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Effect of nanomaterials sizes on the dispersion stability of biodiesel based nanofluids

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ABSTRACT

The effect average alumina nanoparticle sizes on the long term dispersion stability of biodiesel based nanofluids was investigated. Alumina nanoparticles having two different average sizes (~13nm and ~28nm) were dispersed in the Jatropha biodiesel as the base fluids. The effect of alumina (Al_2O_3) nanoparticles sizes on the stability of nanofluids was investigated to achieve more stable nanoparticles dispersed nanofluids having longer duration for potential use in alternative fuel energy applications. Different volume fractions (VF) such as 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% nanofluids were prepared by using two different sizes of alumina nanoparticles (~13nm and ~28nm) by using the surfactants $Span^{80}$ and $Tween^{80}$ in the ratio of 1:1. The results revealed that the nanofluids having the smaller average sizes alumina nanoparticles and 0.1% volume fraction were stable for more than one year as compared to the larger (two times) size nanoparticles having same 0.1% volume fraction. Such long term stable biodiesel based nanofluids can be used as the alternative fuel energy for future automobiles and transportation sectors due to the fuel properties of such nanoparticles dispersed nanofluids retaining the commercial diesel properties. Copyright © 2015 VBRI press.

Keywords: Nanofluids; alumina nanoparticles; size effect; biodiesel; alternative fuel.

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Introduction

Transportation sector is the backbone for the rapid growth of industrialization and also for the existence of the modern civilization, the basic requirement for the transportation sector is the availability of fossil fuels i.e., petrol and diesel. From the last two decades, the prices of these fossil fuels have increased to almost two folds and are still on the rising. The main reason for these high prices is the rapid growth of industrialization and motorization all around the world and also the limited reserves of the fossil fuels. Also apart from the high cost of these fossil fuels, these fossil-fueled vehicles discharge significant amount of pollutants like CO, UBHC, NOx, SOOT, LEAD components and aldehydes which cause environmental degradation **[1-3]** and also severe health problems. In this context, biodiesel has emerged as one of the most potential renewable energy to replace current commercial diesel. Also, it is renewable, biodegradable and non-toxic fuel which can be easily produced through transesterification reaction **[4, 5]**. However, such biodiesel based fuel cannot directly use in diesel engine due to high ignition delay, low cetane number, high brake specific fuel consumption, low calorific value, and low brake thermal efficiency.

It was reported that by addition of nanoparticles to the fuel, the performance and emission characteristics of the diesel engine can be improved **[6]**. Tyagi and et al. **[7]** showed that by addition of aluminum and alumina nanoparticles to the diesel, the diesel engine characteristics such as ignition delay can be improved. They have reported that heat and mass transfer properties of the pure diesel can be increased by dispersion of nanoparticles in the pure diesel and therefore the ignition delay can be improved. Sadhik Basha and R.B. Anand **[8]** conducted experiments on the characteristics of the diesel engine and showed that by using the biodiesel emulsion fuel containing the 51nm alumina nanoparticles the engine performance in term of heat release rate, peak power, ignition delay and emission characteristics of the diesel engine can be improved as compared to the pure biodiesel. However, they had reported that the prepared nanoparticles dispersed fuels were stable for more than five days. Also, there was no one step synthesis of nanofluids, instead nanoparticles were dispersed firstly in DI water and then mechanical agitator was used to prepared nanopartciels blended emulsion fuel. Since, the stability of the nanofluids plays a key role for determining the characteristics of the nanofluids as due to settlement of nanoparticles in the base fluids the properties of the fluids degrade with time and hence cannot retain the same properties as require for the applications **[9, 10].** Hence, the main objective of this work is to study the dispersion stability of nanoparticles dispersed biodesel based nanofluids for achieving the longer stable nanofluids. Since, at nanoscale size matter for determining the properties and stability of the nanofluids **[11, 12].** In this work, the effects alumina nanoparticles sizes on the dispersion stability of the biodiesel based nanofluids are reported. The nanoparticles considered for this work were two different sizes of alumina nanoparticles (~13nm and ~28nm) with the base fluid as jatropha biodiesel and nanofluids were prepared by one step process without any mechanical agitation or addition of DI water. The effect of the different sizes of alumina nanoparticles having different volume concentration nanofluids on the dispersion stability were analyzed by using sedimentation method, UV spectroscopy and Transmission electron microscopy (TEM).

Experimental

Materials

Two different sizes alumina nanoparticles having 99% purity (supplied by Sigma Aldrich, USA) were purchased as dry powder. Jatropha raw oil was purchased from the commercially available dealer (India). Surfactants (Span80 and Tween80 of 99.5% purity) purchased from Hychem Laboratories, India. Alcohols such as Methanol, Propanol, Ethanol and Acetone (99.5% purity) were purchased from Hychem Laboratories, India).

