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Influence on the effect of zinc oxide and titanium dioxide nanoparticles as an additive with *Calophyllum inophyllum* methyl ester in a CI engine

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ABSTRACT

The present experimental work aims at investigating the effect of zinc oxide and titanium dioxide nanoparticles addition in *Calophyllum inophyllum* biodiesel in twin cylinder water cooled direct injection four stroke diesel engine. The nanofluids have been prepared from 50 ppm and 100 ppm concentrations of titanium dioxide and zinc oxide with distilled water through ulrasonication process. Four different *Calophyllum inophyllum* nano emulsions have been prepared with the proportions of 93% of *Calophyllum inophyllum* biodiesel, 5% of nanofluids of zinc oxide and titanium dioxide and 2% of span 80 using mechanical stirrer. The compression ignition engine characteristics were examined with all four *Calophyllum inophyllum* nano emulsions and the results were compared with conventional diesel and pure *Calophyllum inophyllum* biodiesel under various engine loads. The diesel engine operation with CIME nano emulsions improves brake thermal efficiency by 5–17% compared to pure CIME fuel at maximum brake power due to large surface to volume ratio of nanoparticles which exhibit rapid evaporation and better atomization. Further, the CO and HC emissions were reduced drastically for CIME nano emulsions compared to pure biodiesel and conventional diesel fuel. The NOx emission was lower than pure *Calophyllum inophyllum* biodiesel for all CIME nano emulsions but slightly higher than conventional diesel fuel. The smoke emission of diesel engine was reduced drastically for all CIME nano emulsions compared to both pure biodiesel and diesel fuels at all engine loads. Combustion characteristics of in cylinder gas pressure and heat release rate were increased by the addition of nano particles with pure *Calophyllum inophyllum* at all engine loads. Finally, it can be observed that the doping of nano particles with biodiesel has a very good effect on performance characteristics with notable improvement in performances and minimum emissions.

1. Introduction

Increasing energy demands, depletion of fossil fuels and stringent emission norms urged the scientific community to search for alternate fuels such as biodiesel for diesel engine applications which bridge the gap between demand and energy source for automotive sector [1,2]. Moreover from an economic point of view, India spends around 80,000 Cr INR annually for purchase of fuel alone. A shift towards indigenously produced biodiesel fuels helps to reduce the expenditure and this can boost up the country economy [3]. Biodiesels are readily available, bio degradable, portable, nontoxic and renewable in nature. It can be extracted from a variety of natural feedstock sources and globally around 350 crops are recognized as the possible feedstock for biodiesel production. Numerous types of seeds from the plants like pongamia, *jatropha, mahua, castor*, etc are utilized to produce biodiesel which are non-edible in nature. These non-edible oil plants are considered as second generation feedstock due to their economically cheap and easily cultivated in many parts of the world [4,5]. Transesterification is the most feasible and viable technique in which all non-edible oil can be brings down to diesel like properties. *Calophyllum inophyllum seeds* are one of the non-edible feedstock for biodiesel

Abbreviations: BTDC, before top dead center; BSFC, brake specific fuel consumption; BSEC, brake specific energy consumption; BTE, brake thermal efficiency; BMEP, brake mean effective pressure; CIME, *Calophyllum inophyllum* methyl ester; CIME-T50, 93% *Calophyllum inophyllum* methyl ester + 2% span-80+ 5% nanofluid of 50 ppm TiO_2; CIME-T100, 93% *Calophyllum inophyllum* methyl ester + 2% span-80+ 5% nanofluid of 100 ppm TiO_2; CIME-Z50, 93% *Calophyllum inophyllum* methyl ester + 2% span-80+ 5% nanofluid of 50 ppm ZnO; CIME-Z100, 93% *Calophyllum inophyllum* methyl ester + 2% span-80+ 5% nanofluid of 100 ppm ZnO; DI, direct injection; FFA, free fatty acid; BSHC, brake specific unburned hydrocarbon; BSNOx, brake specific oxides of nitrogen emission; BSCO, brake specific carbon monoxide; CIME100, 100% *Calophyllum inophyllum* methyl ester; ppm, parts per million; g/kWh, grams per kilowatt hour; EGR, exhaust gas recirculation; IT, injection timing; CA, crank angle.

