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INFLUENCE OF SYNTHESIZED (GREEN) CERIUM OXIDE NANOPARTICLE WITH NEEM (AZADIRACHTA INDICA) OIL BIOFUEL

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ABSTRACT. Energy demand increases day by day due to the present technological scenario and fossil fuels are also depleting gradually. Therefore, the necessity came into the researchers to identify an alternative renewable resource for compensating the energy demand. The biodiesel appeared to the researchers as an important resource due to its characteristics and ability to compensate for the energy demand. However, some additional improvements are required for the efficient performance of the biodiesel, such improvement is achievable by the blending of an efficient additive with the biodiesel. The present study predominantly focuses to investigate the performance of the biodiesel with two different additives such as cerium oxide nanoparticles and ethanol. The neem (*Azadirachta indica*) oil has been selected as feed stock. The cerium oxide nanoparticles are prepared using the green synthesis process. Four various fuel samples are prepared to examine the effect of additives, (i) PB (pure biodiesel), (ii) BCe (PB+100 ppm CeO_2), (iii) BE (90% biodiesel+10% ethanol) and (iv) BCeE (90% biodiesel+100 ppm CeO_2+10% ethanol). From the experimentation, it is observed that the fuel BCeE achieves the better performance due to the oxygen buffering characteristics and improvement in the atomization by the additives.

KEY WORDS: Additives, Nanoparticles, Neem oil, Emission, Combustion, Heat release rate

INTRODUCTION

In the near future, biodiesel can contribute 27% of the overall energy requirement in the whole world. The transportation alone eliminates nearly 2.1 Gt CO_2, NO_x, HC, etc., per year [1]. The petroleum fuels are gradually depleting and also produces environmental pollution, global warming, etc. However, many countries are affected by the unstable fuel supply. These issues can be sorted out by the appropriate alternative energy resources. The vegetable oil is in the race to become an appropriate alternative for diesel fuel by the calorific heating value. The non-edible oil is not competitive for the edible oil. Therefore, most of the research is concentrated on the non-edible oils [2]. Some of the vegetable oil properties such as viscosity, volatility, density, etc., lead to an improper combustion which causes the scope to the fuel properties modifications. Therefore, the vegetable oil needs to be converted into the biodiesel for the feasible properties [3]. The mono-alkyl ester is the biodiesel which is obtained from the triglycerides of vegetable oil [4]. Different methods are available to prepare the biodiesel which includes thermal cracking, direct use and direct mixing, microemulsions and transesterification. The transesterification process seems to be the most convenient and better choice to produce the biodiesel due to its lower production cost, shorter production time and high productivity [5]. The free fatty acid (FFA) and moisture are the important materials present in the vegetable oil [6, 7]. In future, the neem oil can be the dominating

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*Corresponding author. E-mail: haiterlenina@gmail.com source of energy in India since most of the states cultivate neem trees. A matured tree can cultivate 30-50 kg fruit per year and its cultivation continues up to 150-200 years. The neem oil is also helpful for the medical sector, lubrication and soap production and each part (leaf, kernel, fruit, seed oil, bark, wood, etc.) of neem tree can be used for enormous applications [8, 9]. The neem oil biodiesel shows the positive results in performance, emission and combustion characteristics [10]. However, the flash point and the density of the neem biodiesel is higher than the petroleum diesel [11, 12]. The properties and the performance of the biodiesel was improved by the addition of some additives. The cerium oxide nanoparticle is one of the important additives. It donates the oxygen for oxidizing the carbon monoxide and combusting the unburnt hydrocarbon [13-15]. The volatility is one of the considerable properties of the fuel. The emission of smoke is controllable by the addition of volatile material (ethanol is one among them) with the biodiesel. The fuel with 20% of ethanol can be used in the CI engine without any modifications. Ethanol is a biomass based renewable resource of energy. It is able to derive from the vegetables and wastages. The ignition delay is one of the important parameters. It is mainly dependent on the spray characteristics and latent heat of the fuel. The higher latent heat of ethanol causes the higher ignition delay than the diesel [16-19]. Lenin *et al.* [12, 20] investigated the effect of the blending of pongamia biodiesel with the diesel on the performance and emission characteristics of the engine and they found the useful improvement. The influence of the ionization of the fuel on the performance and emission characteristics has been explored by Thiyagarajan *et al.* [21]. Karthickeyan *et al.* [22] conducted an experiment to investigate the engine performance of the biofuel blend (*Pistacia khinjuk* oil methyl ester in diesel). They observed that the blending of Pyrogallol also influences the engine performance. Jeevanantham *et al.* [23] attained the 45% reduction in NOx emission due to the blending of 10% diethyl ether. Many authors synthesized the biodiesel using various methods and performed the performance, emission and combustion characteristics [24-31]. Hrish and Madhavan [32] experimentally evaluated the influence of the fuel (biodiesel and Al_2O_3 nanoparticles blend) injection timing on the IC engine performance. The study found that the addition of nanoparticles used for varying the effective injection timing. Prabu [33] and also Gopal *et al.* [34] analyzed the effect of various nanoparticles in the working characteristics of DI engines. Hosseinzadeh-Bandbafha *et al.* [35] studied the CI engine performance with the water emulsified fuel. The study identified that the water emulsified fuel contributes to enhancing the performance of the engine. The effect of nanoparticle concentration in the biodiesel evaporation was studied by Jiang *et al.* [36] and they found that the evaporation rate reduces as an increase in the concentration of nanoparticles. Ağbulut *et al.* [37] investigated the effect of the blending of silicon oxide, aluminum oxide and titanium oxide nanoparticles with the fuel in the emission and performance characteristics. The study observed that the nanoparticles helped for the better combustion of the fuel by its highly available oxygen content. Siva *et al.* [38] and Sajith *et al.* [39] performed an analysis to explore the contribution of cerium oxide nanoparticles in the engine performance and emission characteristics. They observed that the cerium oxide positively influenced the engine performance and emission characteristics.

