Properties Study of B20 Palm-Methyl Ester Biodiesel Added with Oxide Nanoparticle Towards Green Marine Fuels

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ABSTRACT

Demand for low carbon emissions in the shipping sector has prompted alternative energy sources to reduce dependence on diesel petroleum for day-to-day operations. Biodiesel fuel has been identified as one of the alternative energy sources that can be used in marine engines. Biodiesel is a plant-based fuel, environmentally friendly, renewable, non-toxic and oxygenated. Despite having many advantages, it nevertheless contributes to a slight reduction in engine power due to its low energy content compared to diesel fuel. Therefore, this study aims to evaluate the effect of using different types of nanoparticle additives with different concentrations on the properties of biodiesel fuel. Nine test samples were prepared by blending B20 palm methyl ester biodiesel fuel with aluminium oxide (Al_2O_3), silicon dioxide (SiO_2) and titanium dioxide (TiO_2) nanoparticle by different concentrations of 50 ppm, 100 ppm and 150 ppm. Several series of fuel property tests were performed on the samples including density, viscosity, calorific value, scanning electron microscope (SEM) and X-ray diffraction (XRD). The test results showed that, the caloric value of B20 biodiesel fuel was increased from 44747 J/g to 45122 J/g, 45090 J/g and 45110 J/g with the addition of Al_2O_3, SiO_2 and TiO_2 nanoparticle, respectively. The viscosity and density properties have also improved with the highest values found on the SiO_2 blend of 3.7792 mm²/s and 820.36 kg/m³. The morphology study revealed that the structure of nanoparticles is in an amorphous state which is expected to contribute a large contact area, good stability and catalytic with a high combustion rate of blend fuel. All of these advantages are expected to contribute as a good catalyst to biodiesel fuel in order to produce optimal combustion of marine diesel engines and further reduce harmful gas emissions.

1. Introduction

The combustion of fossil fuel by marine diesel engines emits harmful gas which is detrimental to humans and the environment [1,2]. More than 3% of global carbon dioxide emissions can be attributed to ocean-going ships which about 1056 million tonnes annually [3]. Exhaust gas emissions from marine diesel engines largely comprise of nitrogen, oxygen, carbon dioxide, and water vapour,

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carbon monoxide, oxides of sulphur and nitrogen, partially reacted and non-combusted hydrocarbons and particulate material [4]. This scenario gives a serious impact on the global air quality and climate. Thus, efforts and techniques in improving combustion and exhaust emissions are becoming critical issues particularly to comply with the restrictions imposed rules by the International Maritime Organization (IMO) along 3 Tier levels [5,6]. In fact, these gases are detrimental to the human health because several health issues may be triggered, such as lung cancer, cardiopulmonary death, bronchitis, and pneumonia. The NOx emissions are believed to be carcinogenic and contribute to photochemical smog formation over cities, acid rain and tropospheric ozone [7].

Shipboard stringent regulations enforcement demand for more viable solutions. Hence, increasing usage of biodiesel fuel appears to be an effective measure in addressing the issue discussed. Biodiesel is a plant-based fuel, easily available, renewable, eco-friendly, bio-degradable, non-toxic and has similar properties to diesel fuel [8-10]. Biodiesel reduces the dependence on the fossil fuels and reduces the greenhouse gas emissions due to its closed carbon cycle [11]. Despite the many advantages of biodiesel revealed, there are also some disadvantages such as an increase in NOx emissions, slightly lower energy content, marginally higher density and poor fuel atomization [12-15]. There is a further scope for enhancement in fuel properties and to overcome the drawbacks by addition of nanoparticles as fuel additives to biodiesel fuel.

