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Full Length Article

Synthesis of stable cerium zirconium oxide nanoparticle – Diesel suspension and investigation of its effects on diesel properties and smoke

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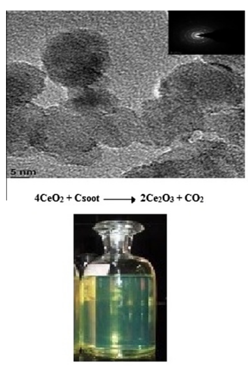
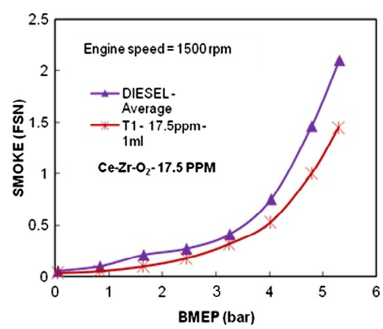
HIGHLIGHTS

- Stable cerium zirconium oxide nanoparticle added diesel for smoke reduction.
- Optimum concentration of catalytic nanoparticles for maximum stability determined based on zeta potential measurement by DLS.
- No significant change in fuel properties with nanoparticle addition.
- Reduction in smoke and improvement of efficiency.

GRAPHICAL ABSTRACT





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ABSTRACT

One of the main problems of diesel engines is the harmful smoke in exhaust and the use of fuel borne catalysts is a good option for controlling the same. Cerium zirconium mixed oxide ($Ce_xZr_{(1-x)}O_2$) nanoparticle is an excellent fuel borne catalyst. Two main issues with the addition of cerium zirconium mixed oxide nanoparticles in diesel are the lack of stability of catalytic nanoparticle in diesel suspension and the influence of these nanoparticles on various properties of diesel. The present work focuses on the synthesis of stable suspension of cerium zirconium mixed oxide nanoparticles in diesel and also on the effect of these nanoparticles on fuel properties, diesel engine performance and exhaust smoke. Cerium zirconium mixed oxide nanoparticle was synthesized by co precipitation method and characterized using Transmission electron microscope and Dynamic light scattering techniques. Catalytic activity of mixed oxide nanoparticles was compared by means of Temperature programmed reduction technique. Nanofluid was prepared by two step method, employing an ultrasonic shaker and oleic acid was used as surfactant to improve the stability of nanoparticle in diesel. The concentration of surfactant was varied from 0.01 to 0.1% by volume and the optimum value was determined by means of UV spectrum absorbance study. The dosing level of nanoparticles in diesel was varied from 2.5 to 20 ppm and the optimum concentration of catalytic nanoparticles for maximum stability was determined based on zeta potential measurement. Various properties of diesel and modified diesel were determined as per ASTM standards. Load tests were carried out on a single cylinder four stroke diesel engine to investigate the effect of catalytic nanoparticles on diesel engine performance and smoke. Performance studies shows 31% reduction in exhaust smoke and 3% enhancement in brake thermal efficiency of diesel engine for a nanoparticle concentration of 17.5 ppm.

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1. Introduction

Diesel engines have wide applications due to its inherent advantage of high thermal efficiency, as compared to petrol engines. One of the main problems associated with diesel engines is its harmful emissions such as carbon dioxide (CO_2), carbon monoxide (CO), particulate matter (PM), soot, and unburned hydrocarbons (HC). Particulate matters in the diesel engine exhaust are very dangerous as it affects the lungs and also has potential effects on heart, whereas carbon monoxide combines with the hemoglobin in blood, restricts the flow of oxygen thereby leading to premature death [2]. HC and NOx emissions in the presence of sunlight react to form photochemical smog and acid rain which causes respiratory problems and eye irritation. Particulate matter causes irritation to the eyes, nose, throat and lungs, resulting in cardiovascular illnesses and possibly premature death [2]. Increase in the global vehicle density necessitates the need for controlling these harmful emissions since the emission norms are becoming more stringent all over the world. Various methods to meet these emission norms include use of alternate fuels and fuel additives, modification of fuel systems and exhaust gas treatment systems, etc. On one side researches are focusing on the development of various types of alternative fuels, whereas on other side, modification of existing fuels with the use of fuel additives is being done. As far as alternative fuels are concerned, biodiesel is a good option to replace diesel thus reducing the consumption of diesel and also for the reduction of harmful emissions. Works has been reported on the preparation of biodiesel from numerous varieties of vegetable oils such as rapeseed, soybean, palm, sunflower and animal fats like beef tallow waste animal fat and lard.

Wide variety of technologies such as diesel oxidation catalyst (DOC), particulate matter filter (PMF), and exhaust gas recirculation (EGR) are being used for reduction of harmful emissions from diesel engines. Two way catalytic convertor used in the exhaust treatment system of diesel engines reduces hydrocarbon and carbon monoxide emissions, with the aid of heat and oxidation catalyst [3,4]. NOx emissions in diesel engines are reduced by employing exhaust gas recirculation [5,6]. Particulate matter traps are used to trap the soot particles in the exhaust gas. In two way catalytic convertor the conversion efficiency of hydrocarbon and carbon monoxide emissions depends on the surface area of the catalyst and also the time available for the catalytic reaction. Addition of catalysts/metal oxide in nanosized form in diesel is a good option for the reduction of these emissions, as the size confinement increases the catalyst surface area. Catalytic nanoparticle catalyzes the combustion reactions in the engine cylinder itself and hence the time for the catalytic reaction also increases as it continues to takes place in the exhaust pipe too.

