



## Development Of Antioxidant Grafted Carbon Nanotube Based Heterogeneous Catalyst For Biodiesel Storage

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***Abstract:***

*The article presents the development of heterogeneous and magnetically separable catalyst based on carbon nanotubes for biodiesel storage. Carbon nanotubes (CNTs) were synthesized having magnetic iron oxide nanoparticles. Antioxidant were grafted in the CNT surface by simple chemical treatment. The antioxidant potency of the developed catalyst was studied by modified DPPH method for nanomaterials. The oxidation stability of biodiesels was studied in details using Rancimat method.*

***Keywords:*** Carbon nanotubes, Iron oxide, Oxidation stability, Rancimat method,

## **Introduction**

The use of antioxidants for long term storage is not new [1-3]. They are used for storage of organic compounds like oils derived from plants, strategic materials like rubber and paints as well as beneficial effect in the living body[4-6]. Most of these antioxidants are organic compounds which may be classified into synthetic and natural antioxidants. One of the important uses of these antioxidants is in storage of plant derived oils. Essential oils extracted from plant sources consist of mono fatty acid methyl esters and high molecular weight glycerin. Essential oils find applications in every sphere of life, from edible oils for cooking to raw material for biodiesel production. The main problem with these oils is their susceptibility to oxidation. The oxidation of oils may be due to its thermal oxidative disintegration in the presence of air and/or moisture. Most of the antioxidants form a homogeneous mixture with these oils when added for storage [7-9] and cannot be separated before end-use thus affecting the overall property of the oils [10]. It is, therefore, necessary to search for new antioxidants which can be removed before end-use and which show enhanced antioxidant activity. This may be possible with the use of heterogenous inorganic antioxidants. Preliminary research of metal nanoparticle antioxidant property was already reported by workers [11-12]. But these antioxidants like silver and gold are costly and hence can not be used in large quantities for storage of oils. Thus cost becomes another criterion in addition to possibility of removal before end-use. Assessing the antioxidant potency of heterogenous antioxidant pose a new challenge due to existence of multiple phases and diversely dispersed conditions. A method for antioxidant potency estimation of insoluble solids was proposed by Serpen et al. [13]. The method was designed for insoluble macroparticles and the thus the validity of the method for nanoparticles may be questioned. It is necessary to design a protocol for antioxidant potency assay which suits nanoparticles for correct estimation of their potency in scavenging free radicals.

The paper aims to design and propose a new protocol for antioxidant potency estimation for nanoparticles, test the antioxidant potency of iron, cobalt and nickel oxide nanoparticles, design and develop a heterogeneous antioxidant using nanopartiles which can be removed after end use, and finally test the designed nanoparticle antioxidant in storage of oil.

## Materials And Method

### *Chemicals and reagents used*

Iron nitrate nonahydrate (grade: purified, 98%), cobalt nitrate hexahydrate (Purified, 97%), nickel nitrate hexahydrate (grade: GR, 97%), urea (grade: extra pure, 99.5%) and oleic acid (grade: pure, 98%) were procured from Merck, India for the synthesis of metal oxide. Nitrogen gas (99.9 %) supplied by Rass cryogenics, India was used for synthesis of MWCNTs. Butylatedhydroxytoluene (Merck, India, grade: AR), Ethanol (grade: absolute for synthesis, 99.9% Merck, India), and 1'-1' diphenylpicrylhydrazyle (DPPH<sup>o</sup>, grade: AR, Merck, India) were used for antioxidant potency estimation.

### *Synthesis of metal oxide nanoparticles*

Metal oxide nanoparticles of iron, nickel and cobalt were synthesized using solution combustion method using similar technique.

### *Synthesis of MWCNTs*

The MWCNTs were synthesized using the CVD technique. *Ricinuscommunis* oil was used as precursor. The synthesis of CNTs was carried out at 850°C. Fe<sub>2</sub>O<sub>3</sub> nanoparticles were used as catalyst for CNTs synthesis. The purification of synthesized MWCNTs was carried out by heating at 450°C for 45 min in open atmospheric condition to remove the amorphous carbon. These MWCNTs were not treated further to remove the catalyst particles.

### *Proposed design of the heterogenous magnetically separable nanomaterial antioxidant*

The proposed design of the nanomaterial antioxidant has three major components: i) a magnetic component, to ease the separation before end use, ii) an antioxidant component, to scavenge the free radicals, and iii) a substrate, to hold both the antioxidant and magnetic component. A schematic of the proposed design is shown the figure 1.

