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Carbon Nanotubes as Nano Additives in Biodiesel: Characterization and Dispersion Stability

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***Abstract* -** In the current global energy situation, fossil fuels are facing issues such as unsustainable demand and environmental concerns. In this approach, the scientific community is looking for alternative fuels such as biodiesel. As compared to petroleum diesel, biodiesel has higher NOx emissions. However, the addition of CNTs to biodiesel as an additive has become a popular way to enhance combustion efficiency for lowering pollution emissions. This study explored the stability characteristics of CNTs with sonication duration into waste cooking oil biodiesel, with the help of UV-Vis spectrophotometer. It was found that regardless of concentration, the CNTs suspension with 3 hours of sonication duration was more stable. The highest absorbance value was found 0.636 for 25 PPM concentration with 3 hours of sonication duration and a minimum value of 0.232 was observed for 25 PPM concentration with 1 hours of sonication duration. The maximum absorbance value with 3 hours of sonication duration was 0.367 and 0.402 for 50 PPM and 100 PPM concentration, respectively.

Index Terms - Additives, Carbon Nanotubes, Biodiesel, Diesel engine.

INTRODUCTION

The world's population has risen dramatically in recent years, reaching 7.7 billion people in 2019 (World Population Prospects 2019). As a result, energy consumption has increased in tandem with population growth, leading in higher levels of greenhouse-gas emissions. The most extensively used energy resources in industry are fossil fuels; unfortunately, these energy resources are not sustainable. Emissions from diesel fuel burning have negative consequences for the environment and human health [1] [2] [3]. Due to its high compression ratio, the diesel engines have a great reputation for low fuel consumption and durability [5]. Diesel and biodiesel fuels, on the other hand, have limitations in terms of producing more NOx [6]. The use of additives to increase biodiesel qualities is gaining popularity as a solution to overcome these limitations, and it has the potential to improve combustion performance while reducing emissions [7] [8] [9].

I. Nano-additives

The specific fuel properties can be improve by using nano-additives to achieve good performance and emission characteristics, without any modification to CI engine. The metal oxides of Cu, Fe, Ce, Pt, B, Al and allotrope of carbon like CNT and GO have been widely used as additives in diesel and biodiesel fuel blends in the reviewed study [10]. Carbon nanotubes (CNTs) are allotropes of carbon that were discovered by Japanese scientist Iijima in 1991. Carbon nanotubes are made up of cylindrical tubes with nano-scale diameters and lengths of many millimeters [11]. Because of their small size and thermal conductivity, they have impressive combustion performance [12]. Depending on the number of graphene layers, it can be single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). The theoretical specific surface area of CNTs is ranges from 50 to 1315 m2/g [9]. Researchers have reported use of waste cooking oil biodiesel as an alternate fuel source for diesel engines, except their poor NOx emission. The use of CNTs as nano-additives to biodiesel has been documented in prior studies, but very few information is available about their inclusion and dispersion stability. As a result, there is a gap in the use of biodiesel with nano-additives, such as waste cooking oil biodiesel. Hence, inclusion and dispersion stability of CNTs as nano additives to waste cooking oil biodiesel at three different dosage levels of 25, 50, and 100 PPM is explored in this study.

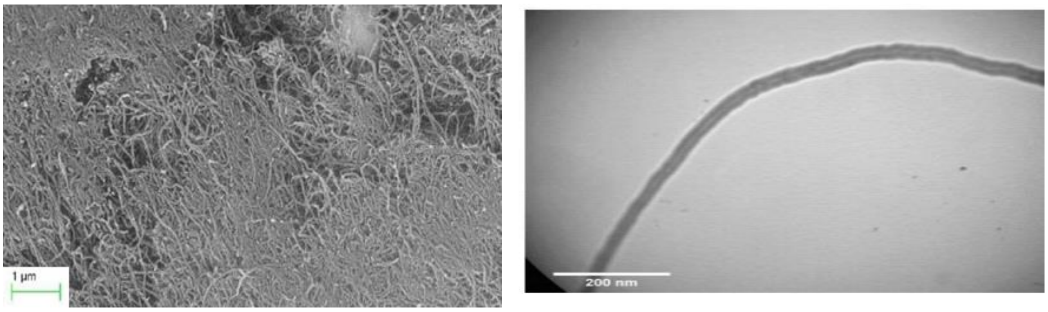
MATERIALS AND METHODS

I. Materials

Multi-walled carbon nanotubes (MWNTs) were obtained from the Ad-nano Technologies with 99% purity and the biodiesel from waste cooking oil (BWCO) was prepared in laboratory by transesterification processes.