From the existing research and literatures, it is identified that the neem oil has an ability to compensate present and future energy demand. It cannot create a food scarcity due to the inedible nature. The availability of neem oil is plentiful in south Asia. India alone produces more than 30000 tons of neem oil per annual [40]. Therefore, the neem oil has been considered for the present study. However, some additives also required to improve the efficiency and performance of the biofuel. From the literature, it has been seen that many nanoparticles were showed the promising improvement in the engine performance and emission characteristics. The cerium oxide is one among them. It shows the useful improvement in the fuel properties, engine performance, combustion and emission. This is the reason behind the consideration of the cerium oxide nanoparticle additives in the present study. Similarly, the blending of ethanol improves the fuel properties such as volatility, viscosity, etc. The present study focuses to explore the combined effect of CeO_2 nanoparticle and ethanol with neem oil biodiesel. The transesterification method is used to prepare the neem biodiesel. The CeO_2 nanoparticle was synthesized using green synthesis process. Four various fuel samples are prepared. The experimentation is performed for the prepared fuel samples. The results are evaluated by various characteristics such as emission, combustion and performance characteristics.

EXPERIMENTAL

Synthesis of cerium oxide nanoparticle (green synthesis)

The cerium oxide nanoparticles can be produced with physical and chemical methods. However, it takes a long time. Therefore, the green synthesis method is preferred for the present study to synthesis the cerium oxide nanoparticles [41]. Many existing researches synthesized the various nanoparticles (iron oxide, cerium oxide nano, silver, etc.) using green synthesis method. They also characterized the nanoparticle with SEM, TEM, XRD, EDX and FTIR [42-43].

The *Moringa oleifera* leaf extract is used as a reduction agent of iron due to the plenty phytochemical contents such as carbohydrate, protein, phenolic compound, etc. The formation of nanoparticles consists of the following three stages: (i) reduction of ions, (ii) clustering, and (iii) nanoparticle growth. Some parameters influence growth and properties of nanoparticles such as nature, concentration, pH value of the reducing agent, stabilizer, ratio between cerium nitrate and reducing agent ratio. The phytochemicals are here to act as a reduction agent to form a cerium oxide nanoparticle [44]. The *Moringa oleifera* leaf was collected from the farm. Then the leaf was separated from the stem. The separated leaves were washed by the water to remove the unwanted impurities presents in the leaves. Then 100 mL of water is taken in the beaker with the 50 g of *Moringa oleifera* leaves and heated till the water reaches greenish colour. Finally, Maan filter No. 40 filter paper is used to take a pure leaf extract without impurities. A 50 mL of *Moringa oleifera* leaf extract was taken in a beaker and heated up to 60 degree Celsius, and then 5 g of precursor was added into the leaf extract at 60 °C. Then the solution was heated continuously, till the solution become a form of paste. The paste has been taken in the ceramic crucible and placed in a muffle furnace to maintain 450 degree Celsius for 2 hours to remove the organic impurities. Finally, the light yellow colour powder was obtained, collected and stored in an airtight container. Figure 1 shows the SEM image of cerium oxide nanoparticles.

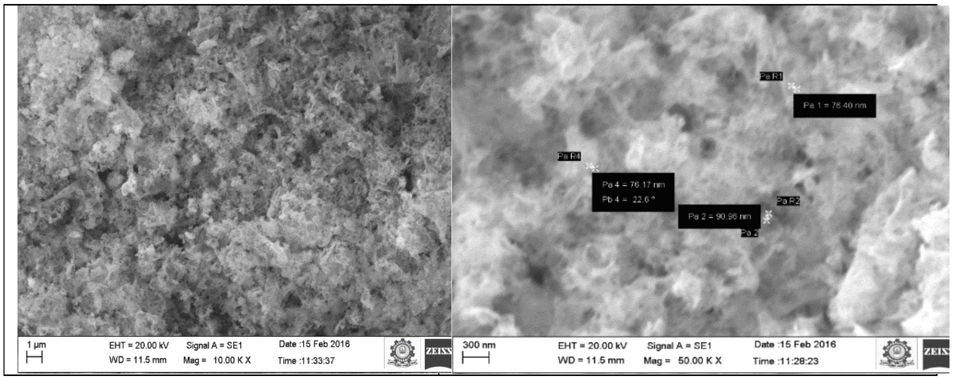

Figure 1. SEM image of cerium oxide nanoparticles.

Characterization of cerium oxide nanoparticles

The synthesized cerium oxide (CeO_2) nanoparticle was characterized using Cu Kα – X-Ray diffractometer for making a conformation of nanoparticles and analyzing the structure. The peak was obtained from the angles 28.465°, 28.589 °, 33.007 °, 47.444 °, 56.311 °, 59.056 °, 69.369 ° and 76.635 ° (Figure 2). The identified peak perfectly matches the JCPDS (Joint Committee on Powder Diffraction Standards) - file no. 34-0394. Therefore, the characterization made a conclusion as the obtained material is the cerium oxide.

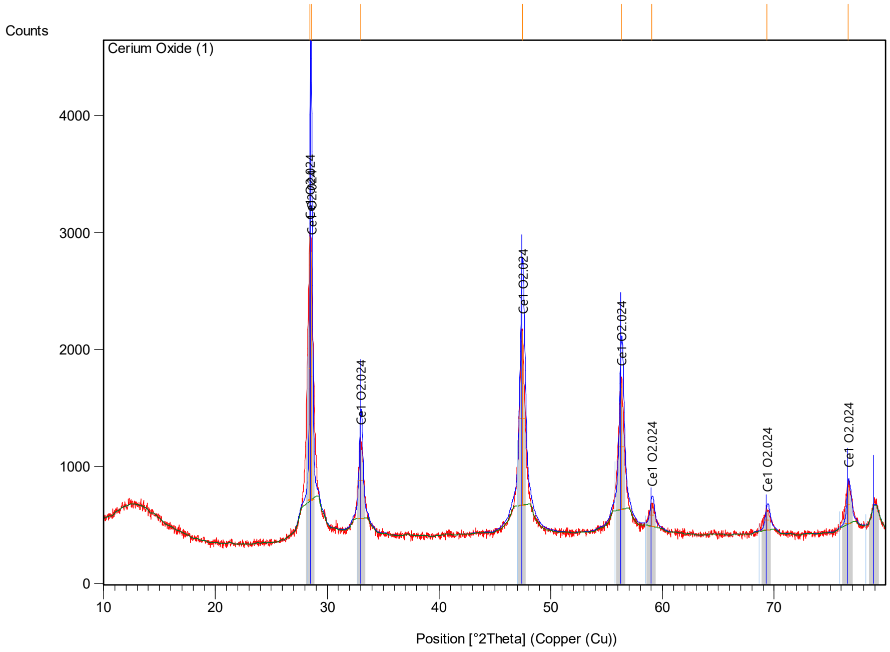

Figure 2. XRD characterization.