The catalyst particles (metal oxide nanoparticles) used for the synthesis of MWCNTs remains trapped inside the MWCNT structure. The oxides of iron, cobalt and nickel innanorange show magnetic properties [14-16]. Thus unpurified MWCNTs (in terms

of catalyst nanoparticles) may act as the substrate for a commercial antioxidant to be attached and may be separated using a magnetic field due to the presence of metal oxide nanoparticles inside the nanotubs.

*Ricinuscommunis* oil was for MWCNTs synthesis. The defects on the walls may be used as locations for grafting the antioxidants, because they have affinity towards such molecules. Butylatedhydroxytoluene (BHT) is a commonly used antioxidant which may be used to in this case. BHT is also used as reference in the study of antioxidant potency of other compounds and materials by researchers [17-18]. For this reason, BHT was selected for the proposed antioxidant nanocomposite.

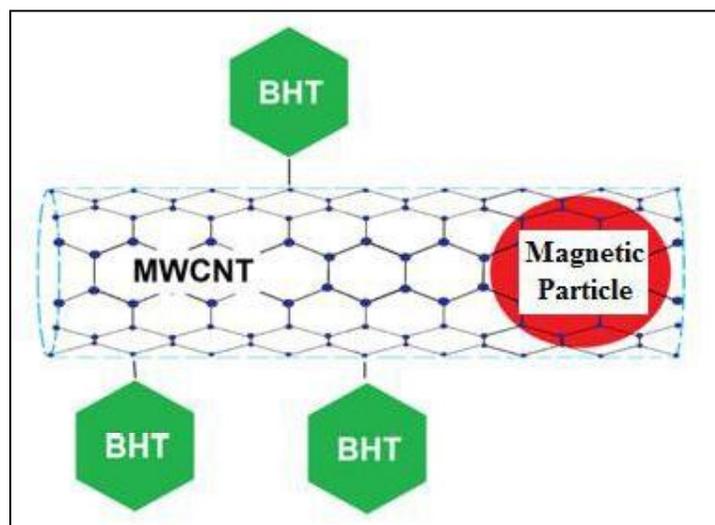


Figure 1: Proposed antioxidant nanocomposite

#### *Grafting of BHT in MWCNT*

BHT is a well known homogenous antioxidant which is used for storage of biodiesels. The process of grafting BHT on the defect sites of MWCNTs was done using ultrasonication. A concentrated 1.0 ml solution of BHT in ethanol was prepared at 40 °C. MWCNT synthesized using *Ricinuscommunis* oil was added to the BHT solution (0.1 g). The mixture was ultrasonicated for 30 minutes at 50 °C. It was centrifuged to collect MWCNTs which were then washed once in DD water and oven dried.

#### *Proposed method for antioxidant potency determination for nanoparticles*

To get the actual antioxidant potency of the engineered nanomaterial, it is desirable to evaluate the antioxidant potency of each nanomaterial individually. Serpen et al. [13] method for estimation of antioxidant potency of non-soluble particles holds for

macroscopic particles. Thus, a modified method is proposed for antioxidant potency assay of the nanoparticles. In the proposed method, nanomaterials/nanoparticles were washed with distilled water to get neutral pH supernatant. 10 mg of the each powdered samples were transferred to separate reaction vial. 1'-1'-Diphenylpicrylhydrazyle (DPPH<sup>o</sup>) reagent (1.7 mL) was added to start the reaction. The mixture was ultrasonicated for 45 min to ease the surface reaction between the nanoparticles and the DPPH<sup>o</sup> reagent. The mixture was centrifuged at 9200 g for 10 min; finally, the absorbance of the supernatant was measured at 517 nm using UV-vis spectrophotometer. The antioxidant potency assays for the metal oxide nanoparticles, MWCNTs and the BHT grafted MWCNTs were investigated using this modified DPPH method for insoluble nanomaterials. All the measurements were carried out after ultrasonication of the insoluble nanoparticles with the DPPH reagent. The scavenging percentage was calculated using the formulae:

$$DPPH \text{ scavenging } (\%) = \left[ \frac{(A_C - A_S)}{A_C} \right] \times 100$$

where,  $A_C$  and  $A_S$  are absorbance of blank DPPH<sup>o</sup> and the DPPH<sup>o</sup> remaining after the test at 517 nm respectively.