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production due to its long existence potency in nature for about 50 years. It has been widely available in many places such as Asia, South Pacific and East Africa etc. [6]. Several research works have been carried on diesel engine with *Calophyllum inophyllum* biodiesel as fuel under various operating conditions.

Rahman et al. [7] have used 5%, 10% and 20% of palm biodiesel and *Calophyllum inophyllum* with diesel as diesel engine fuels under 10%, 12% and 15% loads at low engine speeds of 1000 rpm, 1200 rpm and 1500 rpm. The study revealed that the diesel engine fuelled with *Calophyllum inophyllum* biodiesel had shown higher brake thermal efficiency than that of palm biodiesel under same operating conditions. In addition, the increase in biodiesel concentration in the blends increases the NO_x emissions with lower CO and HC emissions. Ong et al. [4] have produced the *C. inophyllum* biodiesel through three steps transesterification reactions with 98.92% yield. The physical and chemical properties of esterified biodiesel could comply with ASTM D6751 and EN 14214 standards. It was pointed out that 10% of *Calophyllum inophyllum* biodiesel blend had shown 2.3% higher brake thermal efficiency and 3.06% lower specific fuel consumption compare to diesel in diesel engine at all engine speeds. Very recently Nanthagopal et al. [8] have carried out the effect of 200 bar, 220 bar and 240 bar injection pressure of 100% *Calophyllum inophyllum* biodiesel on diesel engine under various loading condition and the experimental results were compared with conventional diesel fuel. The study revealed that there was a reduction in specific fuel consumption at higher injection pressures at all engine loads. Notability, the brake thermal efficiency of 100% CIME fuel at 240 bar injection pressure was comparable to diesel fuel with significant reductions in carbon monoxide and unburned hydrocarbon and smoke emissions. However, the NO_x emissions were higher at all higher injection pressures due to higher combustion temperature. Atabani et al. [9] concluded that *Calophyllum inophyllum* could be a potential and feasible non-edible feedstock for biodiesel production in future due to their excellent physical and chemical properties and environmental friendly in nature.

Many literature reports revealed that biodiesel have poor oxidative stability and high degradability because of its autoxidation quality and its unsaturated fatty acid content. These drawbacks can be easily overcome by adding suitable antioxidants with biodiesel. Several experimental works have been conducted successfully in the past few years on the effect of various antioxidants on biodiesel degradation and stability. 2(3)-*tert*-Butyl-4-methoxyphenol(BHA), 2,6, di-*tert*-butyl-4-methyl-phenol(BHT) and 2-*tert*-butylbenzene-1, 4-diol(TBHQ) are few of the commonly used antioxidants with biodiesel. Fattah et al. [10] used BHA, BHT and TBHQ of 2000 ppm with 20% *Calophyllum inophyllum* biodiesel for its evaluation in diesel engine. It was informed that the addition of antioxidants increased the kinematic viscosity, density and flash point with significant reductions in calorific value. The brake power of the diesel engine has increased by addition of antioxidants with biodiesel. However, the NO_x emission was lower about 1.6–3.6% for all antioxidant addition with biodiesel compared to biodiesel without oxidation inhibitors. Illeri and Kocar [11] have revealed that the addition of 1000 ppm of EHN antioxidant with 20% of canola biodiesel reduced the NOx emission of 4.63% with significant hike in CO and HC emissions. The influence of antioxidant additives, N,N′-diphenyl-1,4-phenylenediamine (DPPD) and N-phenyl-1,4-phenylenediamine (NPPD) with 20% and 100% biodiesel on the reduction of oxides of nitrogen emission was investigated by Varatharajan and Cheralathan [12]. It was noted that nearly 4–10% of NO_x emission has been reduced when the diesel engine fuelled with antioxidant-biodiesel blends.