Biodiesel production process

The neem oil, methanol, KOH, ethanol and cerium nitrate hexa-hydrate are purchased from suppliers. In the present study, the transesterification process is used to prepare the biodiesel from the neem oil. The transesterification is a process to produce mono alkyl ester from the triglycerides due to the reaction between methanol and triglycerides in an appropriate temperature. The neem (one liter) was taken in a beaker, then it was heated up to 60 ºC using an electric heater and stirred with the speed of 500 rpm. Now 200 mL of methanol and 10 g of potassium hydroxide were added to the heated neem oil. The required time needs to be given for the efficient conversion of biodiesel from triglycerides of oil and also for the maximum yield efficiency. Therefore, this process was carried out for an hour with the constant temperature 60 ºC and constant speed 500 rpm. The reacted oil was poured into the separating funnel and placed over 12 hours for the separation of ester and glycerol. This process cultivates two products such as methyl ester and glycerol. The separation has been done by the density and gravitational force acting on the reacted oil. Now the reacted oil was settled in two layers. The biodiesel was settled in the upper layer with golden yellow color and the lower layer contains glycerol with black in color as a byproduct. The glycerol was removed from the separating funnel and utilized for other purposes.

Biodiesel blending and properties

The Table 1 and Figure 3 shows the various biodiesel blends and their properties respectively. PB is pure neem oil biodiesel. The fuel sample BCe is the blending of 100 ppm cerium oxide nanoparticles pure neem oil biodiesel. The fuel sample BE contains 90% volume of pure biodiesel and 10% volume of ethanol. Both cerium oxide nanoparticles (100 ppm) and ethanol (10% in volume) have been mixed with pure biodiesel (90% in volume) in the fuel BCeE. The kinematic viscosity was identified using a red wood viscometer. The calorific value of the prepared biofuel samples was determined using bomb calorimeter. Pensky Martens apparatus is used to find the flash and fire point of the prepared biodiesel samples. The addition of additives shows some positive variations in fuel properties such as Specific gravity, flash point, kinematic viscosity and calorific value. But the ethanol marginally increases the flash point and decreases the calorific value. This action is opposite to cerium oxide nanoparticles.

Table 1. Proportions of biodiesel blends.

Material / Sample	Neem oil biodiesel	Cerium oxide nanoparticles	Ethanol
PB	100%	-	-
BCe	100%	100 ppm	-
BE	90%	-	10%
BCeE	90%	100 ppm	10%

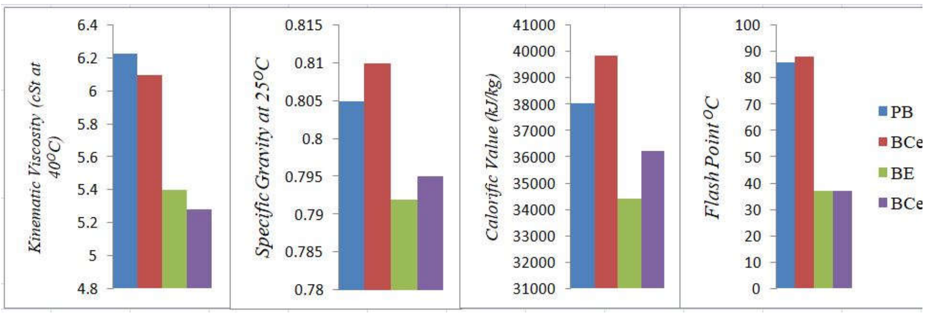

Figure 3. Fuel properties.

Experimental setup

Figure 4 shows the arrangement of the experimental setup specifications of CI engine, respectively. The single cylinder, constant speed, vertical four stroke and air-cooled CI engine is used to conduct an experiment. The rated power and speed of the engine are 4.4 kW and 1500 rpm, respectively. The compression ratio is 17.5:1. The bore diameter and stroke length of the engine are 87.5 mm and 110 mm. The electrical dynamometer (Swingfield) is coupled with an engine for varying the load. The pressure transducer is used to identify the pressure field. The angle encoder is also located along with the flywheel. The burette arrangement was used to analyze the rate of fuel flow of the consumption. The various emissions (unburnt hydrocarbon (UBHC), carbon monoxide (CO) and oxides of nitrogen (NOx)) were measured with the help of an exhaust gas analyzer which was used to estimate. The smoke meter was used to estimate the emission of smoke as a filter smoke number (FSN). This experiment was conducted with five different loads with the constant engine speed of 1500 rpm. This experiment helped to analyze the performance of the CI engine with the prepared various biodiesel samples through some estimated parameters such as brake specific fuel consumption (BSFC), brake thermal efficiency (BTE), emissions, heat release and pressure.

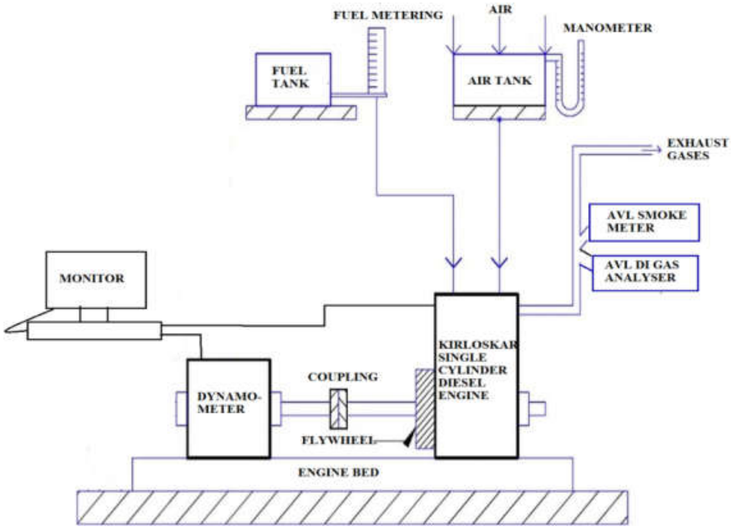

Figure 4. Experimental setup.

RESULT AND DISCUSSION

The present study focuses to analyze the effect of the addition of the CeO_2 nanoparticles and ethanol in the neem oil biodiesel on the performance emission and combustion characteristics. The experiment was conducted with the prepared four different fuel samples. The detailed analyses are discussed in the following sections.