Nanoparticles are defined as materials that have a size or dimension smaller than 100 nm. Oxide nanoparticles are attracting the attention of researchers in various fields because they have unique and novel properties for research [16]. The application of nanoparticles is considered as one of the best fuel additives to improve fuel properties because they have a high surface area, shortened ignition delays and quick evaporation [17]. Most of previous research had focused on the automotive diesel engines. Some finding claimed that adding Cerium oxide nanoparticles (CeO_2) with biodiesel has increases the fuel cetane number and efficiency of diesel engine [18]. Ghanbari *et al.,* [19] had examined the performance and emission of multi cylinder diesel engine by using 5nm carbon nano tubes (CNT) and 50nm nano Silver (Ag) particles added waste cooking biodiesel. The results increase the brake power and torque and decrease the brake specific fuel consumption. The level of CO and HC emission were decreased while the CO_2 and NOx were increased [19]. Perumal *et al.,* [20] revealed that adding Cooper oxide (CuO) nanoparticles to B20 pongamia biodiesel blend leads to enhance the engine thermal efficiency by 4% and reduces the NOx emission by 9.8%. The authors stated that the CuO nanoparticles act as a NOx decomposer by increasing the oxygen stability of fuel [20].

Although previous studies have been conducted on nanoparticles, there is less literature reported regarding the analysis of Al_2O_3, SiO_2 and TiO_2 oxide nanoparticles additives with blended palm biodiesel. In this work, different types and concentrations of nanoparticles incorporated B20 palm-methyl ester biodiesel fuel has been subjected to fuel properties test and characterization. The objective of this study is to determine the fuel properties of biodiesel blend samples by testing density, viscosity, caloric value, in addition to examining the surface morphology of nanoparticles using scanning electron microscopy and X-ray diffraction method. The selection of Al_2O_3, SiO_2 and TiO_2 oxide nanoparticles in this study is because they are more cost-effective and easily available in the market. Palm biodiesel fuel was chosen as fuel for this project due to the abundance of palm oil resources in Malaysia and it is also in line with the Malaysia Biofuel Policy to promote a domestic utilization of palm biodiesel.

2. Methodology

2.1 Fuel Sample Preparation

Preparation of fuel samples was done by blending B20 palm-methyl ester biodiesel with of Al_2O_3, SiO_2 and TiO_2 oxide nanoparticles that have different concentrations of 50 ppm, 100 ppm and 150 ppm as shown in Figure 1. The ultrasonication process has been performed on sample nanoparticles to ensure that the resulting fuel is homogeneous. The agitation of this process takes place for 30 minutes with a rotation speed of 10,000 rpm. The ultrasonication process is the best method to disperse the nanoparticles in the liquid to avoid agglomeration of the nanoparticles [21]. A total of nine fuel samples have been produced namely AL50, AL100, AL150, Si50, Si100, Si150, Ti50, Ti100 and Ti150. All these samples have been sent for property tests such as calorific value, density, viscosity, SEM and XRD test. The B100 and B20 biodiesel were also tested to serve as a baseline fuel for comparison.
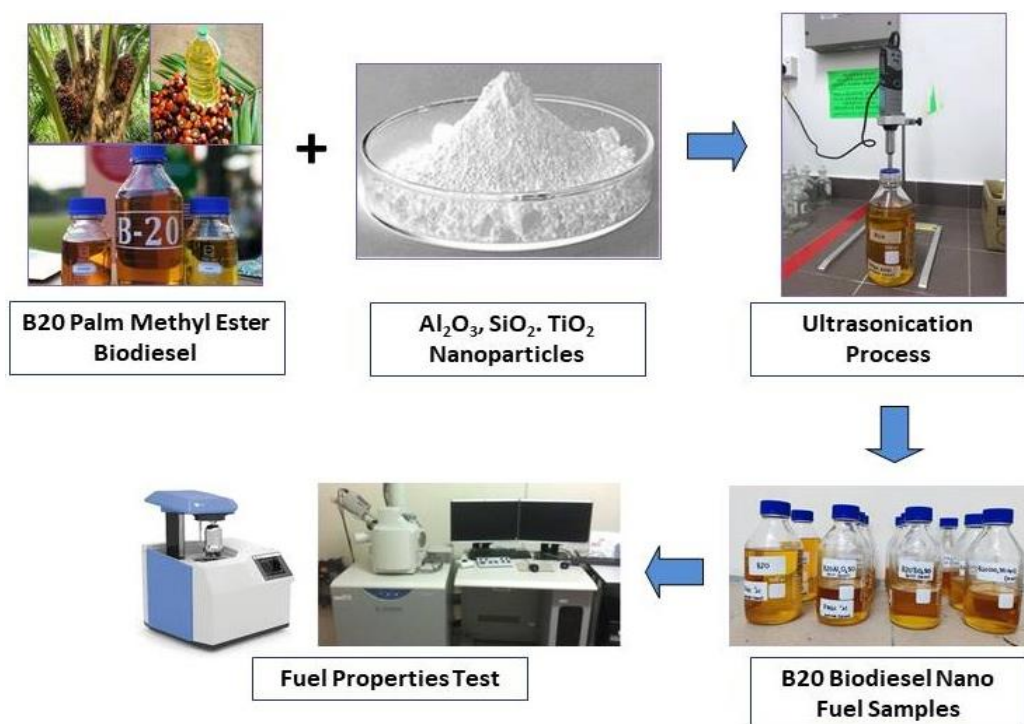