Many scientists revealed that nanoparticle addition with biodiesel and emulsified biodiesel are the best and feasible techniques for emission reductions and better performance in diesel engine applications. Several nano additives have been used with diesel and biodiesel such as Aluminium oxide (Al_2O_3), Titanium dixide (TiO_2), Cerium Oxide, Ferric chlorid (Fe_3O_3), Magnalium (Al-Mg), Cobalt oxide (CO_3 O_4) and carbon nanotube (CNT) in recent years [13]. Yang et al. [14] have introduced a novel emulsified fuel in a multi-cylinder diesel engine which contains 82.4% of conventional diesel and 5% of water along with 12.6% of nano-organic additive on volume basis. The micro-explosion phenomenon of water enhanced the combustion process which resulted in improved barke thermal efficiency compared to diesel fuel. Keskin et al. [15] developed a metallic based additives using resin acid with MnO_2 and MgO and the same has been doped into diesel fuel for diesel engine applications. Metal additives can be completely dissolved in diesel or biodiesel fuel which intern produces hydroxyl radicals and thereby lower the oxidation temperature. When these additives introduced inside the combustion chamber after the combustion process the soot oxidation could takes place and that would reduce the soot emission also [16]. Prabhu and Anand [17] have experimentally studied the effect of Alumina (Al_2O_3) and Cerium oxide (CeO_2) of 10 ppm, 30 ppm and 60 ppm concentrations on jatropha biodiesel properties and the same have been used as diesel engine fuels. Remarkable improvement in thermal efficiency and that too closer to diesel engine efficiency has been observed in this study with significant reductions in CO, HC, NO_x and smoke emissions. Mirzajanzadeh et al. [18] have formed novel synthesized formulated fuel which contains cerium oxides on carbon nanotubes of 30, 60 and 90 ppm in 5% and 20% of waste cooking oil biodiesel and the same has been used as fuels in diesel engine. The presence of 90 ppm CeO_2 in the B20 blend enhances the CO oxidation reaction and thereby reduces the NOx emission by 18.9% and soot emission by 26.3% compared to conventional diesel fuel.

The 25 ppm of alumina nanoparticle were doped into the blend which contains 70% of diesel, 20% of biodiesel and 10% of ethanol by volume and the experiments were conducted in diesel engine under various injection timings of 19° bTDC, 23° bTDC and 27° bTDC by Venu and Madhavan [19]. It has been reported that the addition of 25 ppm of alumina nanoparticle with biodiesel blend at 27° bTDC increased the incylinder gas peak pressure and heat release rate near to TDC along with significant improvement in NOx and HC emissions. However, the results are reversed when the diesel engine fuelled with alumina nanoparticle-biodiesel blend at 19° bTDC injection timing. Shaafi and Velraj [20] investigated the effect of alumina nanoparticle with diesel-soybean biodiesel blend (B20) and diesel-soybean-ethanol blend on performance, combustion characteristics of single cylinder, four stroke diesel engines under various loads. Nanoparticle was mixed with the blend along with surfactant and using an ultrasonicator for achieving stability of mixture. Results outputs indicated that alumina added reformulated fuel has shown higher peak cylinder and heat release rate compared to diesel fuel. A comparative analysis has been carried out by venu and madhavan [21] in diesel engine using 25 ppm TiO_2 (Titanium oxide), ZrO_2 (Zirconium oxide) additives with biodiesel–ethanol blend. As it was pointed out that the nanoparticle addition with biodiesel blend improves the combustion due to higher oxidation rate and thereby minimal emissions. In recent times, Annamalai et al. [22] have introduced a new reformulated fuel which contains 93% of lemon grass oil, 5% of water and 2% of surfactant (span 80) with 30 ppm of cerium oxide (CeO2) in diesel engine for performance and emission investigations and the results have been compared to conventional diesel fuel. The reformulated fuel in diesel engine decreased the HC, CO and NOx emissions by about 15.26%, 26% and 24% compared to diesel fuel. This is because of high latent heat of vaporization of water and oxidation reaction due to the presence of nanoparticle that caused significant reductions in all emissions. However, the peak