#### *Oxidation stability analysis of biodiesel*

Oxidation stability analysis was performed by Rancimat apparatus (Biodiesel Rancimat 873, Metrom, Switzerland). In Rancimat method air is allowed to pass through a reaction tube containing the oil sample, held at a specified temperature (110 °C) in a thermostated aluminum block. The effluent air from the oil sample is then bubbled through a vessel containing deionized water, called the conductivity measurement cell. The conductivity of the water is continuously monitored and stored in an attached PC. During the degradation process (oxidation of oils) volatile organic acids, predominantly formic acid is blown out of the reaction tube which is allowed to pass through the cell and get absorbed in the water. At that time the conductivity of the water in the conductivity measurement cell begins to increase rapidly. Thus more stable oils will result in less conductivity in the conductivity measurement cell in a specific period of time and at a specific temperature and vice versa. In other words more the oil oxidizes more is the conductivity in the conductivity measuring cell. Figure 2 and figure 3 show the schematic diagram and photograph, respectively of the Rancimat apparatus.

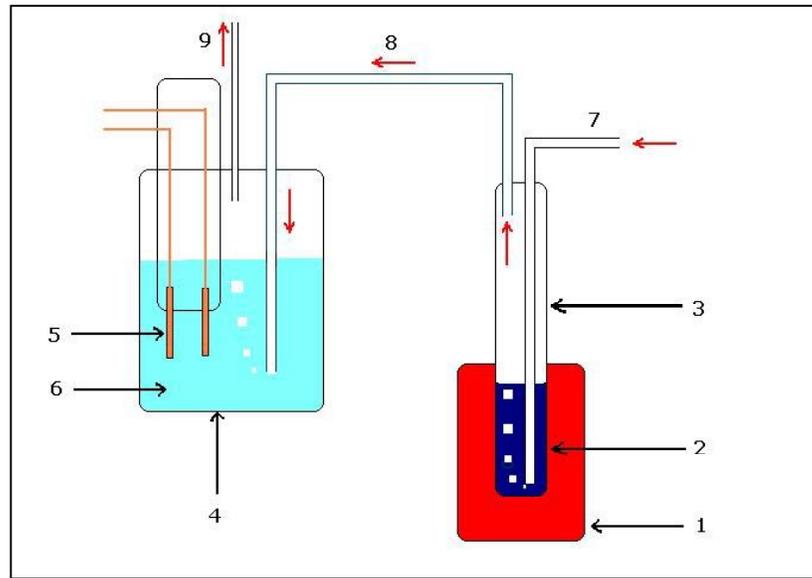


Figure 2: Schematic diagram of Rancimat apparatus. (1) heating block, (2) oil sample, (3) reaction tube, (4) conductivity measuring cell, (5) electrodes to measure conductivity, (6) deionized water, (7) air input, (8) tube carrying air and volatile organic acids from degraded oil in reaction tube and (9) air output.

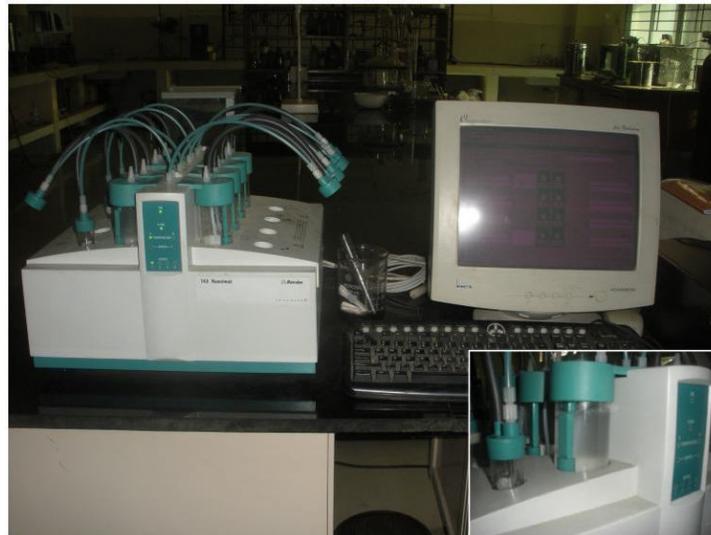


Figure 3: Photograph of Rancimat apparatus

Mesuaferreabiodiesel was taken in separate test tubes (3ml each). Nanoparticles were added to test tube (3.0 mg each). The test tubes were sonicated for 15 min to ensure proper dispersion of iron oxide and BHT grafted MWCNTs in the oil. Two test samples of biodiesel nanoparticle mixtures were transferred to reaction tubes in

Rancimat apparatus. Oxidation stability measurements of oils were performed by Rancimat method at 110 °C with a gas flow of 10 ltr/hr. The time dependent conductivity for all the oils were recorded. For the study *Mesuaferreabiodiesel* without antioxidant was taken as control.