Fig. 1. Sample preparation process

2.2 Fuel Property Test

In this study, a series of property tests were performed on biodiesel blends samples such as calorific value, density, viscosity, scanning electron microscopy and X-ray diffraction analysis. Testing the calorific value of the sample is determined by using a bomb calorimeter model IKA Calorimeter C6000 as illustrated in Figure 2. The combustion reaction in the bomb calorimeter takes place at constant volume and tests were conducted according to ASTM D240 standards. Prior to the test, each 1g of the fuel sample was taken in the crucible and electrically ignited to burn with the presence of pure oxygen. During the combustion, heat was released and a rise in temperature was measured by the equipment. The total energy release in Joule units during the combustion of the fuel sample is obtained based on Eq. (1).

$$q = c_v(T_f - T_i) \tag{1}$$

where q is the heat amount, c_v is the specific heat at constant volume, T_i and T_f are the initial and final temperatures, respectively.
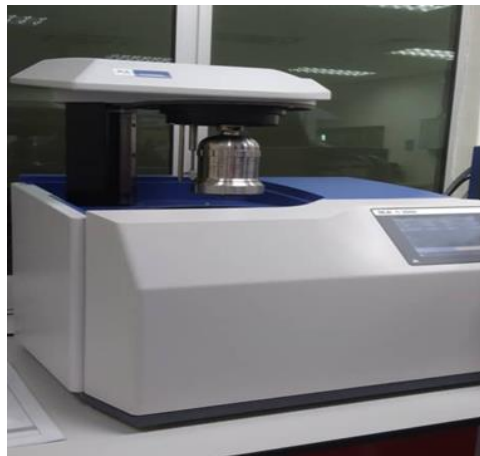

Fig. 2. Bomb Calorimeter equipment

Meanwhile the property of fuel density represents it mass per unit volume. Fuel with higher density has more mass when injected into combustion chamber for the similar volume amount of fuel in turn can produce more power on the engine. Viscosity is a term used to describe liquid resistance to flow due to internal friction. This property plays an important role in the combustion of diesel engines as it relates directly to the characteristics of the fuel injection. Higher viscosity of fuel is responsible for poor injection atomisation and causes the engine to lose power while too low a fuel viscosity may cause a leak in the injection pump [22].

The viscosity and density of fuel was determined by using a Portable Viscometer Anton Paar model SVM 3001 as shown in Figure 3. The measurement principle of this equipment is based on the modified Couette measurement method and it consists of a viscosity cell and a density cell. The measuring cell has a tube that is filled with sample fuel and rotates at a constant speed. The shear force from the sample will drive the rotor and the magnetic force will slow its rotation. After the measurement process starts, the rotor reaches an equilibrium speed and this speed is translated for the calculation of the viscosity of the sample liquid. The kinematic viscosity reading will be determined based on the dynamic viscosity and density of the sample. Kinematic viscosity test of biodiesel can be determined in accordance with ASTM D7042 standards.

