A Comprehensive Review on the Effect of Nano Metallic Additives on Fuel Properties, Engine Performance and Emission Characteristics

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Abstract- Biodiesel is one of the promising substitute source of energy fuel in the transportation sector due to rapid depletion of petroleum reserves on one side and increased energy demand as well as environmental pollution hazards on the other side. In this article, a comprehensive review is conducted highlighting the various available edible as well as non-edible vegetable feed stocks for biodiesel production, metal based additives along with the variations in physio-chemical properties, and its effect on performance and emission aspects. The influence of nano-metallic additives like Al_2O_3, CNT, CeO_3, ZnO_2, TiO_2, CoO_2, CuO, FeO_2, and others with respect to properties, performance and emission were analyzed in detail. Selective and critically archived articles are considered for this review. Based on this review, it is very clear that non-edible oil based biodiesel are one of the best source of energy. The addition of nano-metallic additives to the biodiesel through various forms significantly improves the properties and it contributes to enhanced performance with reduced emissions.

Keywords : Biodiesel, nano-metallic additives, performance, emission, properties.

1. Introduction

The climatic change affects several ecosystems on the earth namely forest ecosystem, marine ecosystem, etc and the major reason for this climate change is global warming. In the past hundred years, the rate of increase in the temperature of earth's atmosphere is drastic on comparison with previous centuries. The major reasons behind these changes are burning of fossil fuels for power generation in thermal power plants and for domestic purposes, increase in use of automobiles and their emissions. Moreover, as a non-renewable source, availability of petroleum as fuel is getting depleted day by day due to the increase in their usage for power generation and transportation. Compression ignition engines are extensively used as energy / power source in variety of applications due to its better mechanical and thermal efficiency, reduced fuel and energy consumption and excellent robustness.

It is estimated that nearly 68% of the country's fuel / oil requirement is fulfilled through import from foreign countries incurring huge foreign exchange affecting the economy. Though the industrial, agricultural and transportation segments mainly rely on petroleum diesel, in spite of its limited availability, the rise in demand is rapid along with increased depletion. Besides the requirement, consequences of its usage results in augmented emission of unburned hydrocarbon (UBHC), carbon monoxide (CO) and oxides of nitrogen (NO_x) at hazardous level causing harmful ecological effects. Exhaust emissions also causes smog and releases greenhouse gases leading to global warming to a large extent.

Some of the common methods followed for improving the performance of diesel engine are engine modification, fuel modification and exhaust gas retreatment. By making some small modifications in the injection timing, valve timing, compression ratio and providing anti wear coatings or linings for the inner parts etc the performance of diesel engine can be improved to some extent. But, engine modifications is not the easy option in all cases, and it also increases the cost of the engine. Fuel modification is carried out by adding catalysts or additives with the base fuel to optimize its physio-chemical properties. The fuel additives are mixed thoroughly with diesel fuel for improving both performance and emission. By using turbocharger or supercharger, the performance of diesel engine can be increased to a great extent which does not require any additional power supply. Techniques like exhaust gas recirculation, catalytic converters and particulate filters etc., are used to treat and control the harmful exhaust gas emissions from diesel engine.

2. Biodiesel and Importance of Additives

Biofuel is one of the best substitute for petroleum diesel fuel. Biodiesel, a mono-alkyl esters of long chain fatty acids which are non-toxic in nature, non-explosive, less flammable and more importantly it is biodegradability. Biodiesel is produced from various available natural sources namely Palm, Jatropha, Pongamia, Grape seed, Mahua, Castor, Cotton seed, Tobacco seed, Rubber seed, Rice bran, Neem, Coconut, Sunflower oil, etc. Neat oil produced from these natural sources are chemically processed by "trans-esterification", in which the alcohol is added to the neat oil under mild condition in presence of a base catalyst. During esterification process, the triglycerides present in the oil gets transformed into alkyl esters and glycerol. The trans-esterification process is carried out in the temperature range of around 50ºC to 80ºC with the addition of methanol or ethanol. The base catalyst commonly used are sodium hydroxide (NaOH) and potassium hydroxide (KOH). The methods used for biodiesel production are ultrasonic reactor method, supercritical process, lipase-catalyzed method and batch reactor method. Generally, the vegetable oil feedstock for biodiesel are categorized into two, namely edible and non-edible sources. Some of the prominent edible and non-edible feedstock available in India are discussed here.

a. Edible feed stocks

Corn belongs to the family of Poaceae with Zea mays as species name. Corn oil is extracted from the germinated maize. It is usually seen in tropical climates having a slow and sluggish growth upto a height of 6 meters. With an oil content of around 40%, solvent extraction process using n-hexane or 2-methyl pentane extracts 85% of corn germ oil from its kernels. Soybean belongs to the family of Fabaceae with annuals as species. Soy is a leguminous and bushy plant producing beans for food and oil industry. It has of 18% to 20% of lipid and oil, 40% of protein along with minimal quantity of cellulose, glucose, ash and fiber. Percolation extraction technique in the presence of n-hexane is used to extract oil from Soybean. Brassica napus (Canola) is capable of producing 75 to 240 gallons of oil in every hectare of cultivation. With an oil content between 35% and 42%, solvent extraction method is widely adopted to extract oil. Arachis hypogaea (Peanut also known as ground nut or goober) is widely grown in tropical and sub-tropical regions with a higher yield in light, sandy loan soil with pH between 5.9 to 7 and soil temperature of 20ºC to 35ºC. The oil content is estimated to be between 45% and 52% of which nearly 50% is extracted by prepressing and the remaining oil is extracted through solvent extraction method. Chamaerops humilis (Palm), a feedstock to extract edible oil from the mesocarp of the fruit, is usually seen in warm and tropical climates. The oil content is estimated to be between 48% and 52% along with high level of beta-carotene. The oil extraction is based on screw pressing technique. Cocos nucifera (Coconut) belonging to the family of Arecaceae is widely grown in the coastal regions with hot and humid climatic conditions. The oil is extracted from the dried kernel (copra) of the coconut. The oil content is found to be between 65% and 72% and it is extracted by employing rotary chucks and oil expellers. Proanthoctandins, an extract from grape seed of Vitis vinifera (Grape) is rich in poly unsaturated fat of about 69.6%. Oryza sativa, a type of Asian rice widely found in asian countries including India is rich in carbohydrates. The oil extracted from the outer hard layer of rice husk is called rice bran oil. It mainly contains oleic acid which is used for edible purpose. Solvent extraction method is adopted to extract oil from the rice bran. Helianthus annus (Sunflower) belonging to the family of Asteraceae is a native of North America and presently widely cultivated as ornamental plant as well as food crop. The kernels of sunflower contains 44% to 50% of oil rich in oleic acid. Compression technique is used to extract oil from seeds of sunflower.

b. Non-Edible feed stocks

Madhuca indica (Mahua), an origin of central and north India, belongs to the family of Sapotaceae. It is one of the most important tree species of Central India producing huge quantity of oleaginous seeds. The oil content of the seed is estimated around 33% to 43%. Rizinus communis (Castor) belonging to the family of Euphorbiaceae is a non-edible, high oil yielding crop mainly found in tropical regions. The castor bean is estimated to contain 40% to 50% of oil which is extracted through high pressure continuous screw press technique with n-heptane as solvent. Millettia pinnata (Pongamia) of Fabaceae family is a semi deciduous, drought resistant, mid-sized tree found mainly in tropical and sub-tropical Asia. It is capable of growing in wide range of soil and climatic conditions. It contains 30% to 40% of oil which is extracted through expeller and cold pressing, and solvent extraction method. Jatropha curcas (Jatropha) belonging to the family of Euphorbiaceae is a tropical and drought resistant plant producing seeds with oil content around 37% to 40%. Recently, Temasek life science lab and JOil Pte ltd, Singapore developed strains of Jatropha curcas with 75% of oleic acid thereby making it as a more suitable biofuel. The oil is extracted by using mechanical press expeller as an oil extraction technique.