## **Results And Discussion**

### *Characterization of nanomaterials*

#### Characterization of iron oxide nanoparticles

The figure 4 shows the TEM micrograph of the iron oxide nanoparticles. The size of the nanoparticles is found out to be 8–40 nm. X-ray diffraction pattern of the samples is shown in the Figure 5. Presence of peaks at angles ( $2\theta$ ), 24.20°, 33.23°, 35.69°, 40.99°, 49.50°, 54.16°, 62.49° and 64.05° portrays the synthesized iron oxide particles to be hematite.

#### Characterization of nickel oxide nanoparticles

TEM image of the synthesized nickel-oxide particles are shown in figure 6. The particle size ranges from 12 to 23 nm. The micrograph reveals that the synthesized particles show almost uniform shape and size. The X-ray diffraction pattern confirms the synthesized particles to be nickel oxide (figure 7). The presence of peaks at  $2\theta$  44.85 and 52.15 confirms the presence of Ni<sub>2</sub>O<sub>3</sub> (hexagonal). The peaks at 37.60, 43.65 and 63.20 are due to the presence of NiO (cubic)

#### Characterization of cobalt oxide nanoparticles

TEM micrograph of the synthesized cobalt oxide nanoparticles shows (figure 8) the particles are of three different sizes, ranging from 12 to 20 nm, 30-35 nm and 40-50 nm. The X-ray diffraction pattern confirms the synthesized particles to be cobalt oxide (figure 9). The presence of peaks at  $2\theta$  42.61 and 57.81 confirms the presence of Co<sub>3</sub>O<sub>4</sub> whereas the peaks at 40.36 and 22.06 are due to the presence of Co<sub>2</sub>O<sub>3</sub>.