Characterization of alumina nanoparticles

Two different sizes of alumina nanoparticles were characterized by using the X-ray diffraction (XRD), Field Electron scanning Microscope (FESEM) and Transmission Electron Microscope (TEM) for their structure and morphology analysis respectively.

Both the alumina nanoparticles were characterized by XRD (D8Advance, Bruker). The XRD images of Alumina nanoparticles are shown in **Fig. 1(a)** and **(b)** respectively. It was confirmed from the XRD analysis that two samples were mixed phases of δ and γ Phase and crystalline in nature.

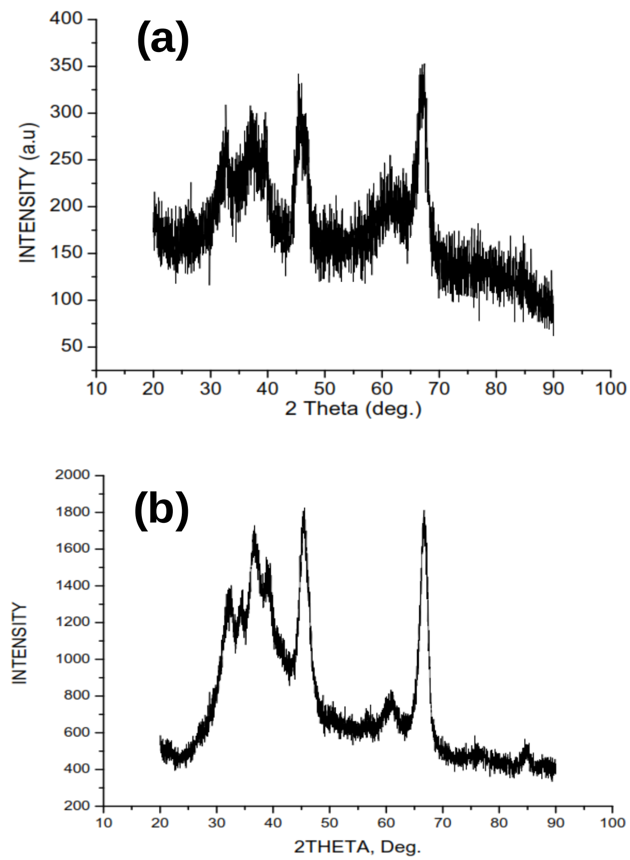

Fig. 1. The XRD spectrum of alumina nanoparticles (a) sample 1 and (b) sample 2.

For purpose of the FESEM analysis, two different sizes of alumina nanoparticles were sonicated 30 minutes in DI water and then one droplet was casted on the cleaned Si substrate followed by drying the sample on a hotplate few minutes to evaporate the DI water. Finally, samples were loaded to Zeiss FESEM to analyze their size and morphology. **Fig. 2 (a)** and **(b)** show the FESEM images of two different sizes of alumina nanoparticles and from these figures, the two samples sizes were confirmed to be ~13nm and ~28nm respectively and having nearly spherical in shapes.

Preparation of nanofluids

The Jatropha Methyl Ester (JME) Biodiesel was synthesized from the Jatropha raw oil through Transesterfication process **[4]**. Initially, the alumina nanofluids test samples were prepared in varying mass concentrations of alumina nanoparticles ranging from 0.5 mg to 10 mg by keeping the biodiesel volume constant i.e. 20 ml. For each sample, the sonification was done for 30 minutes by considering Span80 and Tween80 as the dispersant for the better dispersion stability. In this way, different test samples nanofluids such as 0.1, 0.2, 0.3, 0.4 and 0.5 % volume fraction nanofluids were prepared to evaluate the dispersion long term stability. All the test nanofluids samples were kept in a glass tube and periodically observed for their long term stability. **Fig. 3** shows the photograph of pure biodiesel, 0.1VF, 0.2VF and 0.5VF biodiesel based alumina nanofluids.

