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Review Article

Recent advancements, applications, and technical challenges in fuel additives-assisted engine operations

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ABSTRACT

The rise in technology and population has led to an increase in automobiles and the consumption of fossil fuels. Engine power comes from converting the chemical energy of fuel into work during fuel combustion. Scientists are working to improve engine output by using modifications like fuel injection systems, varying compression ratios, electronic ignition systems, and valve timing systems. However, stringent emission regulations are hindering these advancements in response to ecological challenges. Fuel combustion is linked to greenhouse gas emissions, climate change, global warming, air pollution, and health problems on a large scale. The consumption of fossil fuel resources directly correlates with the population and the welfare of society. The trend toward electric vehicles poses a threat to the use of waste biomass resources. However, biofuels are necessary due to their role in recycling waste biomass sources. The main obstacle to large-scale use of biodiesel fuels in diesel engines is their lower energy content, poor atomization, higher density, and viscosity. These biodiesel characteristics result in higher fuel consumption and NOx emissions due to lower thermal efficiency. Fuel additives are chemical compounds that can help optimize engine power and emissions. Fuel additives can be blended with base fuel, either diesel fuel or biodiesel fuel, to improve the thermo-physical properties of fuel and combustion, leading to lower fuel consumption, less engine wear, prevented failure, and optimized performance in cold weather. According to literature review, blending nanoparticles with fuel generally increases BTE from 1 to 25%, except for magnesium and carbon nanotube additives, which can reduce BTE by up to 4.8%. Hydrocarbon emissions generally decrease from 4 to 60%, while NOx emissions generally decline from 4 to 45%, except for manganese, aluminum oxide,

Abbreviations: $(A/F)_s$, Stoichiometric air–fuel ratio; Ag, Silver; Al_2O_3, Aluminum oxide; AT, A-tocopherol acetate; Au, Gold; Ba, Barium; B, Boron; BP, Brake power; BSFC, Brake specific fuel consumption; BMEP, Brake mean effective pressure; BTE, Brake thermal efficiency; BHA, Butylated hydroxyl anisole; BHT, Butylated hydroxyl toluene; $CaCO_3$, Calcium carbonate; CAGR, Compound Annual Growth Rate; cc, Cubic centimeter; CeO_2, Cerium dioxide; CD, Combustion duration; CCD, Central composite design; CFPP, Cold filter plugging point; CI, Compression ignition; CN, Cetane number; CO, Carbon monoxide; CO_2, Carbon dioxide; $CoCl_2$, Cobalt chloride; COF, Coefficient of friction; Co_3O_4, Cobalt oxide; CP, Cloud point; CR, Compression ratio; CuO, Copper oxide; $CuSO_4$, Copper sulphate; CV, Calorific value; CNT, Carbon nanotubes; DEE, Di-ethyl ether; DPA, Diphenylamine; DPPD, N-diphenyl-1,4-phenylenediamine; DTBP, Di-*tert*-butyl peroxide; DICI, Direct injection compression ignition; EGT, Exhaust gas temperature; EGR, Exhaust gas recirculation; EHN, 2-Ethylhexyl nitrate; EVA, Ethylene-vinyl acetate; EV, Electric vehicle; FAME, Fatty acid methyl ester; Fe, Iron; FP, Flash point; GHGs, Greenhouse gases; GE, Geraniol; GHG, Greenhouse gas emissions; HOME-MWCNT, Honge oil methyl ester-multi walled carbon nanotubes; HCCI, Homogeneous charged combustion; HC, Hydrocarbon; H_2O_2, Hydrogen peroxide; HP, Horsepower; HRR, Heat release rate; HO_2, Peroxyl; ID, Ignition delay; ICP, In-cylinder Pressure; ICT, In-cylinder Temperature; IT, Injection Timing; KV, Kinematic viscosity; kW, Kilowatt; kPa, Kilopascal; LA, L-ascorbic acid; LCA, Life cycle assessment; LHV, Latent heat of vaporization; MgO, Magnesium oxide; Mn, Manganese; MOF, Metal-organic framework; Mtoe, Million tons of oil equivalent; NOx, Oxides of Nitrogen; nm, Nanometer; Mg-Al, Magnalium; NP, Nanoparticle; NPPD, N-phenyl-1,4-phenylenediamine; OECP, Olefin ester copolymer; PL, Pyrogallol; PM, Particulate matter; PMA, Poly methyl acrylate; PPDA, p-phenylenediamine; PG, Propyl gallate; PP, Pour point; ppm, Parts per million; Pt, Platinum; Ra, Surface roughness; ROPR, Rate of pressure rise; ROHR, Rate of heat release; RSM, Response surface methodology; rpm, Revolution per minute; SiO_2, Silicon dioxide; SP, Solidification point; TBHQ, 2-*tert*-butylbenzene-1,4- diol; TiO_2, Titanium dioxide; USA, United States of America; %v, Percent by volume; %wt., Percent by weight; WCO, Waste cooking oil; WPO, Waste plastic oil; WSD, Wear scar diameter; ZnO, Zinc oxide.