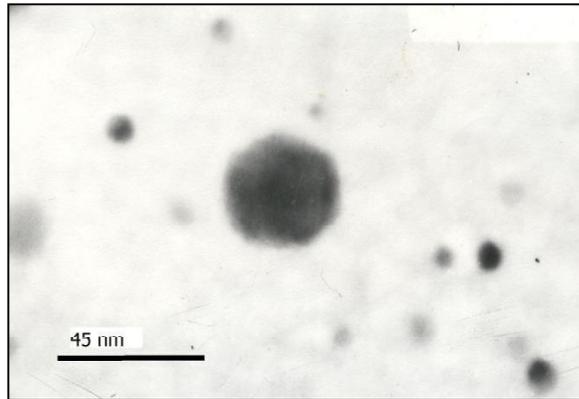


Figure 4: TEM micrograph of iron oxide nanoparticles synthesized at 650 °C

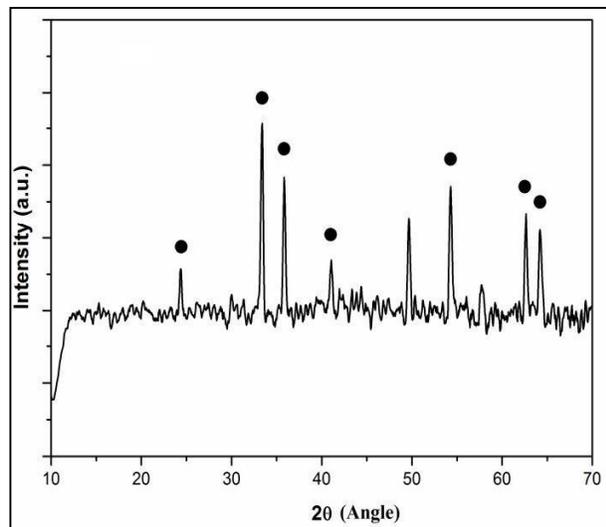


Figure 5: XRD analysis of iron oxide nanoparticles

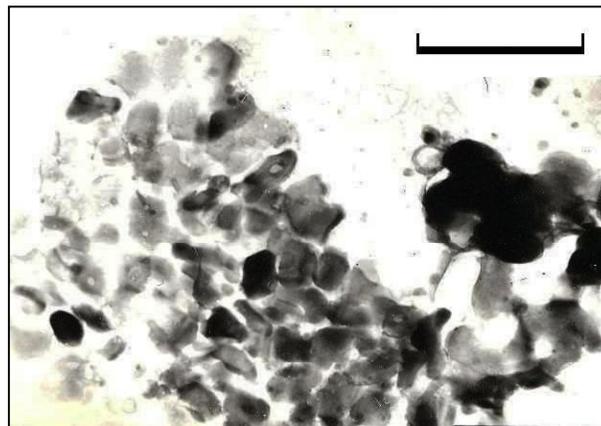


Figure 6: TEM micrograph of nickel oxide nanoparticles synthesized at 650 °C (Scale inset = 100 nm)

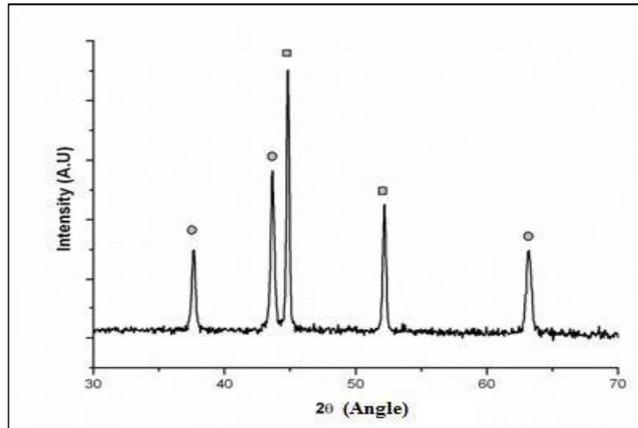


Figure 7: XRD analysis of nickel oxide nanoparticles

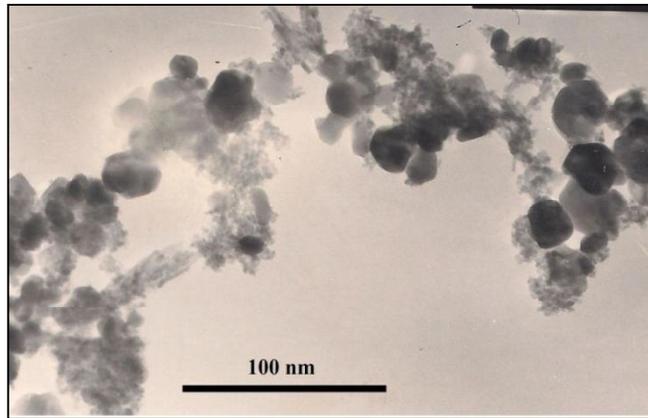


Figure 8: TEM micrograph of cobalt oxide nanoparticles synthesized at 650 °C.

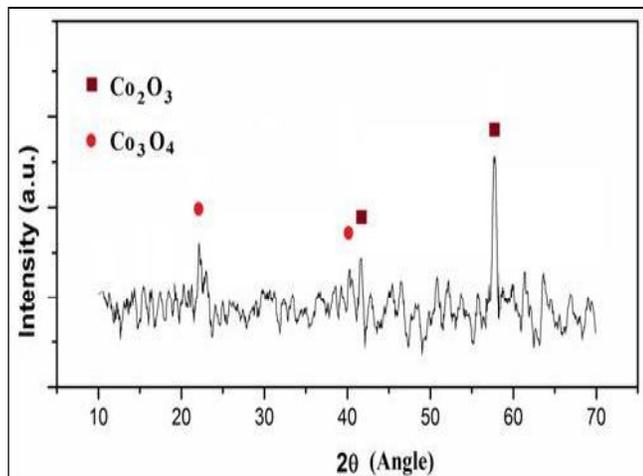


Figure 9: XRD analysis of cobalt oxide nanoparticles

### Characterization of BHT grafted MWCNTs

The TEM micrograph of the pristine MWCNTs and the BHT grafted MWCNTs are shown in figure 10 (a) and (b) respectively. The presence of BHT may be seen on the walls of the nanotube. This suggests that BHT has been attached on the surface of the MWCNT walls successfully.