Fig. 1. Various edible and non-edible biodiesel feed stock

Fig. 2. Metal and metal-oxide nano additives as a performance enhancer

Azadirachta indica (Neem) of Meliaceae family, originated from India is found in all agro-climatic zone with soil pH value of 10 except in cold regions. Mechanical pressing, steam pressing and solvent extraction techniques are used to extract 30% to 50% of oil from the seeds of neem. Simmondsia chinensis (Jojoba) belonging to the family of Simmondsiaceae is a species capable of growing in arid, semi-arid with minimal water and extreme conditions but not suitable for soil prone to flooding and heavy water logging. The seed contains nearly 50% oil which is extracted using mechanical pressing followed by leaching and solvent extraction method. Nicotiana (Tobacco) belonging to Solanaceae family is a non-edible, green leafy plant grown in warm climates with its seed containing oil between 17% and 26%. Oil from the tobacco seed is extracted through solvent extraction and steam distillation methods. Hevea brasiliensis (Rubber tree) belonging to the family and sub-family of Euphorbiaceae and Crotonoideae have their nativity to African and Brazilian countries. Presently it is widely cultivated in Southern Peninsular India. The rubber seed oil mainly contains linoleic and oleic acid which are extracted through mechanical expeller followed by soxhletation process. The various edible and non-edible biodiesel feedstock are shown in Figure 1.

c. Fuel additives and its importance

Additives are organic based or metal based substances which are easily soluble in fuel and its main purpose is to improve, maintain and provide beneficial characteristics to the fuel without affecting the performance and combustion parameters. The fuel additives are added in smaller quantities ranging between 100 ppm to several thousand ppm. The fuel additives are broadly classified as refinery products, distribution system products, and automotive performance enhancement products. They are again subdivided into following categories namely antioxidants, cetane improvers, anti-knocking agents, anti-freezing agents, stability improvers, additives to prevent corrosion, cold flow improvers, fuel borne catalysts, anti-wear agents, etc.

Antioxidants

Biodiesels are fatty acid methyl esters produced by trans-esterification process which are ready to react with oxygen by the process called auto-oxidation. To avoid auto-oxidation of biodiesel in the diesel blend, additives like BHT (Butylated hydroxytoluene), TBHQ (Tert-butyl hydroquinone), BHA (Butylated hydroxyanisole), PG (Propyl gallate), and PA (Pyrogallol) are mixed with diesel-biodiesel blends.

Oxygenated additives

To improve the burning characteristics of fuel with more ignition delay, chemical compounds having more oxygen content are added to that fuel at a trivial quantity. Oxygenated components like ethanol, methanol, biodiesel, dimethyl ether, dimethyl carbonate, di-ethylene glycol diethyl ether, sorbitan monooleate etc., which easily mixes and blends with diesel are used as additive.

Additives to improve cold flow behavior

During cold conditions, the wax content present in the biodiesel begins to freeze and results in crystal like structure which affects the cold filter plug point (CFPP). This situation may be avoided by using additives like ethylene vinyl acetate copolymer, glycerol ketals, glycerol acetates, phthalimide and succinimide copolymers which improves the cloud point property of the fuel.

Additives to improve Cetane number

Cetane number is one of the major factor which determine the fuel quality by representing the ignition capability of the fuel. Fuels with high Cetane number provide better performance with respect to compression ignition engine. Nitrates, nitro alkanes, nitro carbonates, peroxides, etc., are used as additives which improves the Cetane number of the fuel.

Metal based additives

The burning characteristics of the fuel can also be improved by the addition of metals and metal oxides to the fuel in the range of micro or nano sizes through ppm or percentage by weight ratios. Metals like iron (Fe), aluminum (Al), magnesium (Mg), manganese (Mn), silver (Ag), gold (Au), copper (Cu), boron (B), graphene, silica (Si), etc. and metal oxides like aluminum oxide (Al_2O_3), cobalt oxide (Co_3O_4), cerium oxide (CeO_2), titanium oxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO) etc., are used as additives to improve the fuel physio-chemical properties.

Alloys of metals like magnalium (Mg-Al), Carbon nano tubes (CNT) are also used as metal based additive which improves the performance of fuels by changing its physio-chemical properties. Figure 2 shows some of the metals and metal oxides nano additives used as performance enhancers. After several studies, researchers have found that the modification of fuel with respect to its physio-chemical properties yields better results in enhancing the engine performance and controlling the exhaust emissions rather than carrying out engine modifications. With reduced exhaust emissions, ignition delay, cold flow characteristics etc along with comparable performance characteristics, using biodiesel as fuel is found to be favorable. A few literature also reported about the reduction in life span using biodiesel as fuel which can be overcome with the use of fuel additives. In this present review paper, the main focus is to comprehend the knowledge and information related to fuel modification by addition of metal and metal oxide nano additives to improve the performance and reduce the emissions of the diesel engine. The authors have attempted a comprehensive review in listing out various biodiesel, biodiesel with nano-metal based additives and its effect on the engine performance and emission control aspects in a detailed manner. This paper also reports the outcome of several studies carried out by various researchers on the impact of nano-fuel additives on fuel properties, its effect on performance and exhaust emissions at different operating conditions. This review paper on nano-fuel additives for CI engine gives a comprehensive information which would help the students, research scholars, engineers and people working in IC engines.

3. Effect of Nano Metallic Additive on Fuel's Physio-chemical Properties

Attia et al. [1] investigated the effect of B20-Jojoba methyl ester with addition of aluminium oxide nano particle on properties of fuel, performance and emission characteristics of the diesel engine. The result showed that there was a considerable change in fuel properties. It was also noticed that the addition of Al_2O_3 reduced the kinematic viscosity of the fuel along with an increase in density and Cetane number. Prabhu Arockiasamy et al. [2] mentioned that the addition of 30 ppm Al_2O_3 and CeO_2 with Jatropha methyl ester improved the kinematic viscosity, density and calorific value as 4.25 Cst, 875 kg/m^3 and 38.9 MJ/kg for JBD30A blend. JBD30C blend was found to have similar fuel property values as 4.30 Cst, 876 kg/m^3 and 38.7 MJ/kg respectively. The addition of alumina with Jatropha biodiesel improved the fuel properties. Syed Aalam and Saravanan [3] also obtained similar improved fuel properties for B20-Mahua biodiesel by adding aluminum nanoparticles.

Syed Aalam et al. [4] evidently exhibited the enhancement in ZJME25 fuel properties with the addition of alumina nanoparticles. AONP50 gave better results with ZJME25 than AONP25 blend with increased flash point and Cetane number. Shaafi and Velraj [5] used alumina, ethanol and isopropanol as fuel additive for B20-Soybean biodiesel. They mixed 100 mg/l of AONP in D80SBD15E4S1 blend, and noticed a drastic decrease in viscosity and calorific value along with an increase in Cetane number. Anbarasu et al. [6] and Bharathiraja et al. [7] studied the effect of blending

AONP with Canola methyl ester emulsion and straight diesel, and noticed a significant increase in flash point, density along with a significant decrease in viscosity.

Sadhik Basha and Anand [8] compared the fuel properties of JME with and without the presence of AONP and CNT. The result indicated that the addition of CNT with JBD yielded better results with enhanced fuel properties. The flash point of CNT blended Jatropha biodiesel was lowest when compared with neat JBD and AONP blended JBD. Balaji and Cheralathan [9], and Narinder Singh and Bharj [10] mentioned that the addition of CNT with biodiesel resulted in increased flash point, viscosity, calorific value and Cetane number. The values were found to be increasing with increase in amount of CNT concentration. Prajwal Tewari et al. [11] discussed about the change in properties of HOME with the addition of CNT. The author concluded that HOME+50 ppm CNT showed better results than HOME+25 ppm CNT.

Sadhik Basha and Anand [12] studied the CNT blended JME water emulsion and found that flash point for 100 CNT blend was 122^0C, which was lowest among all the blends. With the increase in CNT concentration, viscosity, density, calorific value and Cetane number also showed an increased trend. Karthikeyan et al. [13] mentioned that the addition of ZnO with B20-Grape seed oil methyl ester increased the flash point, fire point, density and viscosity. Rao and Srinivas Rao [14] and Karthikeyan et al. [15] showed that the addition of ZnO and CeO_2 nanoparticles with straight diesel and B20-Pomoline stearin wax biodiesel resulted in increase of calorific value and decrease in flash/fire point. Yanan Gan et al. [17] investigated the burning characteristics of various nanoparticles at dilute and dense concentrations. Iron nanoparticle spherical in shape of size 15 to 80 nm (coated with thin layer of carbon between 2 to 6 nm) and boron nanoparticle non-spherical in shape of size 80 nm were studied.

Kannan et al. [18] highlighted about the addition of FBC ($FeCl_3$) in waste cooking palm oil biodiesel which decreased the flash point, fire point and density values whereas the kinematic viscosity, calorific value and Cetane number showed a significant increase. Nagaraj Banapurmath et al. [19], found that the addition of AgNP with HOME decreased the flash point value whereas, it increased the viscosity, density and calorific values. HOME+50 ppm of Ag showed good results compared to properties of HOME. Bhagwat et al. [21] found that the addition of graphene NP improved the properties of HOME. Among all the blends, HOME+50 ppm graphene showed an enhanced properties. Mohd. Suhail Ansari et al. [22] elaborated the recent trends in nano fluids, its preparation and its applications. Nano fluid synthesis were classified into two types as one stop process and two-step process. Abbas Alli Taghipoor Bafghi et al. [23] studied the performance and emission characteristics of a single cylinder four stroke air cooled diesel engine fuelled with nano ceria added diesel-biodiesel extracted from waste fried oil. CeO_2 of size 10 to 30nm were mixed with diesel-biodiesel blends in the range of 5 ppm to 25 ppm.