Fig. 3. Portable Viscometer

Scanning electron microscopy (SEM) analyses were performed using a Hitachi S-3400N as shown in Figure 4 to investigate the surface morphology of nanoparticles used in this study. The Hitachi S-3400N is a high-performance SEM instrument capable of 3.0 nm resolution in high vacuum mode. The electron beam is produced by an electron gun located at the top of the microscope and it is emitted following a vertical path in the vacuum chamber of the microscope. This device operates under an accelerating voltage of 15 kV. A small amount of fresh catalyst was placed on the surface of a carbon tape, which had been fixed on an aluminium holder of diameter 15 mm.

The structure phase of nanoparticles was study using X-Ray Diffraction (XRD) equipment model RIGAKU Mini Flex II as shown in Figure 5. Changes in XRD diffraction peak positions are used to infer how crystal structure and cell parameters change with changes in nanoparticle size and shape. RIGAKU Mini Flex II is a multi-purpose powder diffraction analysis tool capable of determining crystal phase identification (phase ID), percent (%) crystallinity, crystal size and strain, refinement of lattice parameters and molecular structure on samples.

Fig. 4. Scanning Electron Microscope

Fig. 5. X-Ray Diffraction equipment

3. Results and Discussion

3.1 Calorific Value

Calorific value is a very important property of diesel fuel, because it describes the energy content of the fuel. The higher the calorific value of a fuel it will produce a greater engine output power. The effect of nanoparticle addition on the calorific value of the biodiesel sample is shown in Figure 6. Nanoparticle additive has increased the calorific value of all fuel blends compared to B20 and B100 where the Al_2O_3 150 ppm blend has the highest with 45122 J/g, followed by the TiO_2 blend and SiO_2 which is 45110 J/g and 45090 J/g respectively. The graph also shows the increase in nanoparticle concentration directly proportional to the calorific value of each blend. The addition of oxide nanoparticles has increased the energy value in each sample tested. According to previous studies, the addition of nanoparticles can increase the calorific value, Cetane number and help reduce the flash point of the biodiesel blend [23]. Improvements to the fuel properties of biodiesel can increase the combustion of internal combustion engines and reduce harmful gas emissions. The application of nano additives to the diesel-biodiesel fuel blend is considered an important effort to improve the environment from vehicle emission pollution [13].
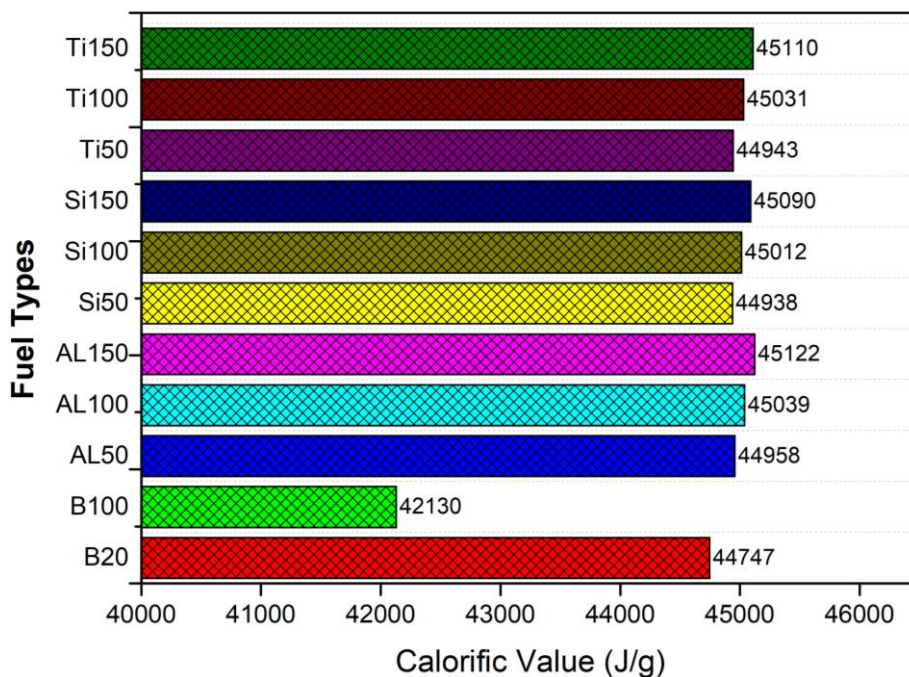
Fig. 6. Calorific value of the test samples