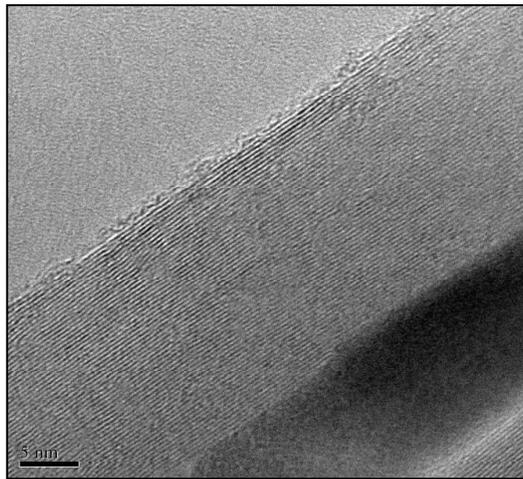


Figure 10(a): Pristine MWCNT

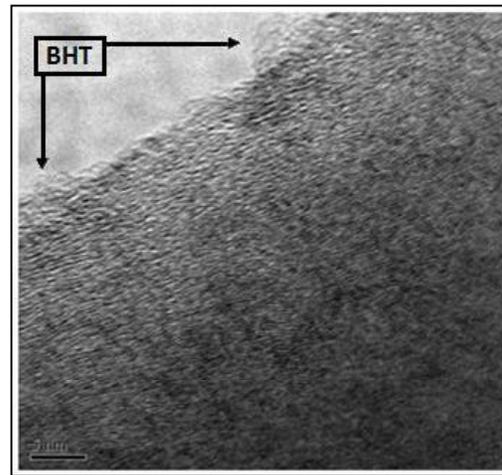


Figure 10(b): BHT grafted MWCNTs

Fourier Transform Infrared Spectroscopy (FTIR) results of BHT, pristine MWCNT and BHT grafted MWCNTs are shown in figure 11. All the samples contain moisture as evident from the peak at  $3630\text{ cm}^{-1}$ . FTIR spectrum of pristine MWCNTs shows peaks at  $1640\text{ cm}^{-1}$  and  $1177\text{ cm}^{-1}$  are due to C=C and C-C of graphitic layers of the tubes. BHT shows peaks at  $3069\text{ cm}^{-1}$ ,  $2956 - 2844\text{ cm}^{-1}$  and  $1436\text{ cm}^{-1}$  corresponds to 'C-H' stretching, 'C-CH<sub>3</sub>' stretching and 'CH<sub>3</sub>' bending. The BHT grafted MWCNT shows peaks at  $1640\text{ cm}^{-1}$  and  $1177\text{ cm}^{-1}$  corresponding to C=C and C-C of graphitic structure of tubes. The peaks at  $2956 - 2844\text{ cm}^{-1}$  and  $1436\text{ cm}^{-1}$  may be due to BHT grafted on the walls of the nanotube structure. The 'C-O' stretching is evident in BHT at  $1756\text{ cm}^{-1}$  is absent in BHT grafted MWCNT sample. This may be due to removal of oxygen from BHT molecule while it is attached to the MWCNT wall. The grafting of BHT in MWCNT showed reduced peak intensities w.r.t transmittance obtained for BHT. The FTIR confirms the attachment of BHT in MWCNT walls.