II. Characterization

The nanotubes was in powdered form and had an average diameter of 10 to 30 nm and a length of 10µm. The specific surface area of carbon nanotube was 110 to 350 m2/g. Fig. 2. shows the images of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of CNTs. The specifications of carbon nanotube is given in the Table I.



(A) **(B)**

FIGURE 1

(A) SEM IMAGE OF AND (B) TEM IMAGE OF CARBON NANOTUBES

III. Preparation of dispersion

Dispersion are made by mixing solid particles with base fluids. Nanofluids are typically prepared using one-step or two-step methods [2]. The manufacturing of nanoparticles and the mixing of nanofluid are done simultaneously in one-step procedure while in two-step approach, the nanoparticles are first dispersed and then using high shear or ultrasonication, it mixed with the base fluid, as illustrated in the Fig. 4.

TABLE I

THE SPECIFICATIONS OF CARBON NANOTUBE

Specification	**Explanations**
Product name	MWCNT
Purity	~ 99%
Outer diameter	R~10-30 nm
Inner diameter	~ 5-10 nm
Length	> 10 µ m
Surface area	110-350 m^2/g
CNT content	95-99 %
Bulk density	0.04 g/cm^3
Chemical formula	C
Material form	Powder

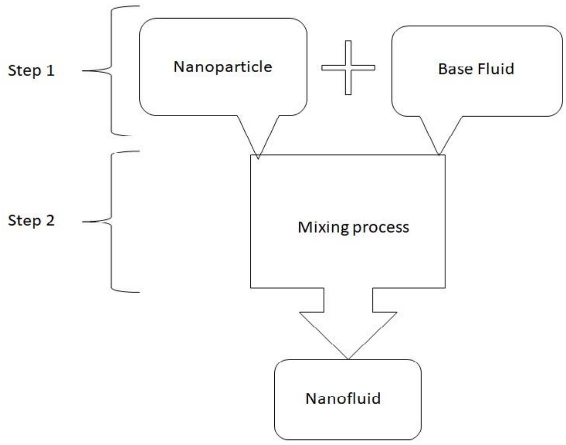
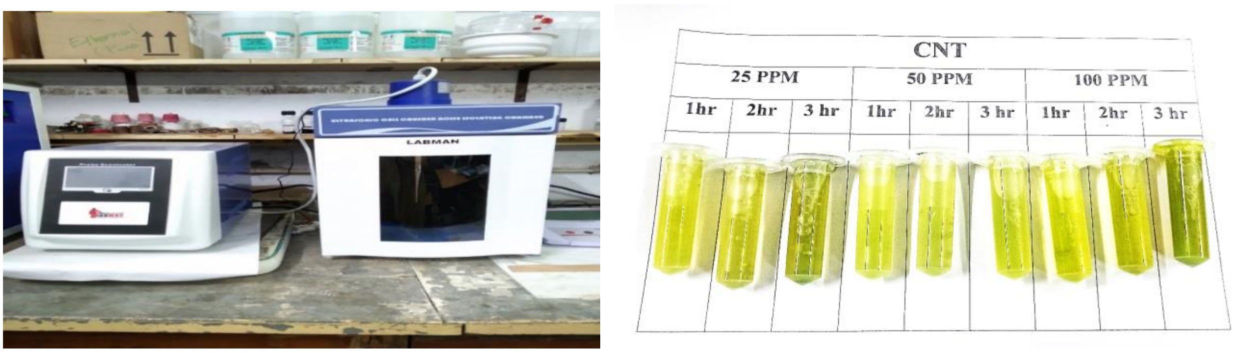


FIGURE 2

TWO-STEP PREPARATION OF NANOFLUID

In this study, the two-step approach was used to prepare the dispersion of CNTs and BWCO. To create a homogeneous dispersion of 25, 50, and 100 ppm, the carbon nanotubes with weight of 1.25, 2.5 and 5 mg were mixed with 50 ml of BWCO. The dispersion were then homogenized for 1 hr, 2 hr, and 3 hr using a probe-based ultrasonicator (make LABMAN) device set to 24 kHz of frequency. Fig. 3. (a) and (b) shows the setup of nanofluid preparation and the dispersed sample of carbon nanotubes in BWCO, respectively.