Sunil Kumar Sharma et al. [24] discussed about the addition of CeO_2 and CNT in JME+TPO blend and found that CeO_2 addition decreased the viscosity and density whereas, the same was increased with CNT addition. Sinem Caynak et al. [25] found that the addition of Mn (12µmol/L) in B25 of pomace oil reduced the viscosity by upto 20.37% and flash point by upto 7%. The pour point got reduced from 0^0C to -15^0C. Table.1 shows the comparison of physio-chemical properties of diesel, bio-diesel and fuel blended with nano metallic additives.

Studies by Demirba et al. [26] and Jayed et al. [27] also showed the importance of adding nano metal additives in biodiesel and its effect in improving the physio-chemical properties of the nano metal blended biodiesel.

a. Discussion on change in physio-chemical properties upon addition of nano metal additives

Addition of CuO and Al_2O_3 nanoparticles with neat diesel increased the flash point and Cetane number whereas, ZnO and CeO_2 reduced the values of flash point [7, 14, 30]. Addition of nanoparticles to the emulsified fuel increased the values of viscosity, density, calorific value and Cetane number [10, 12, 21]. Addition of CeO_2, Al_2O_3, CNT, Al, Ag and graphene nanoparticles with neat biodiesel reduced the flash point values whereas the same increased the viscosity and density values [2, 8, 18, 19, 20, and 21]. Calorific value of neat biodiesel increased with addition of FBC, CNT, graphene and Al nanoparticles [9, 18, and 19]. Addition of ZnO nanoparticles increased the flash point, viscosity, density and calorific value of the fuel. Mn, Mg, aluminum nanoparticles in diesel-biodiesel blends reduced the flash point values [3, 28, and 29].

The reason for adding metal based nano additives to the diesel / biodiesel is to enhance the performance of the engine by improving the properties of fuel. The addition of nanoparticles with diesel / biodiesel blends increased the calorific value and Cetane number of the fuel. In some cases, it also reduced the sulfur content present in the fuel [30]. Addition of CuO and Al_2O_3 with neat diesel reduced the sulfur content [30]. Aluminum nanoparticle with mahua methyl ester reduced the flash point and increased the calorific value and Cetane number [3]. Addition of ZnO with biofuel blends increased the flash and fire point, calorific value and Cetane number [13, 41]. Addition of fuel borne catalysts also reduced the flash and fire point of the fuel [2, 3, 8, 11, 12]. ZnO with neat diesel reduced the flash and fire point values [14]. The calorific value increased with addition of ZnO in all the cases. Addition of CNT with emulsified fuels improved the properties of fuels whereas, Al_2O_3 with emulsified fuels increased the flash and fire point and decreased the calorific value [6, 10, 12]. Graphene nanoparticles gave better fuel improvements in HOME compared to silver nanoparticles [20, 21].

Table 1. Comparison of physio-chemical properties of diesel, biodiesel and nano metal additive blended fuel

S.No	Fuel	Composition of Additives	Flash Point (^0C)	Fire Point (^0C)	Kinematic Viscosity (@ 40^0C cst)	Density (Kg/m^3)	Calorific Value (MJ/kg)	Cetane number	Ref.
1	Neat Diesel		48	-	2.20	835	42.30	-	2
2	Neat Biodiesel		85	-	4.10	873	39.50	-	
3	JBD30A	30ppm Al_2O_3	78	-	4.25	875	38.90	-	
4	JBD30C	30ppm CeO_2	76	-	4.30	876	38.70	-	
5	Diesel		56	-	3	815	42	47	3
6	Mahua Methyl Ester(MME)		136	-	4.90	869	39.95	56	
7	MME20		76	-	3.40	826	41.62	49	
8	MME20+ANP50	50 ppm	71	-	3.37	827.5	41.66	49.5	
9	MME20+ANP100	100ppm	65	-	3.33	829	41.69	51	
10	Diesel		50	-	2.54	833	-	52	4
11	ZJME25		56	-	3.56	846	-	56	
12	ZJME25+25AONP	25ppm	57	-	3.39	849	-	57	
13	ZJME25+50AONP	50ppm	58	-	3.17	853	-	58	
14	Diesel		-	-	2.61	-	44.70	57	5
15	Soybean biodiesel		-	-	4.78	-	41.20	49	
16	D80SBD20		-	-	3.70	-	43	42	
17	D80SBD15E4S1+ Al_2O_3	100mg/l	-	-	3.37	-	42.59	52	
18	Diesel		55	-	3.20	896	-	-	7
19	Diesel+ Al_2O_3	25ppm	57	-	3.05	895	-	-	
20	Diesel+ Al_2O_3	50ppm	59.5	-	2.98	896	-	-	
21	Diesel+ Al_2O_3	75ppm	62	-	2.80	896	-	-	
22	JBD	-	85	-	5.25	895	38.88	53	8
23	JBD25A	25ppm	84	-	5.31	896	39.22	54	
24	JBD50A	50ppm	82	-	5.35	897	39.53	56	
25	JBD25CNT	25ppm	83	-	5.29	895.5	39.50	55	
26	JBD50CNT	50ppm	81	-	5.33	897.9	39.78	57	
27	JBD25A25CNT	50ppm	81	-	5.36	895.2	39.99	57	
28	Diesel	-	75	-	2.30	839.5	44.50	51	9
29	MENO	-	180	-	4.27	890	40.67	53	
30	MENO+100 CNT	-	181	-	4.28	889	40.92	53	
31	MENO+200 CNT	-	181	-	4.28	889	40.92	54	
32	MENO+300 CNT	-	182	-	4.29	888	40.92	54	
33	MENO+400 CNT	-	182	-	4.29	888	40.93	55	
34	Diesel	-	56	-	2-3	-	43	-	11
35	Honge oil methyl ester	-	170	-	5.60	-	36.02	-	
36	HOME25CNT	-	166	-	5.70	-	34.56	-	
37	HOME50CNT	-	164	-	5.80	-	35.10	-	
38	JME	-	85	-	5.05	895	38.88	53	12
39	JME2S5W	-	140	-	5.40	899.8	37.05	51	
40	JME2S5W25CNT	-	130	-	5.43	897.2	37.28	54	
41	JME2S5W50CNT	-	125	-	5.76	897.8	37.35	55	
42	JME2S5W100CNT	-	122	-	5.91	899.4	37.85	56	
43	B20 (Grape seed oil biodiesel)	-	38	45	5.55	841	37.02	-	13
44	B20ZnO50	-	40.3	47	5.82	842	38.12	-	
45	B20ZnO100	-	42.1	50	5.88	844	38.75	-	
46	Diesel	-	52	54	-	-	42.85	-	14
47	Diesel+250ZnO	-	45	48	-	-	42.91	-	
48	Diesel+500ZnO	-	43	45	-	-	42.96	-	
49	Diesel+40CeO_2	-	48	50	-	-	42.892	-	
50	Diesel+80CeO_2	-	46	49	-	-	42.948	-	