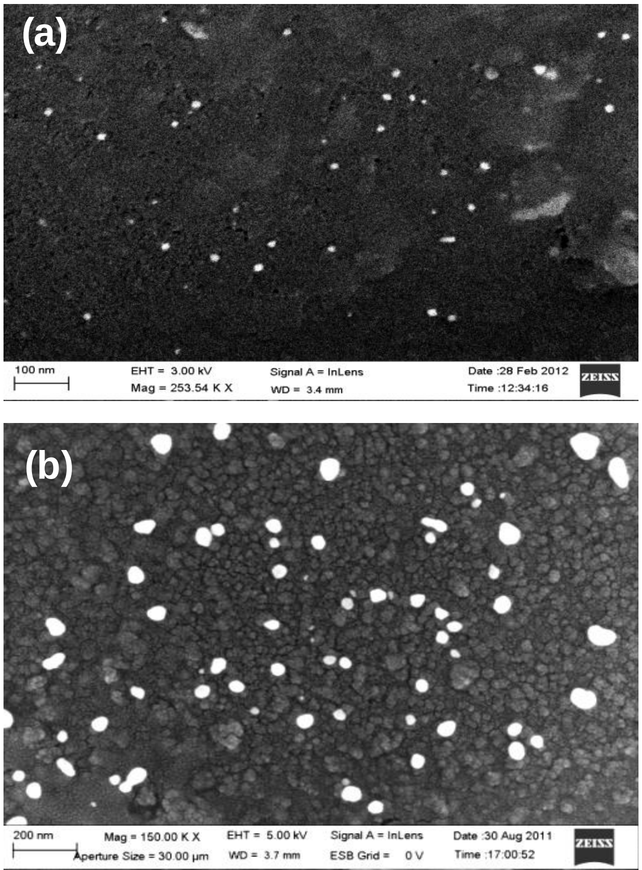

Fig. 2. The FESEM images of alumina nanoparticles (a) sample 1 and (b) sample 2.

Fig 3. Photographic image of alumina nanofluids (a) pure biodiesel (b) 0.1 VF (c) 0.2 VF and (d) 0.5 VF after 30min of preparation.

Results and discussion

It was seen that the dispersion of stability of ~13nm size alumina nanofluids and ~28 nm size alumina nanofluids respectively were different and confirmed from the sedimentation method that all the ~28nm alumina nanoparticles based nanofluids were not even stable for 30min after the preparation, this may be due to the settlement of aggregates nanoparticles as result of gravity. Whereas, the ~13nm size alumina nanoparticles based nanofluids were more stable even for more than one year for the 0.1% volume fraction sample. However, for all the other volume fractions ~13nm size alumina nanofluids the dispersion stability was observed to be not more than 12hrs. Further, the stability of all the 0.1% volume fractions ~13nm sizes alumina nanofluids were carried out by using the Transmission Electron microscopy (TEM) for the agglomeration of the nanoparticles in the biodiesel with time and UV-vis spectroscopy to observe the stability from the absorbance peak ratio of as-prepared and older sample with time. All the as-prepared nanofluids were kept idel in a stand without disturbing them and periodically analyized by using UV-vis spectroscopy for the dispersion stability.

TEM characterization

First of all, one droplet of as-prepared and 1 year old both nanofluids were casted on the carbon coated Cu-grids (200 mesh size) and then heated on a hot plate for 10 minutes to evaporate the biodiesel and for TEM characterizations. **Fig.4 (a)** and **(b)** show the transmission electron micrographs of as prepared nanofluids and one year old. It was seen that both the alumina nanoparticles were individually well dispersed for both as prepared and one year old nanofluids.

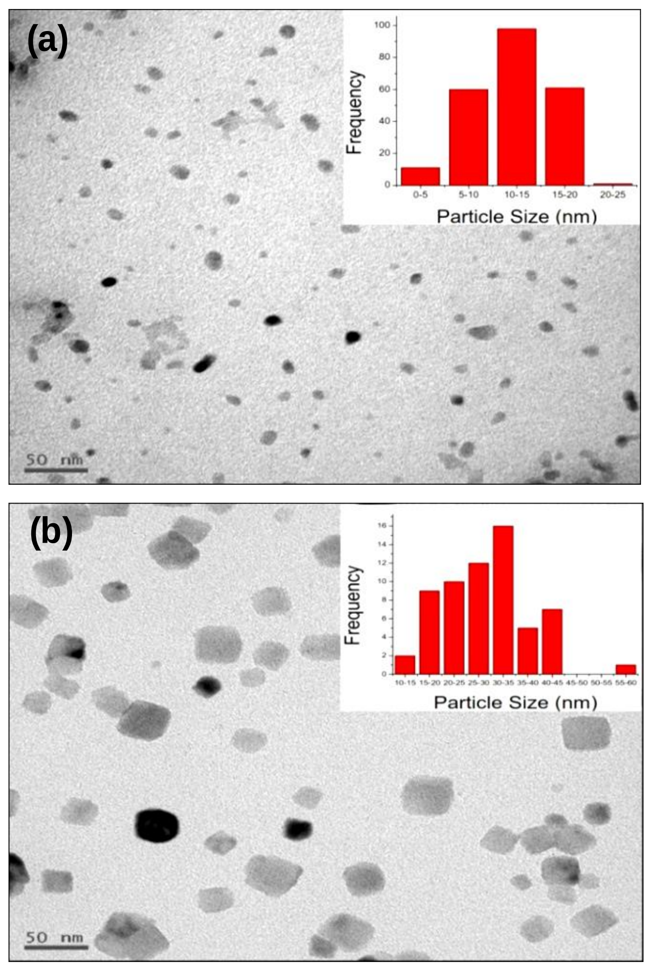

Fig. 4 (a). TEM micrograph of ~13 nm size Al_2O_3 Nanofluids 0.1%VF with (a) as prepared sample (b) 1 Year old sample.