Emission characteristics

The emission characteristic is one of the important criteria that needs to be discussed. The harmful emissions should be minimized. In this section of the study, the effect of blending of the ethanol and CeO_2 discussed in detail.

Unburnt hydrocarbon emission

The unburnt hydrocarbon emission as a function of break power is shown in Figure 5(a) for all the fuel samples. The biodiesel blends BE and BCeE have the unburnt hydrocarbon emission more than the pure biodiesel. However, BCe fuel has reported better emission over the other three biodiesel samples due to the oxygen buffering characteristics of CeO_2 nanoparticles during the combustion. The additional oxygen provided by the cerium oxide can help to oxidize the unburnt hydrocarbon. The cerium oxide also re-oxidizes to Ce_2O_3 as shown in equation 1 [15]. The unburnt hydrocarbon emission of fuel sample BCe is 66.66% and 17.65% lower than the pure biodiesel at 25% and full load conditions respectively.

$$4CeO_2 \leftrightarrow 2Ce_2O_3+O_2 \qquad (1)$$

Carbon monoxide (CO) emission

The carbon monoxide (CO) emission of all the prepared biodiesel samples is shown in Figure 5(b) as a function of beak power. The carbon monoxide has been formed by the incomplete combustion of hydrocarbons. It depends on various factors such as ratio of air fuel mixture, nature of the fuel, combustion chamber design, injection timing, pressure of injection, etc. [44]. The biodiesel blend BCeE produces less CO emission than others. The rich mixture of air-fuel and inadequate oxygen causes the higher CO emission at the full load conditions for all the fuel samples. The CO emission of BCeE and BE is 28% and 14%, respectively, lower than pure biodiesel (PB) at full load condition.

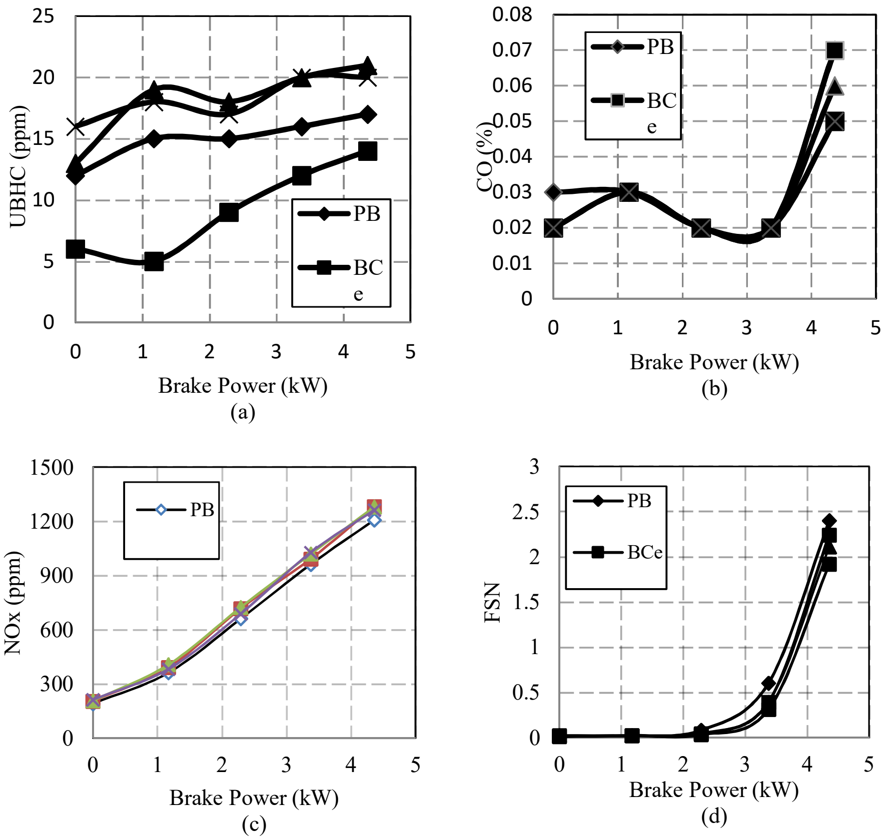

Figure 5. Variation of (a) unburnt hydro carbon (UBHC), (b) carbon monoxide (CO), (c) oxides of nitrogen (NOx) and (d) filtered smoke number (FSN) emissions as a function of break power.

Oxides of nitrogen emission (NOx)

The emission of oxides of nitrogen (NOx) is depicted for biodiesel and its blends as a function of break power in Figure 5(c). Generally, the NOx emission (formed by the reaction between nitrogen and oxygen) is influenced by some parameters such as oxygen content in the fuel, flame temperature and reaction timing. If combustion starts earlier, it will lead to more combustion time that causes the formation of more NOx. The NOx emission increases with engine load. The higher temperature of the combustion and oxygen content at higher load conditions causes the higher NOx emission. The cerium oxide nanoparticles and ethanol donate additional oxygen to react in combustion. Therefore, the fuels BCe, BE and BCeE create more NOx emission than pure biodiesel PB.

Smoke emission

The smoke emissions of various fuels are shown in Figure 5(d). In the present study, the emission of smoke has been measured as filtered smoke number (FSN). The maximum value of smoke emission has been obtained at full load condition for the all-prepared biodiesel samples. FSN increases as an increase in load. The blend BCeE has the lower smoke emission as compared to the other fuel samples and it is 20% lower than the pure biodiesel. Here, the combination of cerium oxide and ethanol helps to reduce the emission of smoke by improving the volatility of fuel and supporting the complete combustion.

Performance characteristics

The present study considered two performance characteristics (BSFC – Brake specific fuel consumption and BTE – Brake thermal efficiency) for observing the effect of CeO_2 and ethanol blend in the neem oil biodiesel. The considered characteristics are elaborately discussed as follows.

Brake specific fuel consumption (BSFC)

The brake specific fuel consumption (BSFC) of prepared all the four biodiesel samples are depicted in Figure 6(a) as a function of brake power. There are different factors affecting BSFC which includes density, viscosity, calorific value, etc. The increase in load of the engine causes the increase in temperature. The higher temperature supports the efficient combustion and better conversion of heat energy to mechanical energy. According to these experimental results, the minimum BSFC was absorbed at 75% load conditions for all the fuel samples and it is also slightly lower than full load condition. The improper burning of fuel at full load conditions can also become a criterion for more fuel consumption. The biodiesel blend BCeE has lower BSFC than others, especially in 50%, 75% and full load conditions.