S.No	Fuel	Composition of Additives	Flash Point (^{0}C)	Fire Point (^{0}C)	Kinematic Viscosity (@ 40^{0}C cst)	Density (Kg/m^3)	Calorific Value (MJ/kg)	Cetane number	Ref.
51	B20 (Pomoline stearin wax biodiesel)	-	46	-	3.10	834	44.07	57	15
52	B20ZnO50	-	47	-	3.10	833	44.33	58	
53	B20ZnO100	-	47	-	3.10	832	44.30	58	
54	HOME	-	187	-	5.60	875	36.10	40	19
55	HOME25Ag	-	160	-	5.80	895	35	-	
56	HOME50Ag	-	158	-	5.80	900	35.50	-	
57	HOME	-	170	-	5.60	880	36.02	-	20
58	HOME50Graphene	-	158	-	5.80	900	35.50	-	
59	HOME50MWCNT	-	164	-	5.80	900	35.10	-	
60	HOME50Ag	-	168	-	5.90	905	34.95	-	
61	JME90TPO10	-	-	-	6.38	868.7	-	-	24
62	JME90TPO10$CeO_2$100	-	-	-	6.39	868.3	-	-	
63	JME90TPO10CNT100	-	-	-	5.24	872.6	-	-	
64	JME80TPO20	-	-	-	6.36	874.1	-	-	
65	JME80TPO20$CeO_2$100	-	-	-	6.40	873.5	-	-	
66	JME80TPO20CNT100	-	-	-	5.35	878.1	-	-	
67	JME70TPO30	-	-	-	6.47	880.4	-	-	
68	JME70TPO30$CeO_2$100	-	-	-	6.38	880.3	-	-	
69	JME70TPO30CNT100	-	-	-	5.29	881.8	-	-	
70	Diesel		73	-	2.60	835	43.76	47	25
71	B25 (Pomace oil)	Mn-12μmol/L	76	-	2.90	828	43.54	49	
72	B60 (Tall oil)		88	-	5.30	-	-	-	28
73	B60-8Mn	8and 12 μmol/L	81	-	4.80	-	-	-	
74	B60-12Mn		80.5	-	4.30	-	-	-	
75	B60-8Ni		85	-	4.90	-	-	-	
76	B60-12Ni		79	-	4.80	-	-	-	
77	Diesel		60	-	3.60	833.5	-	53.8	30
78	Nanodiesel-1	50ppm CuO	66	-	3.50	834.1	-	54.5	
79	Nanodiesel-2	50ppm Al_2O_3	68	-	3.50	834.3	-	54.4	

4. Effect of Nano Metallic Additive on Engine Performance and Emission Parameters

Attia et al. [1] investigated the performance, combustion and emissions characteristics of B20-Jojoba methyl ester and diesel blends with addition of alumina nanoparticles (20 to 50 nm) in the range of 10 mg/L to 50 mg/L. There was a reduction in BSFC by upto 6% when compared with neat diesel and thermal efficiency increased by 7%. NO_x reduced upto 70%, CO reduced upto 75%, UBHC reduced upto 55% and smoke opacity reduced by 5% when compared to B20 blend. Soner Gumus et al. [30] studied the performance and combustion behavior of alumina nanoparticle (27 to 43 nm in size) added with diesel. The test was carried out at full load conditions with throttle valve fully opened and the compression ratio was 20.3:1. Auto ignition temperature increased with the addition of nanoparticle. AIT of CuO blend was higher than the Al_2O_3 blend. Power and torque increased by 1% with 50 ppm addition of nanoparticles for CuO blend and 3.28% for Al_2O_3 blend. BSFC reduced with the addition of nanoparticles and Al_2O_3 blend showed more reduction by upto 1.2%. Mu-Jung Kao et al. [31] analyzed the combustion characteristics of aquas nano alumina blended diesel. Aluminium nanoparticles size in the range of 40 to 60 nm were mixed with water using ultrasonicator to form aquas nano fluid (emulsion). The addition of aquas nano alumina increased the total combustion heat and it reduced the smoke in the exhaust of diesel engine at all the load conditions. However, NO_x emission increased with the addition of nano fluid to the diesel. The BSFC at initial and no load conditions were less for nano fluid diesel and it increased as the load increased.

Senthilraja et al. [32] discussed in detail about the enhancement in thermal characteristics of fuel added with nanoparticles. Al_2O_3 nanoparticles with an average size of 10 nm in addition with water 0.5% by volume ratio gave 100 percent enhancement in thermal conductivity. Yanan Gan and Li Qiao [33] explored the combustion characteristics of n-decane and ethanol with addition of aluminum nanoparticles of various sizes. Aluminum nanoparticles with the size of 80 nm, 5 μm and 25 μm were used in this study. Test was carried out in droplet combustion experiment chamber. Combustion characteristics of all the fuels were compared using spectral images of combustion through various stages with respect to time for each fuel inside the chamber. Ethanol-nano Al showed better combustion characteristics than other fuels.

Prabhu Arockiasamy et al. [2] discussed the combustion and emission characteristics of Jatropha biodiesel with addition of alumina and CeO_2 nanoparticles as additives. Nano particles were added to the biodiesel using ultrasonicator. Both blends were stable without any phase separation upto 48 hrs. BTE increased upto 5% for both the samples. JBD30A showed 9% reduction in NO_x, 33% reduction in UBHC, 20% reduction in CO and 17% reduction in smoke opacity than neat biodiesel. JBD30C showed 7% reduction in NO_x, 28% reduction in UBHC, 20% reduction in CO and 20% reduction in smoke opacity than neat biodiesel. Naresh Kumar, Gurusala and Arul Mozhi Selvan [34] studied the combustion and emission characteristics of nano alumina blended waste chicken fat biodiesel at various blend ratios. The combustion and emission values were compared with values of neat diesel. BSFC was higher for waste chicken oil biodiesel. Addition of nanoparticles to it reduced the BSFC. BTE and peak cylinder pressure values increased with addition of nanoparticles. CO and HC emissions reduced whereas, NO_x emission increased with nanoparticle addition. Smoke reduced by upto 65% for nanoparticle added waste chicken oil biodiesel than waste chicken biodiesel.

Aalam and Saravanan [3] investigated the effect of addition of alumina nanoparticle with mahua biodiesel. Mahua methyl ester was used as the base fuel. Nano particle dosage levels were 50 ppm and 100 ppm. MME with 100 ppm alumina nanoparticle blend showed a slight improvement in engine performance and reduction in emission. Cylinder pressure and heat release rate increased with addition of nanoparticles. BSFC decreased upto 7.66 % for B20ANP100 than B20 blend. BTE increased than diesel for all B20 nano blends. HC and CO emissions were reduced than diesel whereas, NO_x emission increased for all B20 blends than neat diesel. Mathew Jones et al. [35] also investigated the effect of Al nano particle with ethanol fuel and found similar results. Syed Aalam et al. [4] discussed the performance and emission characteristics of diesel engine fuelled with Zizupus jujube biodiesel-diesel blended with alumina nanoparticles. Addition of nanoparticle reduced BSFC compared to ZJME25. BTE increased upto 2.5 % for 50 ppm nano blended fuel. Smoke increased with increase in amount of nanoparticles. ANOP25 showed less NO_x emission than others. CO emission also reduced with addition of nanoparticles.

Shaffi and Velraj [5] analyzed the influence of nanoparticle additives with diesel-soybean biodiesel blend in the diesel engine. Alumina nanoparticles along with ethanol and isopropanol (surfactant) were mixed with diesel-biodiesel blend. The amount of NO_x was same upto 50% load for diesel and nano blended fuel and beyond that it increased than neat diesel. UBHC was very high by 25% than neat diesel and B20, and it was increasing uniformly as the load was increased.

Anbarasu et al. [6] studied the effect of alumina nanoparticle added to canola biodiesel emulsion fuel. Blend consisting of canola biodiesel, water and surfactant was used in this study. CO decreased with AONP addition compared to biodiesel and emulsion fuel. Similarly, HC, smoke, NO_x also decreased with AONP addition compared to biodiesel and emulsion fuel. Syed Aalam and Saravanan [36] also investigated the performance and emission characteristics of a diesel engine fuelled with nanoparticles added to mahua methyl ester-diesel blend. Nishant Mohan et al. [37] explored the performance and emission characteristics of a single cylinder four stroke DI diesel engine fuelled with nano aluminum added diesel. Nano aluminum in the range of 5 to 150 nm was used in this study. The peak cylinder pressure got decreased to 55 bar whereas, it was 62 bar for diesel. BSFC decreased by 7% for nano blended fuel. Further, BTE increased by 9%, CO decreased by about 25% to 40%, HC decreased by 8% and NO_x increased by 3% to 5% for nano added fuel.

Barathiraja et al. [7] studied the performance and emission characteristics of a single cylinder four stroke water cooled diesel engine fuelled with nano alumina added diesel. Nano particle dosage level in diesel were 25 ppm, 50 ppm and 75 ppm. BTE at maximum load was 39.6% whereas, BSFC was higher for all nano fluids compared to plain diesel. Smoke emission was reduced for all nano fluids compared to diesel. CO emission was more for nano diesel and it increased with increase of load. HC emission was also higher than diesel. Sadhik Basha and Anand [8] discussed about the performance and emission characteristics of alumina (average size of 51 nm) and CNT added jatropha biodiesel (JBD). Nano particles were mixed with JBD in various proportions using ultrasonicator. NO_x emissions for JBD, JBD50A, JBD50CNT and JBD25A25CNT were 1282 ppm, 1015 ppm, 1001 ppm and 985 ppm respectively. HC emission for JBD, JBD50A, JBD50CNT and JBD25A25CNT were 60 ppm, 52 ppm, 49 ppm and 46 ppm respectively. The cylinder peak pressure for JBD, JBD50A, JBD50CNT and JBD25A25CNT were 72.3, 69.5, 69 and 68.5 bar respectively. Ramesh Babu and Bharathi Raja [38] also analyzed the performance and emission characteristics of diesel engine fuelled with AONP and found that nano blended fuel increased the BTE.