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silicon dioxide, and carbon nanotubes. This review article comprehensively discusses fuel additives for their potential applications in automotive, making it easier for researchers and manufacturers to select fuel additives for specific purposes. The main objective of this review is to compare the performance and physicochemical properties of multiple fuel additives with biodiesel (base fuel) to extract maximum benefits from biofuels.

1. Introduction

The explosive growth in population with increased consumption of fossil fuel resources to meet energy demands has created an ecological imbalance mainly because of exceeding levels of hazardous emissions. It has become a global priority to look for alternatives to petroleum fuels that are renewable and eco-friendly due to the adverse effects petroleum fuels have on the climate. Global warming is the most devastating manufactured outcome of human activities around the globe, and its effects are much more dangerous. This has resulted in a rise in worldwide entropy and temperature, which has caused a chain of events. Industrialization and rapid consumption of fossil fuel resources are primarily responsible for this global issue.Furthermore, smog is also one of the adverse consequences of global warming, severely affecting the ecosystem. Smog also poses significant health risks to humans, impacting the respiratory system, cardiovascular health, mental health, immune function, and overall well-being. Reducing smog pollution is essential for protecting public health and improving air quality [1].

The CO_2, NOx, CH_4, and water vapors are the most abundant greenhouse gases (GHGs). The significant contributors to GHGs are power plants (25 %) and vehicles (14 %), without which survival is impossible [2]. Also, the transportation sector contributes considerably to air pollution globally, i.e., 28 % of the United States of America's GHGs come from the transportation sector [3]. It is estimated that biofuel consumption will rise to 4.6 million barrels per day in 2040 compared to 1.3 million barrels of oil equivalent per day in 2012 [3]. The petroleum consumption rate is more than four billion tons annually, and the existing petroleum reserves will be consumed entirely by 2052 for similar population growth and crude oil consumption rate [4]. Human activities, notably the burning of fossil fuels like coal, oil, and natural gas, have significantly increased the concentration of CO_2 in the atmosphere [5]. This increase in CO_2 amplifies the natural greenhouse effect, leading to global warming and climate change. The consequences of this warming include rising temperatures, melting polar ice caps, more frequent and severe weather events, changes in precipitation patterns, and disruptions to ecosystems and biodiversity [6].

Das et al. [7] compared the impact of different fuels on the environment regarding the amount of carbon dioxide emitted. They observed that coal, natural gas, biogas, and oil produced 957, 517, 130 and 724 g CO_2/kWh, respectively. The biogas proved the least harmful to the environment because of the lowest CO_2 production upon burning. Larionov et al. [8] obtained synthesis gas with the following composition: H_2 (30–54 vol%), CH_4 (7–26 vol%), CO (20–36 vol%), and CO_2 (12–18 vol%) during oil pyrolysis. Hajderi et al. [9] obtained results, it results that in reduction of CO_2 affect more the fuels B15 (15 % biodiesel in 85 % diesel) up to 11.5 %, M−15 (15 % methanol in 85 % diesel) up to 9 %, FT 15 (15 % Fischer-Tropsch in 85 % diesel) up to 7.5 % and E-15 (15 % ethanol in 85 % diesel) up to 6 %. Also, M 15 has the most significant impact on the reduction of particles and nitrogen oxides with a decrease of 45 % and 30 %, respectively, followed by E 15 with 30 % and 20 % and B15 and FT15 with 30 % and 25. The experimental measurements of the opacity coefficient confirm that using M15 and E15 fuels reduces pollution by 35 % and 25 %.