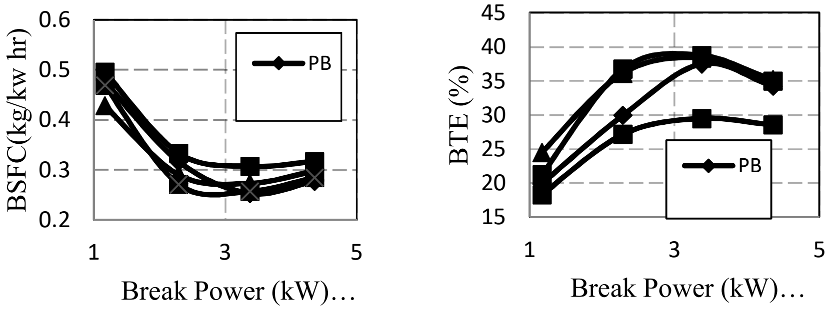

Figure 6. Variation of (a) break specific fuel consumption (BSFC) and (b) brake thermal efficiency as a function of brake power.

Brake thermal efficiency (BTE)

The break thermal efficiency (BTE) is the ratio between the break power and energy that is released during the fuel combustion. The Figure 6(b) illustrates the variation of the brake thermal efficiency with respect to the brake power. The BTE increases with the engine load. The higher value of BTE was obtained at 75% load conditions. Due to the improper burning of fuel, the marginal drop in the BTE is observed at 100% load condition. The fuel sample BCeE produces better thermal efficiency by its good atomization and the combustion of the fuel. The fuel BCe was the lowest performer in break thermal efficiency among all fuel samples due to the inefficient burning of fuel.

Combustion characteristics

The combustion characteristics also need to be discussed. For the present study, the cylinder pressure and rate of heat release are the parameters that are considered and discussed in detail as follows.

Pressure of cylinder

Figure 7 illustrates the pressure acting on the engine cylinder for different crank angles and load conditions. The pressure acting on the cylinder is almost similar to all biodiesel blends at various engine loads. But it has smaller variation among the four fuels used in engine tests. In higher load conditions these variations are very low due to the higher temperature of engine wall and gas. This is responsible for reducing the ignition delay and better combustion of the fuel. Among these four fuels BE and BCe produced the better result and the biodiesel blend BCeE does not make any useful pressure rise. The maximum pressure was obtained for the fuels PB and BCeE at the same angle at no load condition and it was two degrees earlier than the fuel BCe and BE. This change of angle represents the ignition delay also. The peak pressure produced by the fuels PB, BCe, BE and BCeE of 48.946 bar, 48.334 bar, 48.29 bar and 47.362, respectively and the same for 25% load is 53.024 bar, 53.704 bar, 54.122 bar and 52.469 bar, respectively. The pressures 57.979 bar, 58.391 bar, 58.404 and 56.279 bar are produced by the fuels PB, BCe, BE and BCeE respectively during 50% load condition. However, the peaks at load 75% loads are 60.682 bar, 61.482 bar, 61.665 bar and 61.362 bar; for 100% load - 66.039 bar, 66.352 bar, 66.124 bar and 66.796 bar. Generally, the peak pressures were identified from the angle of 5 to 11 degree for all the four prepared biodiesel at all the five different load conditions. Here no major ignition delay or no big change in peak pressure is identified from this experiment. However, the cerium oxide nanoparticle and ethanol produce very some influences on it.

Heat release rate (HRR)

The rate of heat release during the combustion process for the various crank angles has been shown in Figure 8. At the initial stage of combustion, there is a premixing process which causes the negative heat release. The fuel accumulates and vaporizes by absorbing the heat energy present in the cylinder wall and gas. This length of negative heat release phase represents the ignition delay. The fuel started to combust rapidly after the premixed combustion process. Then there is an increase in heat released by the fuel towards the peak and then starts to decrease. However, there is a decrease in ignition delay with increase in load due to the higher temperature of the gas and cylinder wall of the engine. The blending of cerium oxide nanoparticles leads to combustion a little bit earlier than pure biodiesel and it also encourages the initial combustion. At no load condition, more ignition delay was observed by the fuel PB. At the smaller load conditions, the fuel BCe also produced a good peak heat release rate. It also reduces the ignition delay at all load conditions by the ability of CeO_2 to start the combustion earlier and accelerates towards the clean burning of fuel. There is a slightly higher ignition delay with the fuel BE has because of latent heat of the fuel. The latent heat of the fuel has a vital role in the vaporization of the fuel at the very earlier stage of combustion. The fuel BCeE leads to the peak rate of heat release at high load conditions. The different peaks of the rate of heat releases were obtained for various fuels at various loads and different crank angles due to its variations in ignition delay. The addition of additives such as CeO_2 and ethanol has a considerable impact on the rate of heat release during combustion.

