Preparation and characterization of green synthesized cerium oxide nano particle doped with biodiesel blends

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Abstract. The present work focuses on the green synthesis of nanoparticles by using bael leaves. It is a naturally occurring material for synthesizing nano additives. Characterization studies such as particle size analyzer and UV spectroscopy are been used to examine the inherent properties of bale leaf to be used as a nano material. The particle size study confirms that the produced nanoparticle has an average particle size of 50 nm with 200 nm diameter. The study by UV spectroscopy confirms that the nano crystal has a BCC structure with a peak absorption of 9.82 a.u. On the other hand, the physical and chemical properties of nano particle doped with B20 such as kinematic viscosity, calorific value, density and flash point are measured and compared with ASTM standard is presented in this paper.

1. Introduction
In recent days, a country's growth depends on transportation. Energy is one of the most important resources for transport and sustainable development of mankind. In energy consumption after China, USA and Russia, India stands 4th place. The drastic rise in the cost of petroleum based fuels, the rising environmental pollution due to emissions from the automotive vehicles and the severe depletion of fossil fuels thrive the researchers to find an alternative fuel to replace fossil fuels [1, 2]. Despite concerns about environmentally friendly alternative energy sources, biodiesel is one of the possible sources of energy. The addition of nano particles to the biodiesel blends shows the improvement in the engine performance, combustion efficiency and reduces the emission characteristics of diesel engine [3]. The nano diesel proved to be a potential source to improve the combustion efficiency and reduce the air pollutants. It will enhance the fuel properties, better engine performance and the reduction of exhaust emission by doping of nano particles to the biodiesel [4]. Jatroba oil biodiesel blend doped with MWCNT with 40mg/l decreased 40% HC emission due to shortening of ignition delay and with higher surface area to volume ratio of nano particle leads to better air fuel mixing in combustion chamber [5]. The 20.56% of HC emission reduction was achieved with waste cooking oil biodiesel blended aluminium oxide nano particle where the addition of alumina leads to better atomization of fuel due to lowered viscosity and increased surface to volume ratio of nano particle and enhanced heat transfer [6]. The use of zinc oxide nano particle on jatropha oil (B100) biodiesel and observed reduced HC emission due to secondary atomization of fuel blend and effective fuel distribution in combustion chamber leads to complete oxidation of fuel blends [7].
The cerium oxide nanoparticle is used 20 ml cerium chloride (0.5M) solution were stirred at 300 rpm and same amount of ammonium hydroxide solution added to stirred solution and stirred for further 30 minutes. Then this solution heated at a temperature of 110°C to evaporate water content in the stirred solution and produced cerium oxide powder [8]. The super paramagnetic iron oxide nano particles (Fe$_3$O$_4$) is produced by using 1 M of ferric nitrate salt was dissolved with 40 ml of distilled water and 2 M of sodium hydroxide was dissolved with 50 ml of distilled water. Both solutions were mixed together properly and further mixed solution was sonicated for 1 hour to get uniform distribution. After sonication, the moisture content in the synthesized homogenous nano particle was removed by calcinations process at a temperature of 350°C for a period of 1 hour to form iron oxide nano particle [9]. The mahua oil biodiesel (B20) blend doped with copper oxide nano particle with 50 ppm concentration reduced 5.33% HC emission compared with neat B20 mahua oil where nano additive reduces the ignition delay and provides oxygen for complete combustion resulted in lowered HC emission [10].

Many researchers have worked in this theme and reported the influence of various fuel additives such as metal oxide in the nano scale form. The additives with following characteristics are best suited to dope with diesel fuel, a) soluble in the fuel homogeneously during application, b) increase the power output of the engine and c) reduces fuel consumption and exhaust emissions like CO$_2$, NO$_x$, etc. The commonly used nano particles are Aluminium oxide (Al$_2$O$_3$), Titanium oxide (TiO$_2$), Zinc oxide (ZnO), Silicon oxide (SiO$_2$), Ferric oxide (Fe$_3$O$_4$), Nickel oxide (NiO), Cerium oxide (CeO$_2$), Cobalt oxide (CO$_3$O$_4$), Magnalium (Al-Mg) and carbon nanotube (CNT) [11-17]. In recent days, among the above, metal oxide of cerium was found to be more abundant in rare earth family and it possess very good thermal stability. It undergoes redox cycling between the trivalent and tetravalent oxidation state. Based on the literature review in solgel, lubrication chemical method and chemical reaction process but very limited publications in bio- synthesis of nanoparticles.

It is an emerging field where the plant extracts are used as an alternative to produce metallic nano materials. This method involves clean and nontoxic process in which the ecology is not affected. Literature studies reveals that green synthesis of nano materials combined with plant-derived regents as reactive agents for metal salts are in current trend that helps to preserve the nature for future generations. Approaches for the production of nano particles by naturally occurring processes such as plant extract, biodegradable polymers, micro-organisms, etc. are novel [16-17]. When comparing all other methods, the bael leaf extract green synthesized cerium nano particles are simple, one-step, cost-effective, environmentally friendly and fairly reproducible, offering better performance. Conversion of cerium ions into nano particles, which focuses on the application of a green approach to the synthesis of silver nano particles, as an alternative conventional method, is commonly available in India [17]. Cerium nano particles made without the addition of adverse chemicals / physical application methods by using bael leaf extract at low concentration.