3.2 Density and Viscosity Test

Figure 7 and Figure 8 show the changes in density and viscosity among the fuel blends. As shown in the graph, the density of all fuel blends decreases compared to B100 while it slightly improves when compared to B20. The addition of nanoparticle concentration into B20 biodiesel has slightly increased the value of fuel density especially in the SiO_2 blend which has the highest value of 820.36 kg/m^3 but does not show significant changes in other blends. The same effect also applies to the value of kinematic viscosity where the mixture of SiO_2 with a concentration of 150 ppm has the highest value compared to other blends which is 3.7792 mm^2/s. Blending oxide nanoparticles into B20 biodiesel does not make a significant change but has improved the quality of the fuel blends compared to B100.
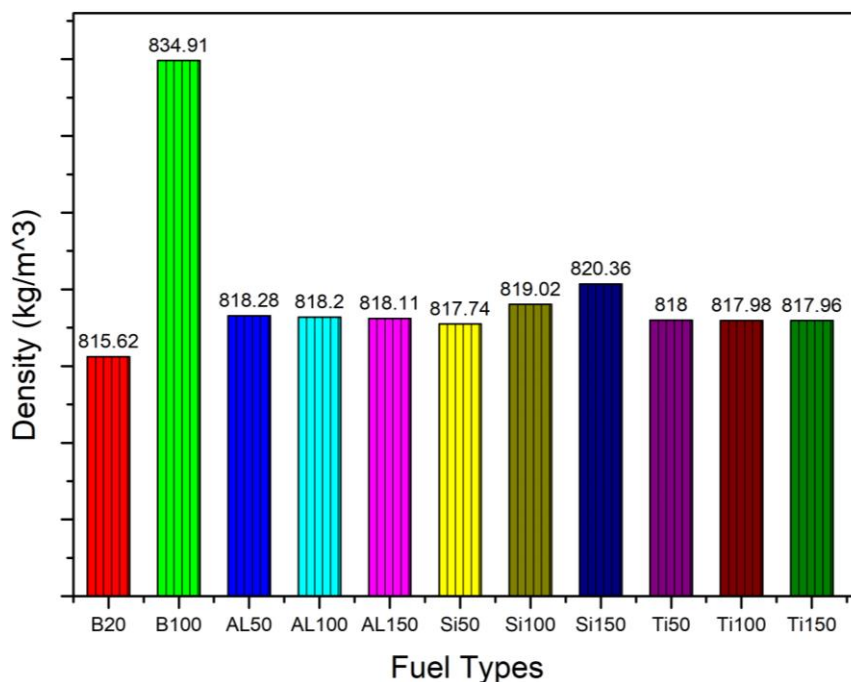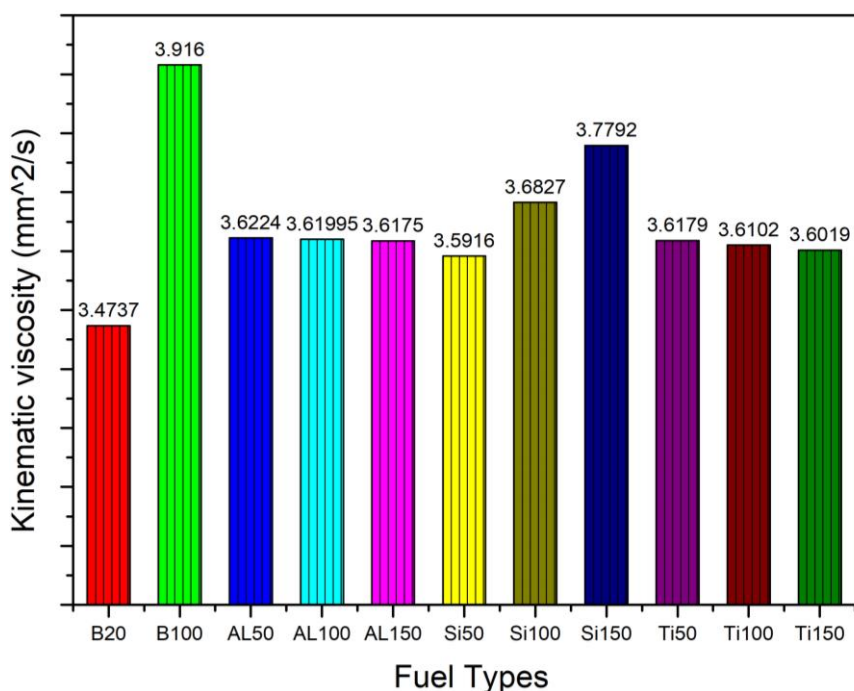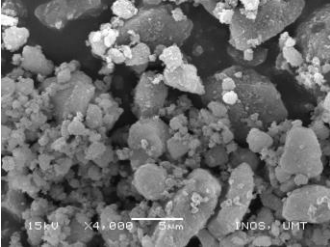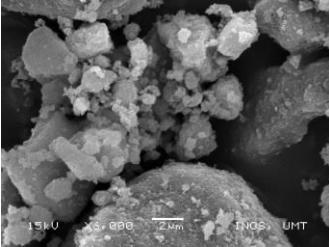
Fig. 7. Density of the test samples
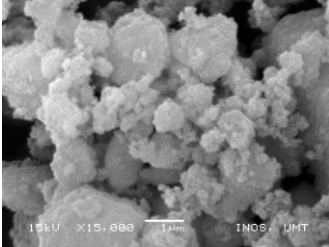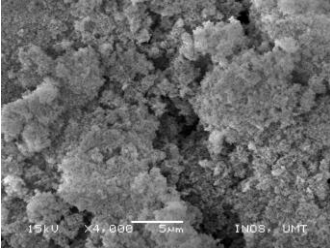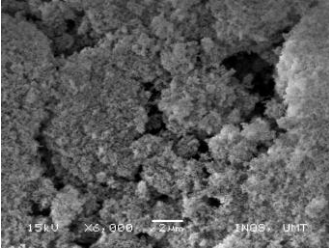
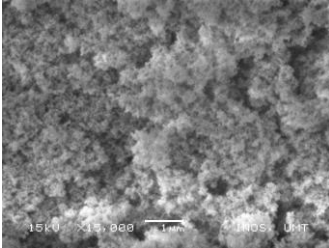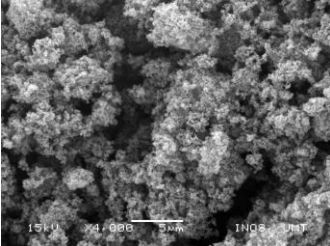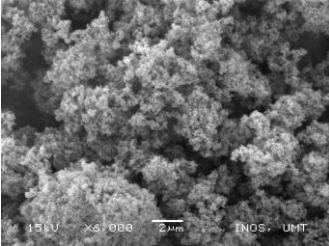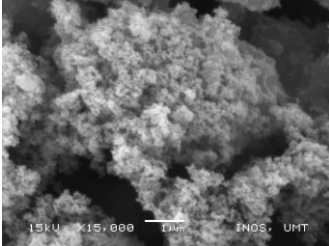**Fig. 8.** Viscosity of the test samples