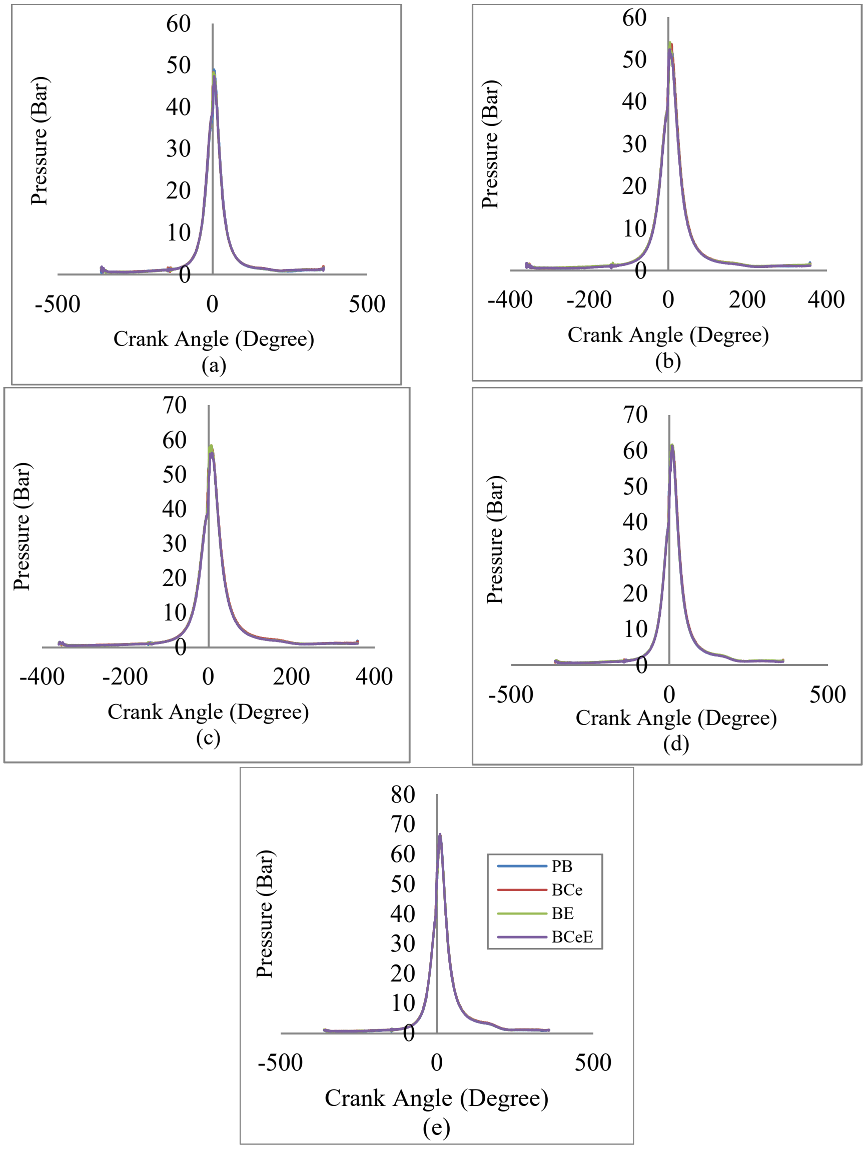

Figure 7. Variation of heat releasing rate as a function of crank angle at (a) no load, (b) 25% load, (c) 50% load, (d) 75% load and (e) 100% load.

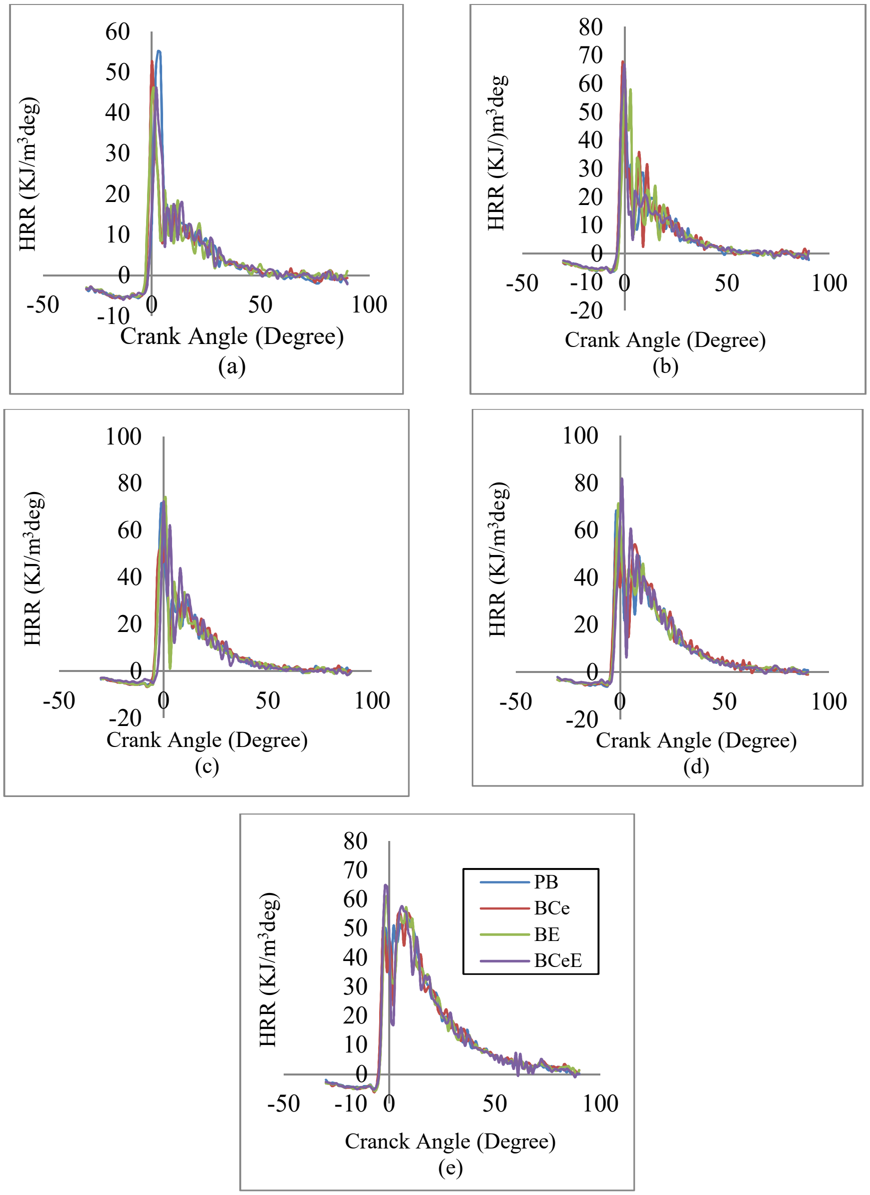

Figure 8. Variation of heat releasing rate as a function of crank angle at (a) no load (b) 25% load (c) 50% load (d) 75% load (e) 100% load.

CONCLUSION

In the present study, the attempt has been made to identify the influence of the addition of cerium oxide nanoparticles and ethanol in the neem oil biodiesel on the performance, emission and combustion characteristics. The combined effect of both additives also is discussed. The neem oil biodiesel was produced by transesterification process. The experimentation was conducted and the effect of the synthesized CeO_2 and ethanol with the neem oil biodiesel was analyzed with various parameters such as performance, emission and combustion. The following result has been obtained by this investigation. (1) In emission characteristics the additives have played a significant role. The cerium oxide alone reduces UBHC emissions. The hybrid cerium oxide nanoparticles and ethanol have produced lowest emission CO and smoke. However, the NOx emissions were increased by the fuel additives. (2) In performance characteristics, the lowest fuel consumption and higher fuel efficiency have been obtained by the fuel BCeE. During the full load condition, the fuel has burnt in an improper way so that the fuel cannot perform in a better manure. (3) In combustion characteristics, the cylinder pressure increases when the load increases. There is no big meaningful variation among the various fuel samples in combustion characteristics. However, the better performance has been obtained by the fuel BCeE in the heat release rate.