Balaji and Cheralathan [9] investigated the performance and emission characteristics of diesel engine fuelled with CNT added NOME. The emission and performance curves were compared with NOME and neat diesel. BTE for CNT added NOME increased upto 2.12% for CNT100, by 4.17% for CNT200 and 3.43% for CNT300. NO_x increased with increase in load. But, addition of CNT decreased the NO_x emission by 2.88% for CNT100, by 7.25% for CNT200 and 4.67% for CNT300. The CO emission was decreased by 8.56% for CNT100, by 16.16% for CNT200 and 11.77% for CNT300. HC emission also decreased by 3.67% for CNT100, 10.39% for CNT200 and 8.15% for CNT300. Narinder Singh and Bharj [10] discussed the combustion and emission characteristics of diesel engine fuelled with CNT added diesel water emulsion. Ultrasonicator and mechanical homogenizer was used for preparing the blends. Blends were prepared by adding 50 ppm, 100 ppm and 150 ppm of nanoparticles. The pressure inside the cylinder and heat release rate for D15W2S was higher than diesel. The BSFC decreased for D15W2S and its maximum decreased upto 0.27 kg/kwhr for D15W2S150N and D15W2S100N. The BTE emissions for diesel, D15W2S, D15W2S50N, D15W2S100N and D15W2S150N were 28.2%, 28.6%, 28.9%, 30% and 30.5% respectively. NO_x emission for D15W2S, D15W2S50N, D15W2S100N and D15W2S150N were 302 ppm, 255 ppm, 224 ppm and 221 ppm respectively. HC emission for D15W2S and D15W2S150N were 45 ppm and 37 ppm respectively. CO emission decreased as concentration of CNT additives increased in the emulsion.

Prajwal Tewari et al. [11] analyzed the combustion and emission characteristics of 1S 4 stroke DI CI engine fuelled with CNT added honge oil methyl ester (HOME). The percentage of BTE for diesel, HOME, HOME25CNT and HOME50CNT were 28%, 23%, 24% and 25% respectively. Smoke opacity at 80% load for diesel, HOME, HOME25CNT and HOME50CNT were 52%, 78%, 63% and 59% respectively. The percentage of CO emission at 80% load for diesel, HOME, HOME25CNT and HOME50CNT were 0.1%, 0.45%, 0.3%, and 0.21% respectively. The NO_x emission at 80% load for diesel, HOME, HOME25CNT and HOME50CNT was 800 ppm, 580 ppm, 600 ppm and 750 ppm respectively whereas, HC emissions at 80% load was 32 ppm, 82 ppm, 70 ppm and 58 ppm respectively. Sadhik Basha and Anand [12] also experimentally investigated the combustion, performance and emission characteristics of diesel engine fuelled with CNT added jatropha methyl ester emulsion. Mehrdad Mirzajanzadeh et al. [39] discussed the combustion and emission properties of six cylinder engine fuelled with CNT added waste cooking oil biodiesel-diesel blend. The emission and performance values of catalyst added blends were compared with B5 and B20 blends. The addition of catalyst reduced the emissions for both B5 and B20 blends. B20 with 90 ppm catalyst reduced NO_x, CO, UBHC and soot particle emissions by 18.9%, 38.8%, 71.4% and 26.3% respectively.

Selvaganapathy et al. [40] investigated the performance and emission properties of a 1S 4 stroke CI engine fuelled with zinc oxide added diesel. BTE, heat release rate and cylinder peak pressure values were increased with the addition of ZnO NP. NO_x and smoke emissions were increased with the addition of ZnO NP at all load conditions. Karthikeyan et al. [13] also reported similar performance and emission characteristics for CI engine fuelled with zinc oxide added grape seed oil methyl ester-diesel blend.

Rao and Srinivas Rao [14] studied the performance and emission characteristics of single cylinder four stroke water cooled CI engine fuelled with ZnO_2 and CeO_2 added diesel. CeO_2 was mixed with diesel in the proportions of 40 ppm and 80 ppm whereas, ZnO_2 nanoparticles were mixed with diesel in 250 ppm and 500 ppm range by using ultrasonicator kept at a frequency of 20 KHz for 15 to 30min. The BSFC for ZnO250, ZnO500 were same as CeO40, CeO80 respectively. BTE increased with addition of nanoparticle. BTE was maximum and it was 29.5% for ZnO500 and $CeO_2$80.

Karthikeyan et al. [15] analyzed the performance and emission characteristics of 1S 4 stroke CI engine fuelled with ZnO_2 nanoparticle added pomoline stearin wax biodiesel-diesel blend. The BSFC decreased for ZnO added blends compared to biodiesel. BTE increased for ZnO blends than biodiesel. The CO and HC emissions were lower than B20 for ZnO added blends. Shaafi et al. [42] reviewed the effect of adding various nanoparticle additives to the properties of various biodiesel and its impact on use as a fuel in diesel engine with respect to performance, combustion and emission characteristics. They concluded that the engine performance was not proportionately increasing with respect to nano additive concentration.

Kannan et al. [18] analyzed the performance and emission characteristics of a 1S 4 stroke DI CI engine fuelled with FBC added waste palm oil biodiesel. Ferric chloride ($FeCl_3$) was added to biodiesel. The results showed that BTE and BSFC improved with the addition of FBC at all operating conditions. NO_x and CO_2 emissions increased slightly with the addition of FBC. Nagaraj Banapurmath et al. [19] discussed the performance and emission characteristics of a single cylinder four stroke DI diesel engine fuelled with silver nanoparticle added HOME. BTE and heat release rate increased with addition of silver nanoparticle to HOME. There was a considerable reduction in HC, CO, NO_x with the addition of silver nanoparticle to HOME.

Manibharathi et al. [44] studied the performance and emission characteristics of a single cylinder four stroke air cooled DI diesel engine fuelled with nanoparticle added pongamia biodiesel. Rhodium oxide (Rh_2O_3) with an average size of 100 nm was mixed with pongamia biodiesel through magnetic stirrer for two hours along with the addition of cetyl trimethyl ammonium bromide as surfactant. The BSEC reduced by 3% at full load condition whereas, BTE got increased. HC, NO_x and CO emissions were reduced by 45%, 37% and 45% respectively.

Banapurmath et al. [20] discussed about the performance and emission characteristics of a single cylinder four stroke water cooled DI diesel engine fuelled with multiple nanoparticle added honge oil methyl ester (HOME). HOME, HOME+50G, HOME+50S, HOME+50CNT blends were prepared. BTE improved with the addition of graphene nanoparticles to HOME. CO, NO_x and smoke emissions were reduced considerably for graphene nanoparticle added HOME. Bhagwat et al. [21] reported similar results with graphene nano particle added to HOME. BTE at 80% load for diesel, HOME and HOME+50 was 28%, 24% and 26% respectively. Smoke opacity was higher for HOME and it was lower for HOME+50. HC, CO, NO_x emissions were decreased for graphene-fuel blend.

Prabhu et al. [45] discussed about the performance and emission characteristics of diesel engine fuelled with titanium oxide added NOME. BSFC lowered with the addition of nanoparticle compared to B20 blend. EGT increased with the addition of nanoparticle. At full load condition, CO, HC and smoke were reduced with the addition of nanoparticle whereas, NO_x increased. Mehta et al. [46] tested the performance and emission characteristics of a 1S 4 stroke DI diesel engine fuelled with multiple metal based nanoparticle added the diesel. Aluminium oxide, ferrous and boron nano particle were selected for this study. BSFC for alumina-diesel and boron-diesel increased whereas, it was nearly same as diesel for Fe-Diesel. CO emission for alumina-diesel and boron-diesel increased upto 30%. HC emission for alumina-diesel was reduced by 8% and for Fe-diesel by 2%. NO_x emission increased for alumina-diesel, Fe-diesel by 5% and 3% respectively.