3.3 SEM and XRD Analysis

The SEM surface morphology of Al_2O_3, SiO_2 and TiO_2 nanoparticles were investigated using the high-performance scanning electron microscope. The resolution and magnification of the SEM were set between 2-5 µm and 4-15K respectively. Photographic SEM images for different nanoparticles with magnifications of 4000x, 6000x and 15000x are displayed in Table 1. Based on the three magnifications, the structure of Al_2O_3 nanoparticles appears to be more crystalline and larger in diameter size compared to other nanoparticles. While the images of SiO_2 and TiO_2 appear to have a

finer size and tend to the amorphous state. The average particle size of the nanoparticles tested was estimated to be in the range of 10 to 25 nm. Amorphous solid refers to the size of each molecule in a substance that is too small compared to the distance between the atoms or molecules of the substance. Amorphous solids have no grain boundaries [24].

Table 1
SEM images of different types of nanoparticles

Nanoparticle	4000x magnification	6000x magnification	15000x magnification
Al_2O_3			
SiO_2			
TiO_2			

The results of XRD patterns for Al_2O_3, SiO_2 and TiO_2 nanoparticles are illustrated in Figure 9, Figure 10 and Figure 11, respectively. The diffraction peaks of Al_2O_3 nanoparticles 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 SiO_2 nanoparticles, the XRD reflection peak has been detected to occur at 26.46°, meanwhile the reflection for TiO_2 were noted at 25.27°, 27.40°, 36.02°, 37.79°, 38.57°, 47.94°, 53.95°, 54.98°, 62.66°, 68.99°, 70.35°, and 74.89° correspondingly to planes (101), (110), (103), (004), (200), (105), (211), (220), (213), (116), (215), and (301). XRD analysis of oxide nanoparticle samples shows that Al_2O_3, SiO_2 and TiO_2 nanoparticles have an amorphous structure which contributes to a large contact area for the fuel blend. The nature of the fuel additive that has a higher surface contact area will produce higher chemical reactivity and resulting in effective combustion in the engine cylinder [21].
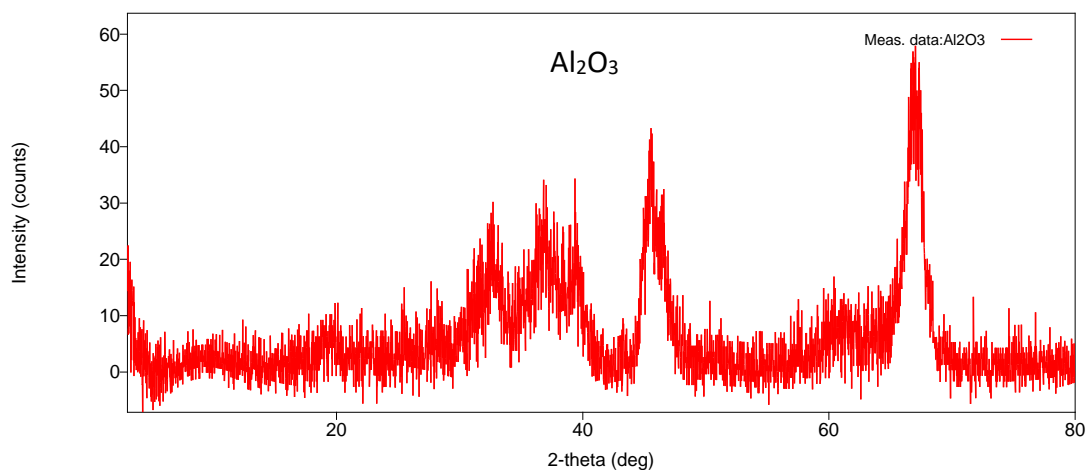
Fig. 9. XRD pattern of Al_2O_3 nanoparticles