From this investigation work, it is concluded that the hybrid cerium oxide nanoparticles and ethanol show the better significant performance results due to their better atomization and oxygen buffering character. Therefore, the fuel BCeE has been suggested by the present study and further optimization is required to get a better performance.

REFERENCES

1. Atabani, A.E.; Mofijur, M.; Masjuki, H.H.; Irfan Anjum Badruddin, Kalam, M.A.; Chong, W.T. Effect of *Croton megalocarpus*, *Calophyllum inophyllum*, *Moringa oleifera*, palm and coconut biodiesel–diesel blending on their physico-chemical properties. *Ind. Crops Prod.* **2014**, 60, 130-137.
2. Borodina, V.G.; Mirgorod Yu, A. Kinetics and mechanism of the interaction between HAuCl4 and rutin. *Kinet. Catal.* **2014**, 55, 683-687.
3. Venkanna, B.K.; Venkataramana Reddy, C. Biodiesel production and optimization from *Calophyllum inophyllum* Linn oil (honne oil)–A three stage method. *Bioresour. Technol.* **2009**, 100, 5122-5125.
4. Demirbas, A.; Demirbas, M.F. Importance of algae oil as a source of biodiesel. *Energy Convers. Manag.* **2011**, 52, 163-170.
5. Ma, F.; Hanna, M.A. Biodiesel production: a review. *Bioresour. Technol.* **1999**, 70, 1-15.
6. Nabi, M.N.; Akhter, M.S.; Shahadat, M.M.Z. Improvement of engine emissions with conventional diesel fuel and diesel–biodiesel blends. *Bioresour. Technol.* **2006**, 97, 372-378.
7. Silitonga, A.S.; Ong, H.C.; Mahlia, T.M.I.; Masjuki, H.H.; Chong, W.T. Biodiesel conversion from high FFA crude jatropha curcas, calophyllum inophyllum and ceiba pentandra oil. *Energy procedia.* **2014**, 61, 480-483.
8. Ragit, S.S.; Mohapatra, S.K.; Kundu, K.; Gill, P. Optimization of neem methyl ester from transesterification process and fuel characterization as a diesel substitute. *Biomass Bioenerg.* **2011**, 35, 1138-1144.
9. Parmar, B.S. Industrial uses of neem and future commercialization. *Neem in Sustainable Agriculture.* Scientific Publishers: Jodhpur, India; **1997**, pp. 251-260.
10. Dhar, A.; Kevin, R.; Agarwal, A.K. Production of biodiesel from high-FFA neem oil and its performance, emission and combustion characterization in a single cylinder DICI engine. *Fuel Process. Technol.* **2012**, 97, 118-129.
11. Baitiang, T.; Suwannakit, K.; Duangmukpanao, T.; Sukjamsri, C.; Topaiboul, S.; Nuwong Chollacoop, N. Effects of biodiesel and jatropha oil on performance, black smoke and durability of single-cylinder diesel engine. *J. Met. Mater. Miner.* **2008**, 18, 181-185.
12. Lenin Haiter, A.; Thyagarajan, K. Performance evaluation of a diesel engine fueled with methyl ester of pongamia oil. *IJEE* **2012**, 3, 939-948.

13. Ribeiro, N.M.; Pinto, A.C.; Quintella, C.M.; da Rocha, G.O.; Teixeira, L.S.; Guarieiro, L.L.; do Carmo Rangel, M.; Veloso, M.C.; Rezende, M.J.; Serpa da Cruz, R.; de Oliveira, A.M. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. *Energy Fuels* **2007**, 21, 2433-2445.
14. Selvan, V.A.M.; Anand, R.B.; Udayakumar, M. Effect of cerium oxide nanoparticles and carbon nanotubes as fuel-borne additives in diesterol blends on the performance, combustion and emission characteristics of a variable compression ratio engine. *Fuel* **2014**, 13, 0160-167.
15. Vairamuthu, G.S.; Sundarapandian, C.; Kailasanathan.; Thangagiri, B. Experimental investigation on the effects of cerium oxide nanoparticle on *Calophyllum inophyllum* (Punnai) biodiesel blended with diesel fuel in DI diesel engine modified by nozzle geometry. *J. Energy Institute* **2016**, 89, 668-682.
16. Qi, D.H.; Chen, H.; Geng, L.M.; Bian, Y.Z. Effect of diethyl ether and ethanol additives on the combustion and emission characteristics of biodiesel-diesel blended fuel engine. *Renew. Energy.* **2011**, 36, 1252-1258.
17. Tse, H.; Leung, C.W.; Cheung, C.S. Investigation on the combustion characteristics and particulate emissions from a diesel engine fueled with diesel-biodiesel-ethanol blends. *Energy* **2015**, 83, 343-350.
18. Hulwan, D.B.; Satishchandra, V.J. Performance, emission and combustion characteristic of a multicylinder DI diesel engine running on diesel–ethanol–biodiesel blends of high ethanol content. *Appl. Energy* **2011**, 88, 5042-5055.
19. Qi, D.H.; Chen, H.; Geng, L.M.; Bian, Y.Z.; Ren, X.C. Performance and combustion characteristics of biodiesel–diesel–methanol blend fuelled engine. *Appl. Energy* **2010**, 87, 1679-1686.
20. Haiter, A.L.; Azhagesan, N.; Berlin Selva Rex, C.R.; Thyagarajan, K. Performance of diesel engine operating with pongamia methyl esters as biodiesel. *Asian J. Sci. Res.* **2012**, 5, 153-161.
21. Thiyagarajan, S.; Herfatmanesh, M.R.; Geo, V.E.; Peng, Z. Experimental investigation into the effect of magnetic fuel reforming on diesel combustion and emissions running on wheat germ and pine oil. *Fuel Process. Technol.* **2019**, 186, 116-124.
22. Karthickeyan, V.; Ashok, B.; Thiyagarajan, S.; Nanthagopal, K.; Edwin Geo, V.; Dhinesh, B. Comparative analysis on the influence of antioxidants role with *Pistacia khinjuk* oil biodiesel to reduce emission in diesel engine. *Heat Mass Transfer* **2020**, 56, 1275-1292.
23. Jeevanantham, A.K.; Nanthagopal, K.; Ashok, B.; Ala'a, H.; Thiyagarajan, S.; Edwin Geo, V.; Ong, H.C.; John Samuel, K. Impact of addition of two ether additives with high speed diesel-Calophyllum Inophyllum biodiesel blends on NOx reduction in CI engine. *Energy* **2019**, 185, 39-54.
24. Ravichandran, V.; Vasanthi, S.; Shalini, S.; Shah S.A.; Harish, R. Green synthesis of silver nanoparticles using *Atrocarpus altilis* leaf extract and the study of their antimicrobial and antioxidant activity. *Mater. Lett.* **2016**, 180, 264-267.
25. Yadav, G.; Sekar, M.; Kim, S.H.; Geo, V.E.; Bhatia, S.K.; Sabir, J.S.; Chi, N.T.; Brindhadevi, K.; Pugazhendhi, A. Lipid content, biomass density, fatty acid as selection markers for evaluating the suitability of four fast growing cyanobacterial strains for biodiesel production. *Bioresour. Technol.* **2021**, 325, 124654.
26. Vedagiri, P.; Martin, L.J.; Varuvel, E.G.; Subramanian, T. Experimental study on NOx reduction in a grapeseed oil biodiesel-fueled CI engine using nanoemulsions and SCR retrofitment. *Environ. Sci. Pollut. Res.* **2020**, 24, 29703-16.
27. Praveena, V.; Martin, M.; Edwin Geo, V. Experimental characterization of CI engine performance, combustion and emission parameters using various metal oxide nanoemulsion of grapeseed oil methyl ester. *J. Therm. Anal. Calorim.* **2020**, 139, 3441-3456.