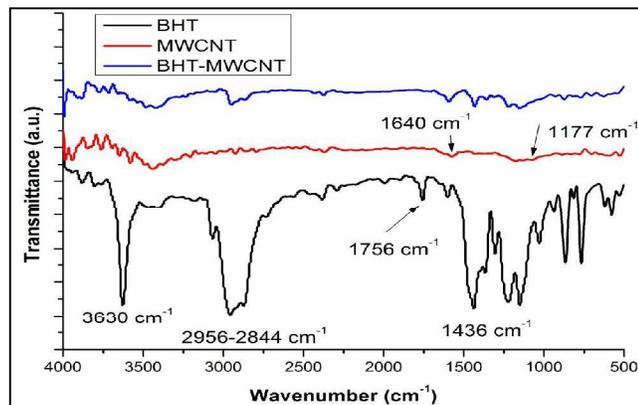


Figure 11: FTIR of BHT, pristine MWCNT and BHT grafted MWCNT

#### Antioxidant potency assay

The antioxidant potency estimation of individual metal oxide nanoparticles has also been carried out. It is expected to help in designing the proposed antioxidant. The method discussed followed to explore the antioxidant potency of the nanoparticles. Thenanoparticles quenched the DPPH<sup>o</sup> free radicals in a time-dependant manner (Figure 12). The DPPH<sup>o</sup> scavenging activities for iron-oxide nanoparticles is higher as compared to cobalt and nickel oxide nanoparticles. For direct comparison SC 50 values are calculated from the absorbance value. SC 50 is defined is the amount of sample required for 50% scavenging of the free radicals. The SC 50 values of the metal oxide samples calculated were 37.98 mg/ml, 64.44 mg/ml and 149.89 mg/ml for iron oxide, nickel oxide and cobalt oxide nanoparticles, respectively. The results show that the antioxidant potency of iron oxide nanoparticles is highest among the three metal oxides tested. Though, macroscopic particles of iron, cobalt and nickel oxides are known oxidants but the result reveals that at nano-scale the oxidant nature of these metal oxides revert to antioxidant. Though the potency of these metal oxide nanoparticles were very less as compared to BHT (SC 50<sub>BHT</sub> = 12.0 mg/l). Out of these the metal oxides iron suits the best as it shows better antioxidant potency compaired to other metal oxides used and is magnetic in nature. Based on the study, it is obvious to use iron oxide nanoparticles in the proposed antioxidant as “magnetic particle”. The observed antioxidant property might be due to the neutralization of free-radical character of DPPH<sup>o</sup> by transfer of an electron by these nanomaterials [19].

The antioxidant potency of the proposed grafted antioxidant was also done (figure 12). They also showed antioxidant activity. The antioxidant potency of BHT grafted

MWCNT is higher than the metal oxides, as evident from the graph. The SC 50 value of the BHT grafted MWCNT is found to be 14.45 mg/ml. Antioxidant properties of BHT grafted MWCNT particles implies feasibility of their use in increasing the longevity of strategic materials (like biodiesel, edible oil, paint, rubber and its composites). The proposed antioxidant was thus found to be potent and was finally tested for biodiesel storage as discussed in the next section.

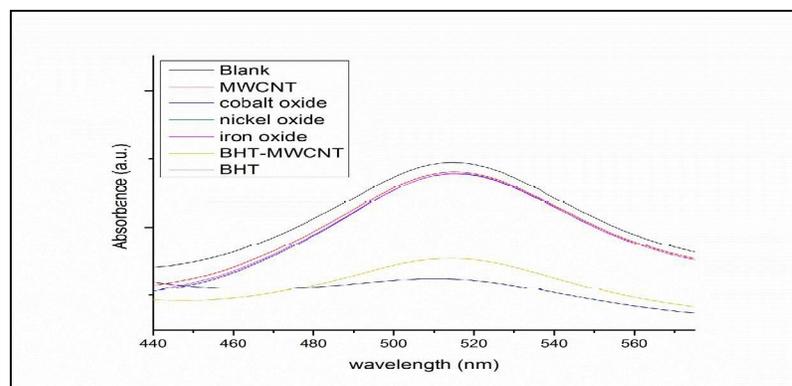


Figure 12. Antioxidant potency assay of synthesized nanoparticles and prepared nanocomposite showing absorbance after 45 min. ultrasonication with DPPH.

#### Oxidation stability analysis

BHT grafted MWCNTs nanoparticles scavenge free radicals in vitro. The antioxidant potency of these nanoparticles were tested long term storage of *Mesuaferreabiodiesel*. During the degradation process (oxidation of biodiesel) volatile organic acids, predominantly formic acid is blown out of the reaction tube which is allowed to pass through the cell and get absorbed in the water. As discussed, this increases the conductivity of water in the conductivity measurement cell and stable oils will result in less conductivity in the conductivity measurement cell in a specific period of time and at a specific temperature and vice versa. Figure 13 shows the graphical representation of conductivity-time data obtained from the conductivity measuring cell for the nanoparticles. The rate of degradation (oxidation) of the control and the biodiesel containing BHT grafted MWCNTs mixture is slow at the beginning of the experiment as evident from figure 13. With time the degradation of the oils increases in all the samples. In comparison to the control the oil sample containing BHT grafted MWCNT nanoparticles showed less degradation (oxidation). The nanocomposite containing biodiesel show enhanced stability from the very beginning.

The prominent difference in the conductivity in control from the oil samples containing nanoparticles suggests that nanoparticles have significantly increases the stability of the biodiesel. Though, the addition of the nanoparticles could not stop the degradation completely, but, addition of the proposed antioxidant nanocomposite is found to be potent antioxidant as it could enhance the stability of the biodiesel substantially. As the potency of iron oxide nanoparticles is very less, it could not stop the oxidation process.