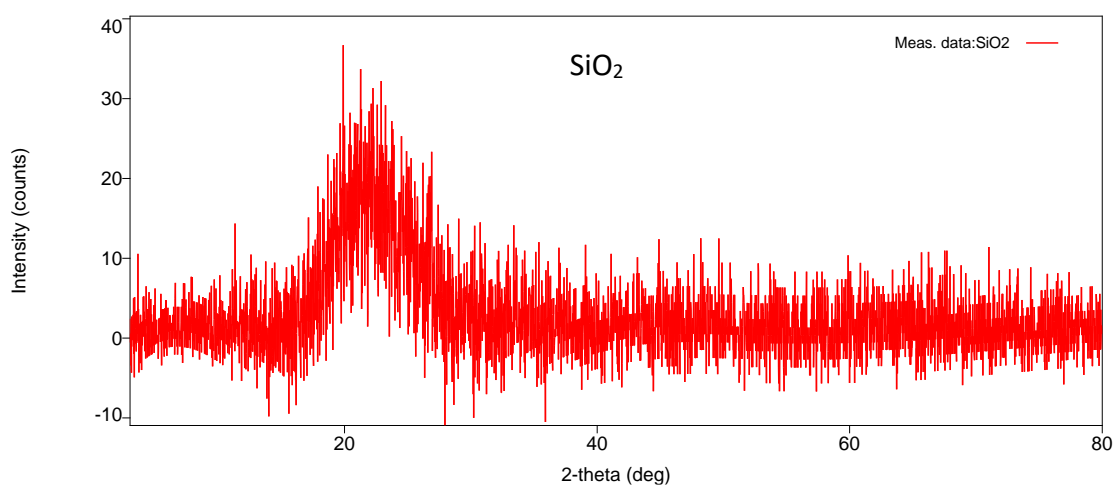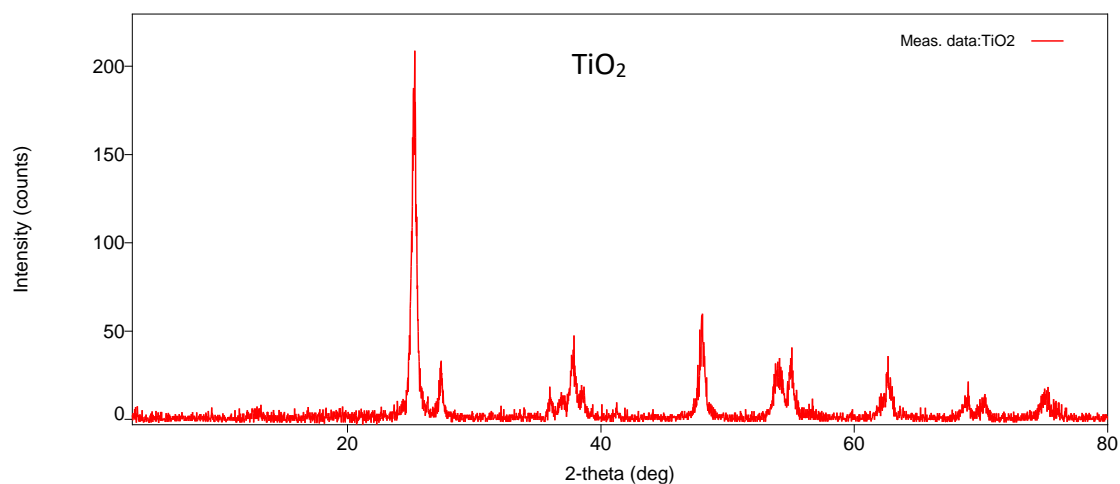**Fig. 10.** XRD pattern of SiO_2 nanoparticles

Fig. 11. XRD pattern of TiO_2 nanoparticles

4. Conclusions

Property tests on B20 palm-methyl ester biodiesel fuel added with different types of nanoparticle additives were investigated in this study. Some observations from the study can be concluded as follows. The addition of nanoparticles has enriched the calorific properties of B20 fuel where the

Al_2O_3 mixture with a concentration of 150 ppm has the highest value of 45122 J/g. It was found that density and viscosity of palm biodiesel fuel have been improved by using nanoparticles as additives when compared to B20 fuel, as it increased by 1% and 4%, respectively among the test fuels. The obtained result of SEM and XRD revealed that Al_2O_3 have hexagonal crystalline structures while TiO_2 and SiO_2 are much finer in structure. The results of the morphological study show that the nanoparticle structure is in an amorphous state and is suitable for blending with biodiesel fuel. The amorphous state of nanoparticles provides a large contact area on the fuel additive material. These features are expected to improve combustion quality in the engine and reduce exhaust gas emissions, further contributing to green fuel for marine diesel engine applications. Based on the results of the property test and morphological study on nine biodiesel fuel samples, the Al_2O_3 sample with a concentration of 150 ppm has been identified as the optimal blend in this study. In further studies, these samples will be tested in marine diesel engine to determine their effect on engine performance, emissions and combustion characteristics.

Acknowledgement

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