28. Praveena, V.; Martin, L.J.; Edwin Geo, V.; Subramanian, T. Experimental study on NOx reduction in a grapeseed oil biodiesel-fueled CI engine using nanoemulsions and SCR retrofitment. *Environ. Sci. Pollut. Res.* **2020**, 27, 29703-29716.
29. Edwin Geo, V.; Sonthalia, A.; Subramanian, T.; Aloui, F. NOx-smoke trade-off characteristics of minor vegetable oil blends synergy with oxygenate in a commercial CI engine. *Environ. Sci. Pollut. Res.* **2018**, 25, 35715-35724.
30. Mrad, N.; Paraschiv, M.; Aloui, F.; Varuvel, E.G.; Tazerout, M.; Nasrallah, S.B. Liquid hydrocarbon fuels from fish oil industrial residues by catalytic cracking. *Int. J. Energy Res.* **2013**, 37, 1036-1043.
31. Kamraj, R.K.; Raghuvaran, J.G.T.; Panimyam, A.F.; Allasi, H.L. Performance and exhaust emission optimization of a dual fuel engine by response surface methodology. *Energies.* **2018**, 11, 3508.
32. Harish, V.; Madhavan, V. Effect of Al_2O_3 nanoparticles in biodiesel-diesel-ethanol blends at various injection strategies: Performance, combustion and emission characteristics. *Fuel.* **2016**, 186, 176-189.
33. Prabu, A. Nanoparticles as additive in biodiesel on the working characteristics of a DI diesel engine. *Ain Shams Eng. J.* **2018**, 9, 2343-2349.
34. Gopal, K.; Arindam Pal, N.; Charan Samanchi, S.; Sathyanarayanan, K.; Elango, T. Investigation of emissions and combustion characteristics of a CI engine fueled with waste cooking oil methyl ester and diesel blends. *Alex. Eng. J.* **2014**, 53, 281-287.
35. Hosseinzadeh-Bandbafha, H.; Khalife, E.; Tabatabaei, M.; Aghbashlo, M.; Khanali, M.; Mohammadi, P.; Shojaei, T.R.; Soltanian, S. Effects of aqueous carbon nanoparticles as a novel nanoadditive in water-emulsified diesel/biodiesel blends on performance and emissions parameters of a diesel engine. *Energy Convers. Manag.* **2019**, 196, 1153-66.
36. Jiang, G.; Yan, J.; Wang, G.; Dai, M.; Xu, C.; Wang, J. Effect of nanoparticles concentration on the evaporation characteristics of biodiesel. *Appl. Surf. Sci.* **2019**, 492, 150-6.
37. Ağbulut, Ü.;, Karagöz, M.; Sarıdemir, S.; Öztürk, A. Impact of various metal-oxide based nanoparticles and biodiesel blends on the combustion, performance, emission, vibration and noise characteristics of a CI engine. *Fuel.* **2020**, 270, 117521.
38. Shiva, K.; Dinesha, P.; Rosen, M.A. Effect of injection pressure on the combustion, performance and emission characteristics of a biodiesel engine with cerium oxide nanoparticle additive. *Energy.* **2019**, 185, 1163-1173.
39. Sajith, V.; Sobhan, C.B.; Peterson, G.P. Experimental investigations on the effects of cerium oxide nanoparticle fuel additives on biodiesel. *Adv. Mech. Eng.* **2010**, 2, 581407.
40. Karmakar, A.; Karmakar, S.; Mukherjee, S. Biodiesel production from neem towards feedstock diversification: Indian perspective. *Renew. Sustain. Energy Rev.* **2012**, 16, 1050-1060.
41. Kandasamy, S.; Sorna Prema, R. Methods of synthesis of nano particles and its applications. *J. Chem. Pharm. Res.* **2015**, **7**, 278-285.
42. Al-Ruqeishi, M.S.; Mohiuddin, T.; Al-Saadi, L.K. Green synthesis of iron oxide nanorods from deciduous Omani mango tree leaves for heavy oil viscosity treatment. *Arab. J. Chem.* **2019**, 12, 4084-4090.
43. Li, L.; Yang, L.; Lin, Y.; Zhang, X. A compressive review on high-and low-temperature performance of asphalt modified with nanomodifier. *Adv. Mater. Sci. Eng.* **2021**, 2021, Article ID 5525459.
44. Dutta, D.; Mukherjee, R.; Patra, M.; Banik, M.; Dasgupta, R.; Mukherjee, M.; Basu, T. Green synthesized cerium oxide nanoparticle: a prospective drug against oxidative harm. *Colloids Surfaces B: Biointerfaces* **2016**, 147, 45-53.