Table 2. Comparison of performance parameters under various test conditions for nano metal additive blended fuel

S.No	Engine Type	Test Condition	Base Fuel	Nano Additive	BTE	BSFC	CP	Ref.
1	1-cylinder 4-stroke AC CI engine	1300-1500 rpm at 0, 25, 50 and full loads	B20-JME	Al_2O_3 at 10-50mg/l	↑ upto 7%	↓ upto 6%	-	1
2	1-cylinder 4-stroke WC CI engine	At moderate speed	Diesel	CuO and Al_2O_3 25-100 ppm	-	↓ 1% and 3.28% for CuO and Al_2O_3.	-	30
3	1-cylinder 4-stroke AC CI engine	-	JME	Al_2O_3 and CeO_2 30ppm	↑ by 5% for both	↓	↑	2
4	1-cylinder VCR engine 5:1- 20:1	-	B20, 40-WCFB	Al_2O_3	↓ with addition of NP	↑	↑	34
5	1-cylinder 4-stroke CRDI diesel engine	-	B20-MME	Al 50, 100 ppm	↑ by 1.58% to 7.66% for ANOP	↓ by 7.6% - ANOP100	↑	3
6	1-cylinder 4-stroke AC CRDI diesel engine	-	ZJME25	Al_2O_3 25 and 50 ppm	↑ by 2.5% for 50ppm	↓ by 6% - 50 ppm	-	4
7	1-cylinder 4-stroke AC DI CI engine	25%, 50% and full load	D80SBB15E 4	Al_2O_3 100 mg/l	↑ BTE at high load	↓ at high load	-	5
8	1-cylinder 4-stroke WC DI VCR engine	1500 rpm	CBD emulsion	Al_2O_3 100 ppm	↑ by 31.7%	-	↑	6
9	1-cylinder 4-stroke AC CRDI diesel engine	At full load	B20-MME	Al_2O_3 and Fe_2O_3	40AONP blend shows ↑ BTE	↓ with Alumina blend	-	36
10	1-cylinder 4-stroke AC CI engine	-	Diesel	AONP 0.5%wt	↑ by 9%	↓ by 7%	↓ 55 bar	37
11	1-cylinder 4-stroke WC CI engine	-	Diesel	Al_2O_3 25-75 ppm	↑ by 39.6% at max load	↑ for NP blend	78 bar for 75ppm blend	7
12	1-cylinder 4-stroke WC DI diesel engine	0, 20, 40, 60, 80 and full loads	Diesel-water emulsion	CNT 50, 100 and 150 ppm	Higher for 150ppm blend	↓ at full load	↑ and engine noise reduced	10
13	1-cylinder 4-stroke AC CI engine	-	JME emulsion	CNT - 25,50,100 ppm	28.45% for 100NP blend	↓ with addition of NP	74.11 bar for 50 NP blend	12
14	1-cylinder 4-stroke WC diesel engine	-	Diesel	ZnO 250 ppm & 500 ppm	-	-	78 bar for 500NP blend	40
15	1-cylinder 4-stroke WC diesel engine	0, 50 and full loads	Diesel	ZnO - 250, 500 ppm & CeO - 40, 80 ppm	29.5% for both ZnO500 and CeO80	↓ With both blends.	-	14
16	1-cylinder 4-stroke WC DI diesel engine	0, 50 and full loads	Diesel	Al_2O_3 & Co_3O_4	D25 shows higher BTE at all loads	-	D35, 15 gives peak cylinder pressure	62

S.No	Engine Type	Test Condition	Base Fuel	Nano Additive	BTE	BSFC	CP	Ref.
17	1-cylinder 4-stroke WC DI diesel engine	-	WCPBD	Ferrous, Copper and Cobalt	↑ for all nano blends	↓ for all NP	Higher at full load	18
18	1-cylinder 4-stroke AC DI diesel engine	50% and full load	Jatropha BD	Al-Mg and Co_3O_4	↑ with addition of NP	↓ by 3% - 2% for NP	-	63
19	1-cylinder 4-stroke AC DI diesel engine	-	Pongamia BD	Rh_2O_3	↑	3% reduction at full load	-	44
20	1-cylinder 4-stroke WC DI diesel engine	Full load	B20-NOME	TiO_2 250ppm, 500ppm	↓ with the addition of NP	↑ for all blends than diesel	-	45
21	1-cylinder 4-stroke DI VCR engine	At BMEP 0.44 MPa	Diesel	CeO_2 and Water based ferrofluid	↑ 5.33 to 12.17% for 0.8% ferrofluid blend.	↓5.06 to 10.85 %	-	65
22	1-cylinder 4-stroke DI VCR engine	At BMEP 0.44 MPa	Diesel 70%, Ethanol 20%, Castor oil 10%	CeO_2 - 25 ppm	↑ at all loads	Lowest	D+25 ceria - 10.2 bar DEC+25 ceria - ↑	50
23	1-cylinder 4-stroke AC DI diesel engine	At full load	JME and TPO	CeO_2 and CNT	J90T10 Ceria blend shows ↑ BTE	SFC ↑ with addition of NP	-	24
24	1-cylinder 4-stroke AC diesel engine	-	Diesel-JME -Ethanol	CeO_2 - 30 - 50 mg/l	↑ for NP high CP	↓ as 0.328 for NP	↑ 63.70 bar for nano blend	51
25	1-cylinder 4-stroke AC CI engine	At constant BMEP	B20-GSME	CeO_2 - 50, 100 ppm	B20, ceria100 gives ↑ BTE	BSFC minimal	-	52
26	4-cylinder 4-stroke WC DI diesel engine	At 16.1:1 CR 1000-2400 rpm	B25 - Pomace oil	Mn - 12 μmol/L	↑	-	-	25
27	1-cylinder 4-stroke AC DI diesel engine	At 2400 rpm	B60 - TME	8, 12 μmol/L Ni and Mn	-	↓ with 12 μmol/L for NP	-	28
28	1-cylinder 4-stroke AC DI diesel engine	At 18.1:1 CR	B10 - WCFBD	Mg – 0 to 16 μmol/L	↑	↓	-	29

↓ Decrease by : ↑ Increase by

Soukht Saraee et al. [47] analyzed the performance and emission characteristics of a six cylinder air cooled DI diesel engine fuelled with silver nanoparticle added diesel with sorbitan monooleate as surfactant. Fuel consumption, engine speed, peak cylinder pressure and exhaust emissions values were compared with diesel as base line reading. Rashedul et al. [48] reviewed the various biodiesels, various types of fuel additives and its effect on the characteristics of biodiesel on addition. Oxygenated additives was suggested to control the cylinder temperatures. Co, Mg, Mn, Ni metal additives increased the exhaust emissions. Sajeevan and Sajith [49] mentioned about the performance and emission characteristics of a single cylinder four stroke naturally aspirated water cooled CI engine fuelled with ceria nanoparticle added diesel. BTE increased with the addition of nanoparticles. Diesel with 35 ppm ceria added blend showed lesser NO_x and CO emissions compared to other blends and neat diesel.

Arul Mozhi Selvan et al. [50] analyzed the performance and emission characteristics of a single cylinder four stroke DI diesel engine fuelled with ceria nanoparticle added diesel. The results showed an improvement in BSFC and BTE of diesel-biodiesel-ethanol blend with the addition of ceria nanoparticles. Sunil Kumar Sharma et al. [24] analyzed the performance and emission characteristics of the diesel engine fuelled with nano ceria (20 to 30 nm in size) and CNT (200 nm) added tire pyrolysis oil mixed jatropha methyl ester. BTE increased with the addition of both ceria and CNT. CO and HC emissions decreased with the addition of ceria and CNT whereas, NO_x and smoke increased. Shaafi Tajudeen and Velraj [51] also obtained similar results and elaborated about the performance and emission characteristics of a diesel engine fuelled with nano ceria (15-30 nm) added to diesel-jatropha biodiesel-ethanol blend.