(A) (B)

FIGURE 3

(A) PROBE-BASED ULTRASONICATOR AND (B) NANOFLUID

IV. Stability of the dispersion

The stability characteristics of CNTs in fuel suspension were investigated in this section. The dispersion stability was assessed by observing the variation of concentrations over time with the help of UV-Vis spectroscopy, which is commonly used to determine sample concentrations. The absorption bands of scattered CNTs in the range of 190–1100 nm is reliable [13]. The stability investigation for various concentration of CNTs and sonication time was conducted for four days by using a V-730 UV-Visible spectrophotometer (make JASCO) in the range of 200-1000 nm, scan speed of 400 nm/minute and a slit width of 5 nm. The baseline is set using BWCO as the reference sample and CNTs nanofuels as the specimen sample. The absorbance of the dispersion was measured at the end of each day while they were kept in static conditions. The V-730 UV-Vis spectrophotometer is shown in Fig. 4. and its specification is given in Table II.

FIGURE 4

V-730 UV-VISIBLE SPECTROPHOTOMETER

TABLE II

THE SPECIFICATIONS OF UV-VISIBLE SPECTROPHOTOMETER.

Specification	**Explanations**
Optical System	Double beam type
Light source	Deuterium lamp
Wavelength range	190 to 1100 nm
Wavelength accuracy	+/-0.2 nm (at 656.1 nm)
Wavelength repeatability	+/-0.1 nm
Detector	Silicon photodiode

RESULTS AND DISCUSSION

The influence of sonication time and CNTs concentration on nanofuels stability as a function of time is presented in this section. The influence of sonication duration on the stability for different concentrations of CNTs can be seen in Fig. 5., Fig. 6. and Fig. 7. The decrease in absorbance indicates that the CNTs began to cluster and settle with time for all concentrations and sonication durations.

It is quite worth noting that as the concentration of nanomaterials increased, the suspension stability decreased, which is due to the generation of dense solution, which sediments faster than less dense particles [14]. Regardless of concentration, the CNTs suspension with 3 hours of sonication was more stable. Rashmiet et. al. investigated the influence of sonication time on MWCNTs suspension stability in the presence of gum arabic found that the blends stability was proportional to sonication time; however, extended sonication may shorten nanotube length and affect thermophysical properties.

The absorbance values of CNTs nanofuels for all concentration are shown in Fig. 8. and Fig. 9. The highest absorbance value found was 0.636 for CNTs concentration of 25 PPM and 3 hours of sonication time, and a minimum value of 0.232 was observed for CNTs concentration of 25 PPM and 1 hours of sonication time on of first day. The maximum absorbance value for 50 PPM and 100 PPM concentration was 0.367 and 0.402 respectively, for 3 hours of sonication time on first day. The percentage drop in absorption after four days of sample preparation of 25 and 100 PPM concentration for 3 hours of sonication period was 4% and 6% respectively, it shows that even after four days, the sample with 25 PPM concentration was more stable than the 100 PPM concentration.