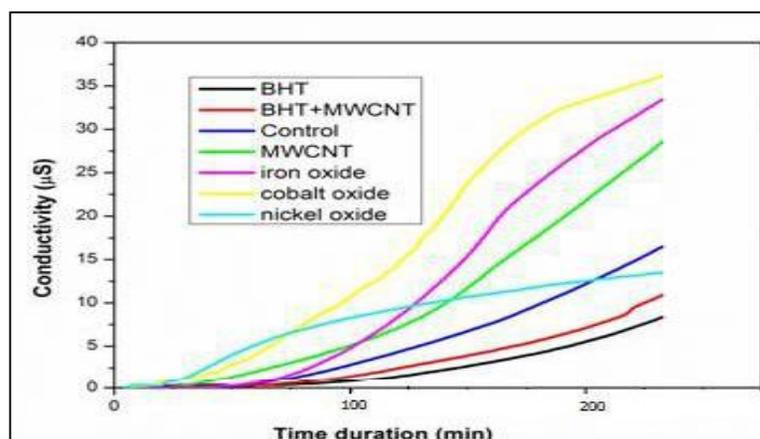


Figure 13: Rancimat oxidation stability test of biodiesel, at 110° C

The induction time (the time that elapses until the start of oxidation) for the samples obtained by Rancimat method were 233.15 min, 187.2 min, 122.01 min, 114.80 min, 60.32 min, 41.20 min, 31.83 min for BHT, BHT grafted MWCNT, Control, MWCNT, iron oxide, nickel oxide and cobalt oxide respectively. The prepared antioxidant showed antioxidant activity and could control oxidation of biodiesel. The potency of the prepared nanoparticle composite is less than the BHT but it could be compensated by adding more amount of nanocomposite in the biodiesel. The enhanced amount of antioxidants may not have any bad effect as it is designed to be removed before end use. For separating the BHT grafted MWCNT from the oil sample magnetic field may be applied. A test was conducted for this by keeping the samples in ethanol medium. Figure 14 (a) and 5.14 (b) respectively show the effect of before and after the application of magnetic field.

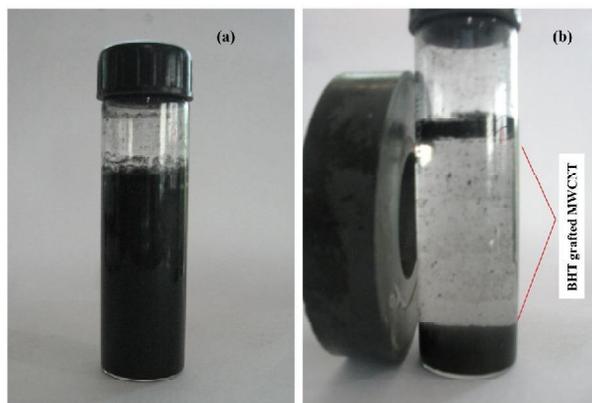


Figure 14: BHT grafted MWCNT in ethanol (a) before and (b) after application of magnetic field to demonstrate the magnetic severability of the antioxidants

### Conclusion

The study shows that the metal oxide nanoparticles (iron oxide, nickel oxide and cobalt oxide) scavenge free radicals but, the antioxidant potency of the metal oxide nanoparticles is feeble as compared to BHT. The SC 50 values for the metal oxide nanoparticles obtained were 37.98 mg/ml, 64.44 mg/ml and 149.89 mg/ml for iron oxide, nickel oxide and cobalt oxide nanoparticles, respectively. The variation in surface area due to size of the difference in size of the metal oxide nanoparticles may be ignored because of large differences in the SC 50 values.

The grafting of BHT in MWCNT was successfully demonstrated. The BHT grafted MWCNT showed higher potency compared to the metal oxides with SC 50 value of 14.45 mg/ml. It is established that the proposed nanoparticle may be used as antioxidant. The degradation study of *Mesuaferrea* biodiesel is studied and it is found that BHT grafted MWCNTs is a potent antioxidant and can enhance the shelf life of biodiesels. The potency of BHT grafted MWCNT is less than BHT but, this can be overcome by increasing the amount of the nanoparticle in the biodiesel sample for storage. It has been demonstrated that the nanoparticles can be separated magnetically. This is the primary study where an heterogeneous antioxidant is used, thus there is no result for direct comparison is available.

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