Karthikeyan et al. [52] used nano ceria added grape seed methyl ester (GSOME)-diesel blend in a 1S 4 stroke diesel engine for performance and emission analysis. The BTE increased for B20+$CeO_2$100 at constant BEMP and the CO emission was decreased for B20+$CeO_2$100. EGT, HC and NO_x decreased for B20+$CeO_2$100 blend. Zhipeng Xin et al. [53] synthesized CeO_2, $CeZr_xO_2$, $CeCu_xO_2$, $CeMn_xO_2$ and $CeCo_xO_2$ nanoparticles and then mixed them with diesel-grape seed oil methyl ester blend for studying the performance and emission characteristics. Sinem Caynak et al. [25] used manganese (Mn) as fuel additive in B25-pomace oil methyl ester. 12 µmol/l of Mn was added to diesel-pomace biodiesel blend. They noticed an average reduction in performance by 1.54 % for B25 nano blend compared to diesel. Metin Guru et al. [29] analyzed the performance and emission characteristics of a single cylinder four stroke air cooled DI CI engine fuelled with Mg added diesel-waste chicken fat biodiesel blend. 16 µmol/l of Mg was mixed with B10-waste chicken fat biodiesel fuel blend. The results showed a considerable reduction in CO and smoke emissions by upto 13% and 9% respectively whereas, NO_x increased by 5% with Mg added blend compared to neat diesel. Various proportions of biodiesel blended with copper oxide nanoparticles were analyzed at the rated speed of CI engine which resulted in an increase in BTE at lower blends at full load along with lower emission levels [54]. Al_2O_3 and CeO_2 at proportion of 10, 30 and 60 ppm were blended with jatropha biodiesel and tested in a single cylinder four stroke compression ignition engine. Remarkable improvement in BTE was noticed at increased concentration of nanoparticle along with reduction in NO_x, UBHC, CO and smoke [55]. Cerium oxide nanoparticle blended with lemongrass emulsion oil was fuelled to the constant speed CI engine to analyze its performance, emission and combustion parameters. The LGO emulsion was prepared with water, LGO and span 80 solutions with the HLB value of 4.2. The emulsified fuel owing to its larger surface area, enhanced the atomization thereby leading to better mixing and faster evaporation rate resulting in better performance and reduced emissions [56]. The influence of nozzle geometry was studied in a four stroke tangentially mounted single cylinder compression ignition engine fuelled with methyl esters of calophyllum inophyllum-ultra low sulphur diesel–cerium oxide nanoparticle. The brake thermal efficiency and brake specific fuel consumption were also found to be favorable due to better atomization [57].

The effect of zinc oxide nano particle on degummed jatropha biodiesel was studied in a direct injection compression ignition engine in dual fuel mode. NO_x emission was found to detoriate with the addition of nano particle [58]. Experimental performance and emission parameters were compared with the theoretical model in terms of nano particle concentration and load. Fe_3O_4 was dispersed in 0.4% and 0.8% concentrations by volume for testing at under variable loading condition. ANOVA method with 95% confidence level and regression fitted models were adopted to predict the performance parameters, 0.4% nano concentration was found to be optimal with reduced emission levels [60]. The effect of various injection strategies in CI engine fuelled with biodiesel-ethanol-nano particle blends were experimentally studied. Al_2O_3 was synthesized and characterized using ultra-sonicator and SEM / XRD techniques. The retarded injection timing of 19° bTDC was noticed to produce optimal combustion, performance and emission [61]. Roshith Oommen George et al. [62] reported about the performance and emission characteristics of a 1S 4 stroke air cooled direct injection diesel engine fuelled with alumina and cobalt oxide mixed diesel. NO_x was lower and HC emission for D25:25 showed constant values at all loads. The CO emission decreased by 20% for D25:25 and HC decreased by 15.20% than neat diesel. Ganesh and Gowri Shankar [63] reported the performance and emission characteristics of a single cylinder air cooled DI diesel engine fuelled with nanoparticle added jatropha biodiesel. Magnalium (Al-Mg) and cobalt oxide (Co_3O_4) with average size of 38 to 70 nm were used as additives. BSFC for neat biodiesel was higher compared to diesel. With the addition of nanoparticles to it, it was reduced by 2% for Co_3O_4 blend and 3% for Al-Mg blend at full load conditions. 1% improvement in thermal efficiency was achieved for Al-Mg blended biodiesel compared to neat biodiesel. HC emission was reduced considerably with both the blends than neat biodiesel. Ranaware and Satpute [65] discussed the performance and emission characteristics of single cylinder four-stroke DI CI engine fuelled with nano fluid mixed diesel. Cerium oxide and water based Ferro fluid were added to diesel fuel in the proportions: CeO_2 - 25 ppm, Ferro fluid - 0.4%, 0.8% in volume of diesel. BSFC reduced with the addition of both CeO_2 and Ferro fluid. BTE reduced with the addition of CeO_2 whereas, it increased with the addition of Ferro fluid. CO emission increased whereas, NO_x reduced with the addition of Ferro fluid. Recently, studies were carried by several researchers [68-73, 76, 77, and 78] in using nano metal based additives to the fuel with the focus on improving the performances and reducing the emissions of compression ignition engines.

a. Discussion on performance parameters

Ignition delay period and BSFC reduced with Al_2O_3 and CuO when added to neat diesel [30]. BTE and peak cylinder pressure values were increased with the addition of Al, Al_2O_3 nanoparticle in plain diesel [7, 37, and 62]. The addition of ZnO, CeO_2, and Ferro fluid with plain diesel increased BTE and reduced BSFC [14, 40, 62, and 65]. Al_2O_3 and CNT with emulsified fuels increased BTE and reduced BSFC [6, 12]. Al_2O_3, Al, CNT increased the BTE and reduced BSFC when added with diesel-biodiesel blends [1, 3, 4, 6, 10, 34 and 37]. Addition of TiO_2 in diesel biodiesel-blend increased the BSFC [24, 45].

Table 3. Comparison of emission parameters under various test conditions and additives

S. No	Engine Type	Test Condi-tion	Base Fuel	Nano Additive	UBHC	CO	NO_x	Smoke	Ref
1	1-cylinder 4-stroke AC DI diesel engine	At all loads	B20 JME	Al_2O_3	↓ by 55%	↓ by 75%	↓ by 70%	↓by 5%	1
2	1-cylinder 4-stroke WC DI diesel engine	Full load	Diesel	Al_2O_3 and CuO	↓ by 13%	↓ by 11%	↓ by 6%	-	30
3	1-cylinder 4-stroke AC DI diesel engine	-	JME	Al_2O_3 and CeO_2	↓ by 28-33%	↓ by 20-30%	↓ by 7-9%	↓ by 17 to 20%	2
4	1-cylinder VCR engine	-	B20-WCFB	Al_2O_3	↓	↓	↑ with addition of NP	↓ upto 65%	34
5	1-cylinder 4-stroke AC CRDI diesel engine	-	MME	Aluminium	ANP100 - ↓ by 26.04%	ANP -↓ by 26%	ANP - ↓ by 2.6-7.9%	-	3
6	1-cylinder 4-stroke AC CRDI diesel engine	-	ZJME	Al_2O_3	-	AONP 25 3.951g/kWhr	AONP25 - Lowest	↑ with NP	4
7	1-cylinder 4-stroke AC DI diesel engine	-	Diesel, SBD	Al_2O_3 100mg/l	↑ with load	-	↑ with load	-	5
8	1-cylinder DI WC VCR engine	-	CBD-water emulsion	Al_2O_3	↓	↓	↓	↓	6
9	1-cylinder 4-stroke AC CRDI diesel engine	-	B20 MME	Al_2O_3 and Fe_2O_3	AONP - 81 ppm IONP - 83 ppm	AONP 40, 80 - ↓ by 19, 20%	AONP 40, 80 - 1118, 1120 ppm	↓	36
10	1-cylinder 4-stroke AC diesel engine	Full load	Diesel	Aluminium	↓ by 8%	↓ by 25 - 40%	↑ by 3 - 5%	-	37
11	1-cylinder 4-stroke AC DI diesel engine	-	JME	Al_2O_3 and CNT	46 ppm for JBD25A 25CNT	-	985ppm for JBD25A 25CNT	57% for JBD25A 25CNT	8
12	1-cylinder 4-stroke WC DI diesel engine	-	NOME	CNT 100, 200, 300ppm	CNT ↓ by 3.67 – 8.15%	CNT ↓ by 8.56 to 11.7%	CNT ↓ by 2.8 to 3.4%	CNT ↓ by 3.2 to 5.7%	9
13	1-cylinder 4-stroke AC DI diesel engine	80% load	HOME	CNT 25,50 ppm	50CNT – 58 ppm	50CNT 0.21%	25CNT 600ppm	50CNT 59%	11
14	1-cylinder 4-stroke AC diesel engine	-	JME water emulsion	CNT	JMEE100CNT - of 57 ppm	JMEE100CNT - 49%	JMEE100 CNT - 910ppm	JMEECNT100 - 49%	12
15	1-cylinder 4-stroke WC diesel engine	At various loads	Diesel	ZnO	-	-	↓ NOx at full load	↑ addition of ZnO	40
16	1-cylinder 4-stroke AC DI diesel engine	-	Diesel	Al_2O_3 and Co_3O_4	D25, 25 Moderate emission	D25, 25 - ↓ CO	Lower for D25, 25	-	62