However, it was also identified that after one year, the initial ~13nm size alumina nanoparticles size and shape changed to higher size i.e. 30-50nm and nearly cubical shape. To understand the growth mechanism and morphology change more depth study is still underway, however, the preliminary results suggested that the initial smaller size alumina nanoparticles in biodiesel medium with Span^{80} and Tween^{80} as stabilizing surfactant (1:1 ratio) may aggregation occurred and they coagulate to form the new size and shape and still showing stability due to the present of surfactants.

UV-vis spectral analysis

It is a very reliable method to evaluate the stability of nanofluids since there is a linear relationship between the suspended nanoparticles and absorbance of the suspended nanoparticles. All the prepared alumina nanofluids were periodically analyzed by UV-vis Spectroscopy measurement using the standard size of cuvette (path length 10mm). Initially, the baseline was fixed considering the Jatropha Biodiesel as the reference sample as well as the specimen sample. After fixing the baseline, Jatropha Biodiesel was taken as the reference sample and the alumina nanofluids was considered as the specimen sample and the data were obtained for the different stability time of alumina nanofluids.

Fig. 5 shows the UV-vis spectra of alumina NP-13nm of 0.1%VF as prepared sample and different stability time respectively. It was clearly observed that as the sediment time increases the absorbance decreases due to fraction of alumina nanoparticles aggregate and settled down at the bottom of the glass tube, hence less concentration as compared to the as prepared sample. However, it was also observed that even for one year old sample that alumina nanoparticles were still dispersed in the biodiesel as there was no indication of absorbance flattering, which is generally occurred when the nanoparticles were no longer dispersed in the base fluids.

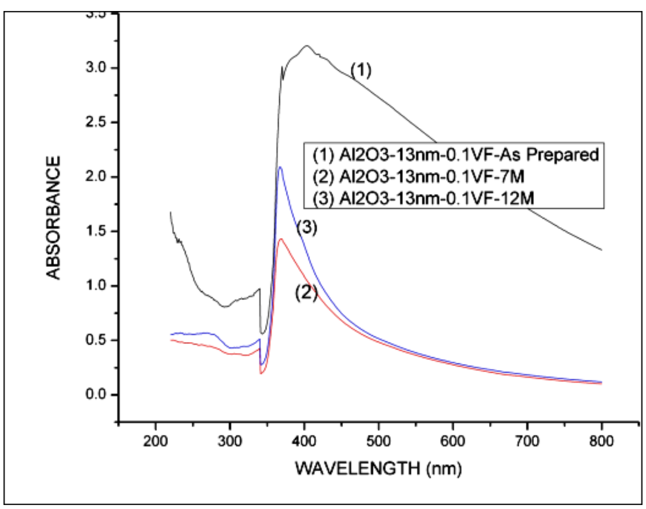

Fig. 5 The UV-vis spectra 0.1%VF of Al_2O_3NP-13nm size alumina nanofluids with different stability time.

Therefore, our one year older ~13nm size alumina nanofluids of 0.1% volume fraction are still stable which also good agreement with the TEM results. This may be due reason that the smaller size alumina nanoparticles having higher surface area and larger solid/liquid interface as compared to the larger alumina nanoparticles. Also, it was noticed that higher volume fractions more than 0.1%, ~13nm size alumina nanofluids were not showing stability and settled down with in one day of preparation because it may exceed the saturation limit volume fractions and hence nanoparticles start to coagulate and settled down within one day. Our preliminary results also revealed that incase of the one year old stable having ~13nm size alumina nanoparticles having 0.1 % volume fraction alumina nanofluids, the alumina nanoparticles sizes were increased in the range of 30-50nm and also the shape changed from the nearly spherical to the cubical shape. The growth mechanism of the dispersed nearly spherical alumina nanoparticles to different shape (cubical) and increasing in size in the biodiesel based nanofluids is still not clear and more depth study is underway for understanding clearly the nanoscale phenomena which may responsible for such unique morphology change of the alumina nanoparticles.

Conclusion

The size effect of the alumina nanoparticles on the dispersion stability of biodiesel based nanofluids was investigated. It was observed that average ~13nm size alumina nanoparticles based biodiesel nanofluids having 0.1 % volume fractions were showing more than one year stability whereas, the larger size (~28nm) alumina nanoparticles based nanofluids having same volume fractions were not even showing stability for 30min and settled down within few minutes of after preparation. Since, achieving the long term dispersion stability in nanofluid is key to retain the properties of nanofluids, such longer duration stable jatropha biodesel nanolfuids can be used as alternative fuel in diesel engine transportation applications.

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