2. Material and Methodology

2.1. Preparation of Bio Diesel
In this work, methyl ester of pungamia oil used as a feedstock. The methyl ester of pungamia oil (biodiesel) was prepared by esterification process. In this reaction, potassium hydroxide act as a catalyst concentration of 0.7 wt/wt% of oil, molar ratio of ethanol to oil as 8:1, maintained the mixing speed of 550 rpm with the temperature of 65°C for one hour. At this optimized process parameters, mono esters (bio diesel) capitate of 91±0.3 % was attained.

2.2. Preparation of Bael Leaf Nano-Particle
From the basics of easily available and environmentally friendly nature, fresh green bael leaf extract was preferred to make cerium oxide nanoparticles. The bael leaves were collected and washed with distilled water for removing the impurities. After the removal of impurities from the bael leaves, it is cut thinly and again it is washed with distilled water. Figure 1 represent the photographic view of bael
After completion of cleaning process, the 30g of bael leaves is mixed with 120ml of Deionized water. The mixture is poured to the beaker and allowed for boiling process for one hour. After the boiling process the mixture is filtered to remove the wastes and for the extraction of aqueous leaf extract. In this experiment, the nano particles is extracted from the aqueous bael leaf extract is shown in figure 2.

![Figure 1. Bael leaf.](image1)

![Figure 2. Leaf soup.](image2)

**2.3. Procedure for Green Synthesis of Cerium Oxide Nanoparticles**

The bael leaves soup is interacted with 25 mg of CeO$_2$ and 120 ml of distilled water. The mixture was stirred at a constant speed of 85 rpm for 4 hours to achieve a homogeneous reaction and to obtain cerium oxide nano particles in dry form. For the separation of cerium nano particles, the soup is centrifugated for 6000 rpm for 20 minutes. For better partition of nano particles, the stirring operation is repeated until the expected free substance is extracted. A hot air oven at a temperature of 720°C is utilized for the sanitating the particles. After the reaction of bael soup and CeO$_2$ solution, these cerium nano particles is obtained as shown in figure 3.

![Figure 3. Green Synthesized Nano particles.](image3)

Now a days, for the blending of B20 nano particles in diesel-bio diesel blends, ultrasonicator is used. Then, 1 litre of diesel-bio diesel blends and 1g of green synthesis nano particles is added into a beaker. It is allowed to ultrasonic apparatus for uniform dispersion for half an hour.

**3. Result and Discussion**

3.1. Particle Size Analysis
Analysis of particle size is achieved through dynamic light scattering technique. The dynamic range is 0.3 nm to 8μm, depending on the physical properties of the sample. The lower limit is determined by the size, the intensity of the sample, and the presence of large and unwanted particles. The sample density affects the upper limit as DLS is based on all motion from Brownian movement and not gravitational force. The same instrument can also be used to calculate the molecular weight of polymers, other molecules and the second viral coefficient. The size of the particle is analysed with the help of the particle size analyser and it is found and is given in the figure 4.

![Particle Size Analysis](image)

**Figure 4. Particle Size Analysis.**

It is clearly prove that the size of the particle is found to be 200nm that shows an imaginary peak. In PSA test, the peak observed at the optimum relative intensity is considered as the diameter of the particle. It is seen that the particle size of cerium oxide nanoparticle is 200 nm.

3.2. **UV spectroscopy**

The optical properties of nanoparticles are sensitive to shape, size concentration, agglomeration state and refractive index near the surface of the nanoparticles, making UV / VIS / IR spectroscopy a powerful tool for defining, characterizing and studying these materials. UV spectroscopy is a method in which the shape and orientation of the nano sized crystal is measured in relation with the absorbed UV radiation and is shown in the figure 5.

The figure 5 shows the variation of wavelength (nm) with respect to absorption coefficient of nanoparticles. The peaks obtained from the graph proves that the nanoparticle is formed and has Body-centric lattice and the absorption rate is 9.82 a.u for the peak wavelength of 312 nm. It proves sizer of nanoparticles within the nano range.
4. Fuel Properties

The test fuel properties of diesel, B20 bio diesel blends dopped with green synthesized nanoparticles of 5 and 10 ppm cerium oxide nanoparticles are compared and presented in the table 1.

| Properties                             | Diesel | Methyl ester of Pungamia B20 | B20 + 5 ppm GS CeO₂ | B20 + 10 ppm GS CeO₂ | ASTM standards of bio diesel |
|----------------------------------------|--------|-------------------------------|---------------------|----------------------|-----------------------------|
| Kinematic Viscosity (cSt) at 40°C       | 2.5    | 3.1                           | 3.1                 | 3.2                  | 1.9 – 6.0                   |
| Calorific value (MJ/kg)                | 43.8   | 43.3                          | 43.4                | 43.6                 | > 40                        |
| Density (kg/L)                         | 0.832  | 0.831                         | 0.831               | 0.828                | 875-900                     |
| Flash point (°C)                       | 52     | 63                            | 62                  | 62                   | >130                        |

Nevertheless, all the properties are significantly increased compared to diesel when green synthesized nano particles are doped with diesel-bio diesel blends. The properties of test fuel in table 1 indicate that they are all within the biodiesel standard range.

5. Conclusion

Based on the experimental investigations of green synthesized bale leaf extract nanoparticles, the following conclusions were made.

- Nanoparticles of cerium oxide were prepared by bael leaf extract of green synthesized method and particle size of 50 nm and diameter 200 nm is obtained.
• It is obtained from the UV spectroscopy results that the nano crystal has BCC structure with peak absorption of 9.82 a.u.
• Particle size analyser and UV spectroscopy results proved that produced nanoparticles size and orientation are within the nano range.
• The physical and chemical properties of B20 biodiesel dopped with green synthesized nanoparticles are within the ASTM standards range.

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