S. No	Engine Type	Test Condi-tion	Base Fuel	Nano Additive	UBHC	CO	NO_x	Smoke	Ref
17	1-cylinder 4-stroke WC DI diesel engine	-	WCPBD	FBC - $FeCl_3$	↓ with addition of FBC	↑ with addi-tion of FBC	↓ with addition of FBC	↓ with addition of FBC	18
18	1-cylinder 4-stroke AC DI diesel engine	-	HONG	Ag	↓ by addition of Ag.	HOME 50 less	HOME5 0 less	-	19
19	1-cylinder 4-stroke AC DI diesel engine	Full load	POME	Rh_2O_3	↓upto 45%	↓ upto 45%	↓ upto 37%	-	44
20	1-cylinder 4-stroke AC diesel engine	Full load	B20-NOME	TiO_2	19 ppm for B20T250	0.04% for B20T2 50	↑ with addition NP	2.4% for B20T25 0	45
21	1-cylinder 4-stroke AC DI VCR engine	At 0.44 BMEP	Diesel	CeO_2 and Ferro fluid	DC25 - ↓ than diesel DF0.4% - ↑ DF0.8% - ↑	DC25 - ↓ DF0.4 % - ↑ DF0.8 % - ↑	DC25 - ↑ diesel DF0.4% - ↓ DF0.8% - ↓	-	65
22	1-cylinder 4-stroke AC DI VCR engine	At 0.44 BMEP	Diesel, COME and ethanol	CeO_2	DCE25 ↓	↓ with NP	↑ with addition of NP	-	50
23	1-cylinder 4-stroke AC DI diesel engine	Full load	JME and TPO	CeO_2 and CNT	↓ with addition of NP	CNT ↓ CO emissio ns	↑ CeO blend	↑ with load	54
24	1-cylinder 4-stroke AC DI diesel engine	At 2400 rpm	B60 - TOME	8, 12 µmol/L Ni and Mn	-	↓ by 64.28% for NP	Lowest for 8Ni and 12Ni blends	↓ maximu m with 12 Mn blend	28
25	1-cylinder 4-stroke AC DI diesel engine	At 18.1:1 CR	B10 - WCFFB	Mg – 0 - 16 µmol/L	-	↓ by 13%	↑ by 5%	↓ by 9%	29

↓ Decrease by: ↑ Increase by

Addition of Al_2O_3, Fe_2O_3, Al-Mg, Co_3O_4, CuO, Rh_2O_3, and Fe2O3 increased the BTE and reduced the BSFC when added with neat biodiesels [2, 18, 36, 44 and 63]. When the temperature increases inside the cylinder, the nanoparticles presents within the fuel began to ignite and releases higher amount of heat, which increases the engine performance. This review covered the researches carried out on fuels added with the following nanoparticles: Al_2O_3, CeO_2, ZnO, CuO, $FeCl_3$, $CuCl_2$, $CoCl_2$, $CuSo_4$, Co_3O_4, Al, Mn, Mg, Ni, Ag, Cu, CNT and metal alloys etc. The BTE of the engine increased mostly with all the above mentioned nanoparticles at higher loads. The addition of Al_2O_3 with all the base fuels increased the BTE. ZnO and ceria nanoparticles increased the BTE slightly. CNT gave good results on engine performance. Except few nanoparticles, all the above mentioned nanoparticles reduced the fuel consumption at partial and maximum load conditions when compared to diesel or base fuel used and the details are given in Table 2. Due to the presence of nanoparticles, the BSFC was higher than base fuel at initial load conditions. But, it decreased with the increase in load. Al_2O_3, Al, Ferro fluid, CeO_2 nanoparticles in addition with base fuel showed a higher BSFC reductions than all other nanoparticles. Addition of excess or lesser quantity of nanoparticle with the diesel or diesel blend did not make any changes in the performance or reduced the performance. Adding the nanoparticles with lower calorific value fuels will help in improving the fuel properties and thereby, improves the performance of CI engine.

b. Discussion on emission parameters

Co_3O_4, Al_2O_3, Al added diesel reduced UBHC and CO emissions. NO_x was reduced with Co_3O_4, Al_2O_3 added diesel whereas it increased with Al [30, 37, 62]. Ferro fluid added with neat diesel increased CO and HC emissions whereas, it reduced NO_x emission [65]. Al_2O_3 and CNT added emulsified diesels reduced all emissions including smoke [6, 12]. NO_x increased with the addition of Al in neat biodiesel. All emissions were reduced with the addition of Rh_2O_3, Ag, and CNT in neat biodiesel [8, 9, 11, 19, and 44]. Similarly, all emissions were reduced with the addition of Al_2O_3, Fe_2O_3, Mn and Ni in diesel-biodiesel blends [1, 28, 29, 36]. NO_x increased with the addition of TiO_2, Mg, and CeO2 in diesel biodiesel blends [29, 34, 45, 50] as given in Table 3. The cause of UBHC was due to incomplete combustion of the fuels. The flame produced inside the cylinder could not propagate throughout the cylinder in some cases, so that incomplete combustion occurs. Normally, the addition of nanoparticles with the base fuel improved the combustion process thereby it reduced the UBHC emissions. Addition of Al_2O_3, CNT, ZnO and CeO_2 with diesel or other base fuels decreased the UBHC emissions considerably. Cause of CO emission was due to insufficient oxygen supply during the combustion process. CO emission were reduced with the addition of nanoparticles and other oxygenated additives. In some cases like using emulsified fuels added with FBC, CO emission increased slightly. During combustion process, the reaction occurring between the nitrogen and oxygen at higher temperature led to nitric oxide and nitrogen oxide emissions. In general, NO_x emission increased with the addition of nanoparticles. This was due to the addition of nanoparticles which improved the combustion process and thereby releasing higher heat release rate. At higher temperature, the formation of NO_x increased, but it can be controlled with the addition of small quantity of ethanol. Smoke was a combination of partially burnt fuels, liquid fuel droplets, gases, etc. emitted during combustion process. Smoke was an unavoidable byproduct of combustion process. The intensity of smoke was reduced or controlled with the addition of nanoparticles. As complete combustion was achieved by using nano particle blended fuel, smoke was reduced considerably.

5. Conclusion

Based on the review, it is understood that the addition of nanoparticles plays a major role in improving the fuel properties and enhancing the performance of CI engine as well as reducing the exhaust emissions. Addition of nanoparticles increases BTE which depends upon the base fuel used, amount of nanoparticle added, how well they are mixed with the base fuel, and operating condition of the CI engine. Nanoparticles like Al_2O_3, Al, CNT and CeO_2 shows good results as additives with diesel and biodiesel blends in all aspects. ZnO also gives better results but, more amount of ZnO should be added than other nanoparticles to get an equivalent performance and the use of ZnO as fuel additive increases the cost of fuel. The performance enhancement cannot be achieved with every amount of nanoparticle addition. Therefore, selecting optimal range of nanoparticle addition is key to get good results on enhanced performance and reduced emission in a CI engine. Some nanoparticles gives good results with every base fuel with which it is added, but in some cases it fails to improve neither performance nor emissions. Size of the nano particle is also a criteria to be considered in using nano metal additives for improving the fule properties. Therfore, selecting the nanoparticles based on the properties of the fuel to be improved will help us to attain better results and lot of researches should be done on this area to select the suitable nano metal additive based for the fuel.

Abbreviations

Al_2O_3	Aluminum oxide
CNT	Carbon nanotube
CeO_2	Cerium oxide
ZnO	Zinc oxide
ZnO_2	Zinc peroxide
TiO_2	Titanium di-oxide
CoO_2	Cobalt di-oxide
CuO	Copper oxide
FeO_2	Ferrous oxide
UBHC	Unburned hydrocarbon
CO	Carbon monoxide
NO_x	Oxides of nitrogen
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
BHT	Butylated hydroxytoluene
TBHQ	Tert-butyl hydroquinone)
BHA	Butylated hydroxyanisole
CFPP	Cold filter plug point
B20	Blend of Diesel (80%) and biodiesel (20%)
AONP	Aluminum oxide nano particle
JBD	Jatropha biodiesel
SBD	Soyabean biodiesel
HOME	Honge oil methyl ester
AIT	Auto ignition temperature
CRDI	Common rail direct injection
BSFC	Brake specific fuel consumption
BMEP	Brake mean effective pressure
BTE	Brake thermal efficiency
BSEC	Brake specific energy comsumption
EGT	Exhaust gat temperature
CP	Cylinder pressure
MENO	Neem oil methyl ester
CTAB	Cetryl trimethyl ammonium bromide
JME	Jatropha methyl ester
WCFB	Waste chicken fat biodiesel
MME	Mahua methyl ester
CBD	Canola biodiesel
WCPBD	Waste cooking palm biodiesel
NOME	Neem oil methyl ester
TPO	Tire pyrolysis oil
GSME	Grape seed oil methyl ester
TME	Tail oil methyl ester
NP	Nano particle

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