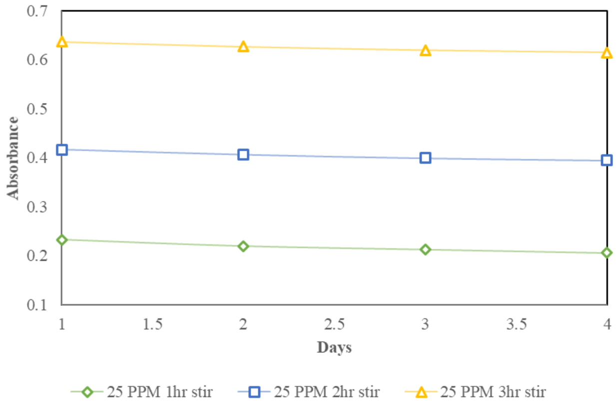


FIGURE 5

STABILITY CHARACTERISTICS OF 25 PPM BWCO

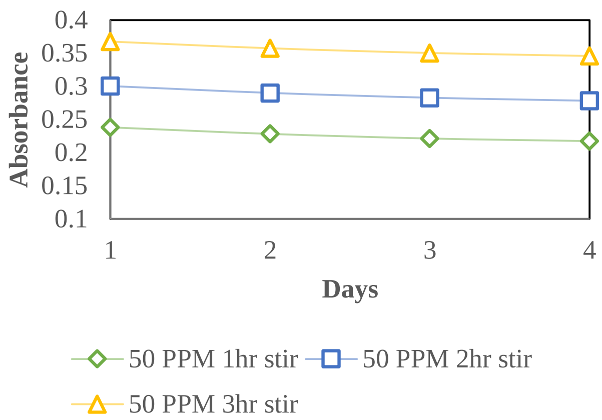


FIGURE 6

STABILITY CHARACTERISTICS OF 50 PPM BWCO

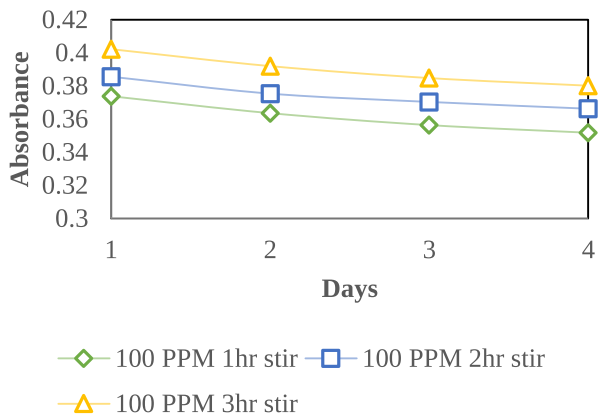


FIGURE 7

STABILITY CHARACTERISTICS OF 100 PPM BWCO

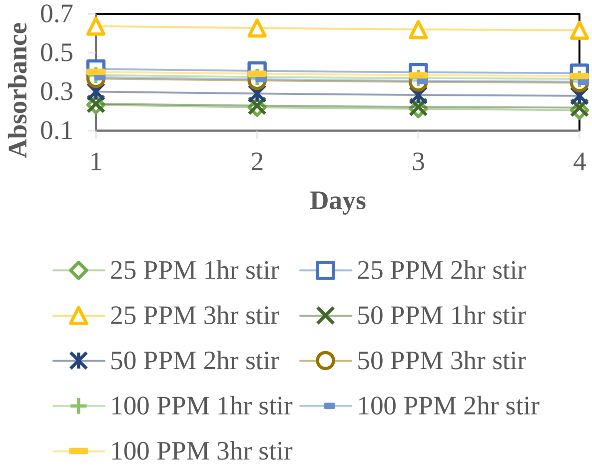


FIGURE 8

STABILITY CHARACTERISTICS OF CNT BWCO FOR ALL CONCENTRATION

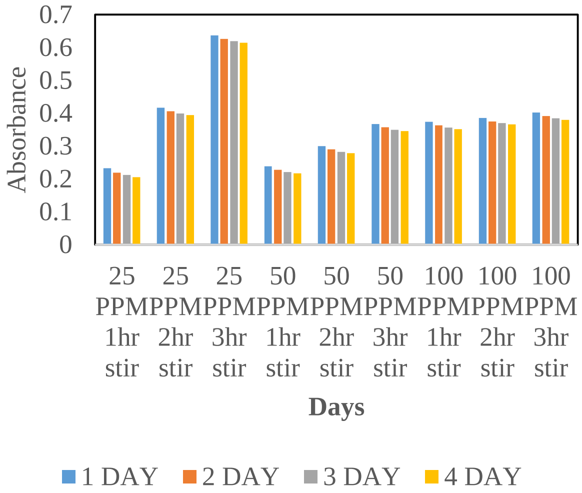


FIGURE 9

STABILITY CHARACTERISTICS OF CNT BWCO FOR ALL CONCENTRATION

CONCLUSION

This article studied the effects of CNT nano-additives stability in biodiesel fuel for different concentration and sonication duration. A UV-Vis spectrophotometer was used to study the sedimentation of CNTs nanofuels. The recent investigation yielded the following conclusions:

- CNT began to cluster and settle with time for all concentrations and sonication durations.
- Regardless of concentration, the CNTs suspension with 3 hours of sonication duration was more stable.
- The highest absorbance value found was 0.636 for 25 PPM concentration with 3 hours of sonication duration and a minimum value of 0.232 was observed for 25 PPM concentration with 1 hours of sonication duration.
- The maximum absorbance value for 50 PPM and 100 PPM concentration was 0.367 and 0.402 respectively, for 3 hours of sonication duration.

- The percentage drop in absorption after four days of sample preparation of 25 and 100 PPM concentration for 3 hours of sonication period was 4% and 6% respectively, it shows that even after four days, the sample with 25 PPM concentration was more stable than the 100 PPM concentration.

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