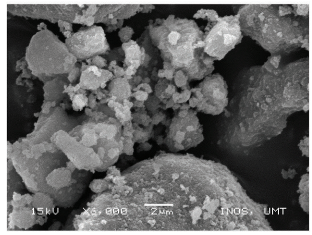


Figure 5: Changes in heating value between fuel blends

(a) (4,000x) (6,000x)





(c)

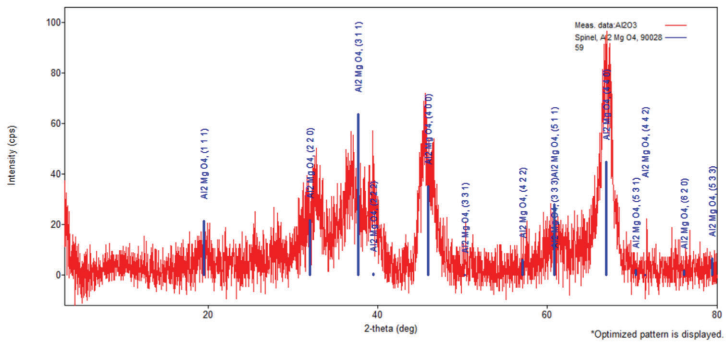
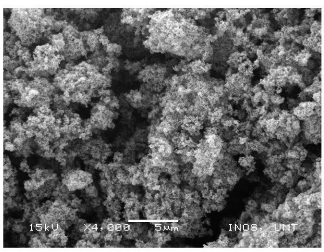
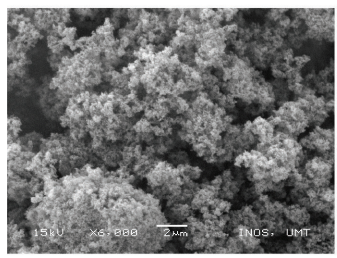


Figure 6: Al2O3 nanoparticles (a) and (b) SEM image of 4,000x and 6,000x, and (c) XRD image

(a) (4,000x) (6,000x)





(c)

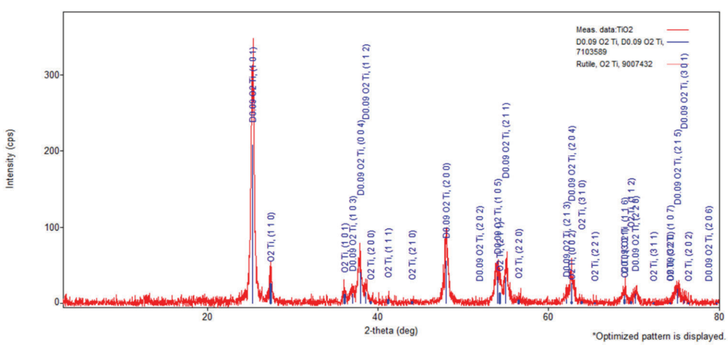
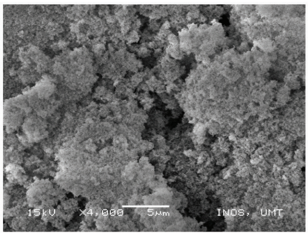
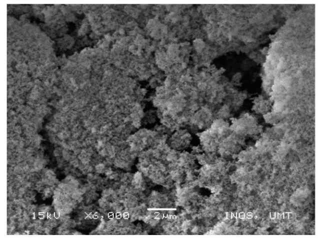


Figure 7: TiO2 nanoparticles (a) and (b) SEM image of 4,000x and 6,000x, and (c) XRD image

(a) (4,000x)



(b) (6,000x)



(c)

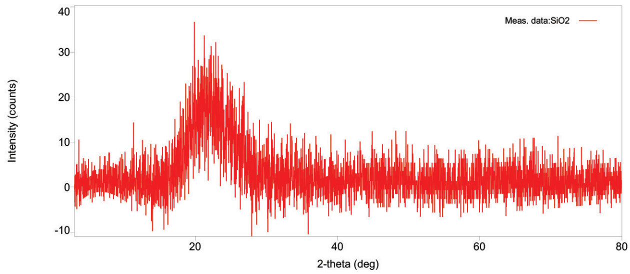


Figure 8: SiO2 nanoparticle (a) and (b) SEM image of 4,000x and 6,000x, and (c) XRD image

the SiO_2, the peaks were noted at 26.46°. This confirmed that the nanoparticles present in the PMEB fuel blends.

Conclusions

From this study, the experiments were done to show the effects of Al_2O_3, TiO_2, and SiO_2 nanoparticles as additives to B20 palm methyl ester biodiesel fuel blend on fuel characteristics properties test Al_2O_3, TiO_2, and SiO_2 at different concentrations of nanoparticles (50, 100, 150 ppm) were added to PMEB B20 blend. Al_2O_3, TiO_2, and SiO_2 were synthesised and characterised by Scanning Electron Microscope (SEM) and X-ray diffraction (XRD). The fuel properties of the prepared palm methyl ester with nano additives were found to confirm the ASTM standards. Based on the results, the density and viscosity of PMEB fuel have been improved by using nanoparticles as additives when compared to B20 fuel, as it increased by 1% and 4.2%, respectively. The structure under SEM revealed that Al_2O_3 have hexagonal crystalline structures while TiO_2 and SiO_2 are much finer. This presents the intercorrelation of XRD for both nano biodiesel blends (Al_2O_3 and TiO_2) for similar high absorbance in the dispersion stability. The interrelation of Al_2O_3 additives has enriched the calorific of B20 fuel properties as it increases the combustion of marine diesel engines and reduces the catastrophic gas emissions due to their large contact area, good stability, and a raid combustion rate. This is shown where the Al_2O_3 mixture with a concentration of 150 ppm has the highest heating value of 45,122 J/g. Further studies on biodiesel-nanoparticle effects in experiments will focus on engine performance, engine emissions, and engine combustions of marine diesel engines. By combining nanoparticles with palm biodiesel fuel, engine performance, emission and combustion can be significantly enhanced, providing a practical substitute fuel for marine diesel engines without needing to modify the engines.

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Conflict of Interest Statement

The authors declare that they have no conflict of interest.

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