Various works has been reported on the addition of metal oxides such as aluminum oxide [7], copper oxide, manganese oxide [8] and cerium oxide [9–12,32] in diesel. But among these, cerium oxide is an excellent catalyst because of its ability to switch between two oxidation states i.e. CeO_2 (+4) and Ce_2O_3 (+3), via a relatively low-energy reaction [1]. Cerium oxide simultaneously reduces HC, soot and NOx emissions, in the diesel engine exhaust, because of this peculiar ability of transformation. Cerium oxide has lot of applications, which includes heterogeneous catalysis in automotive exhaust gas conversion, solid oxide fuel cells (SOFC's) [13–16] and recently in biomedicine for applications in spinal cord repair and other diseases of the central nervous system [17]. Cerium (IV) oxide (CeO_2) or Ceria can be used as a fuel additive as it is stable up to 2400 °C. Various methods being adopted for the synthesis of cerium oxide based solid oxide nanoparticles includes sonochemical method [18], hydrothermal method [19], and precipitation method [20] and so on. Ceria exhibits better physical, chemical and electrical property, high thermodynamic affinity for oxygen and sulfur, good reactivity and sinterability, especially in nano sized form. Higher temperature leads to the degradation of cerium oxide in its pure form, resulting in poor oxygen storage capacity. Oxygen storage capacity of cerium oxide can be enhanced by coating or doping it with metals such as Ca, Nd, Pb, and Zr. Mixed oxides of cerium are synthesized by coating/doping of cerium oxide with copper [21], zirconium [22], titanium [23], etc. Zirconium oxide is a thermally stable ceramic material existing in nature in monoclinic crystalline structure with a melting point of 2713 °C. The addition of isovalent zirconium cations into FCC cell of ceria leads to defective fluorite structure with higher oxygen mobility [24].

Cerium oxide is a theoretically and experimentally proven redox catalyst used for the reduction of harmful emissions from diesel engines. Zhnag et al. [25] studied the impact of dosing of cerium oxide nanoparticle additive (Envirox®) in diesel, on engine performance and pollutant emissions. An improvement of fuel efficiency up to 5.6% was observed with the use of this additive. Use of Envirox also resulted in 5.6% reduction in CO_2 emissions, 10.6% in CO emissions and 24.4% reduction in particulate matters, 32% increase in ultrafine particles and 9.3% increase in NOx emissions. Sajeevan and Sajith [10] and Sajith et al. [11] reported the use of cerium oxide nanoparticle as diesel additive and reported an improvement of 5% and 1.5% in brake thermal efficiency, respectively. An average reduction of 45% in HC emission was observed, with the use of cerium oxide nanoparticles in diesel.

Two issues to be addressed with the use of metal/metal oxide nanoparticles in diesel are the influence of these fuel additives on various properties of fuel and the stability of nanoparticles suspended in fuel. Properties of fuel depend on the molecular structure of the hydrocarbons. Important properties of diesel are flash and fire point, cloud and pour point, cetane number, density, viscosity, etc. Various additives such as lubricity improvers, deformers, detergents and metal oxides like aluminum oxide, copper oxide, iron oxide, cobalt, manganese oxide, and cerium oxide are being used for the alteration of these properties. Sajith et al. and Sajeevan [10,11] reported an increase in flash point and kinematic viscosity of diesel on addition of cerium based metal oxide additives. Guru et al. [26] used Mn, Mg, Cu and Ca metals organic based metal additives and observed a reduction in the freezing point. Cetane number, viscosity and flash point of diesel were found to increase on increasing the dosing level of additives. Ying et al. [27] reported that addition of DME (dimethyl ether) in diesel results in the reduction of aromatic fractions, calorific value, and kinematic viscosity of blend fuels. However, C/H ratio, Cetane number, and oxygen content of the blends are enhanced, which is favorable for combustion. Keskin et al. [28] developed metallic-based additives doped in diesel with MnO_2 or MgO and both additives enhanced the properties of diesel such as flash point, viscosity, cloud point and pour point. Lenin et al. [8] has done experiments with Manganese oxide (MnO) and Copper oxide (CuO) nanoparticles doped diesel. Kinematic viscosity of diesel was found to be decreased by 6% and 17% and flash point was decreased by 8% and 16% respectively, on addition of MnO and CuO nanoparticles in diesel.

Stabilization of nanofluids, in other words the stability of nanoparticle dispersed in the base fluid, is one of the major issues in the practical application of nanofluids. Nanofluids are defined as engineered fluids in which particles in the size range of 1–100 nm dispersed in base fluids [29] and can be synthesized either by single step or two step method depending on application. Catalytic nanoparticle dispersed in diesel was the nanofluid used in the present work and two step method was adopted for the synthesis of diesel based nanofluid. Stability of nanofluids can be improved by steric or electrostatic stabilization. Stability of nanofluids is estimated by the measurement of zeta potential using Dynamic light

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