Crude oil fulfils the annual energy consumption of 12.2×10^9 tons globally, projected to rise to 1.75×10^9 tons in 2035 [10]. The transport sector consumes 50 % of fossil fuels to meet energy demand [11,12]. The transport sector is the backbone of oil consumption. The transport sector will contribute 50 % of greenhouse gas emissions until 2030 [13]. The higher efficiency of diesel engines is responsible for their critical role in a wide range of applications in the industrial and automobile sectors. However, the wide applications of diesel engines have also increased the concern for the depletion of fossil fuel sources. Fig. 1 represents the global energy consumption from 1970 to 2050. As per Bloomberg New Energy Finance, New Energy Outlook [14], it can be concluded that petroleum fuel contributed almost 62 % of annual energy consumption during 2020. However, the contribution of fossil fuels to the energy mix is decreasing due to the adoption of renewable energy sources. However, petroleum fuels will hold a significant place in the energy mix as they will contribute 25 %, as per projection.

Furthermore, the rapid depletion of fossil fuel sources is an alarming situation. Although diesel engines possess potential excellent attributes, they may also produce air pollution and exhibit cancer-causing threats to humans [15]. Therefore, exploring alternate and clean energy sources is crucial to meet energy requirements. Bio-energy commercialization can be a solution to the current challenges, along with exploring distinct additives to improve engine performance.

Electric vehicle (EV) technology is emerging due to its carbon–neutral nature and zero emissions. As per Statista's report for electric vehicles in Asia [16], compared to 2020, sales of new electric cars more than doubled in 2021, with an increase of 51.8 %. EV sales increased to about 5 % of global passenger car sales in 2021. The unit sales of electric vehicles exceeded 6.5 million, and the market realized a total revenue of US$ 350 billion. Electric vehicle market unit sales are expected to reach 9.30 million in 2028. The forecasted compound annual growth rate (CAGR) of the revenue between 2017 and 2027 will be 28.9 %. Biodiesel is a reliable substitute for compression ignition (CI) engines. They are a clean fuel from plant-based (edible and non-edible) and animal-based sources, such as animal fats, vegetable oils and microalgae [17–19]. Biodiesel may also be synthesized from cooking oil and agricultural waste [20,21]. The biofuel demand has grown 5 % per year on average between 2010 and 2019, and the Net Zero Emissions by 2050 [22]. An average growth of 14 % per year is projected by 2030.

Furthermore, biofuels are increasingly produced from feedstocks such as wastes and residues, which do not compete with food crops. In Net Zero Emissions by 2050 [22], the biofuels produced from these resources will meet 45 % of total biofuel demand by 2030. In 2020, only 7 % of biofuels came from waste and residues. Therefore, biodiesel production from waste sources is more advantageous for energy conservation through waste recycling. The dumping of huge volumes of waste, which would otherwise pollute the ecosystem, will be the main issue. Both diesel fuel and biodiesel possess similar fuel properties, and the benefits of biodiesel in terms of higher combustion efficiency, cetane rating, biodegradability, flash point, lubricity and lower sulphur and aromatic content make it an ideal alternative to diesel fuel [23].

Although biodiesel feedstocks are abundant, biodiesel-fueled diesel engines have faced many issues, including lower fuel economy, higher density, poor fuel atomization, cold start cranking problems, higher corrosive issues, and piston ring sticking [24]. The potential solution to these issues is blending biodiesel with diesel fuel, which can be fueled into diesel engines without significant modification [25]. Biodiesel blended fuel is cheap and safer because it does not harm the ecosystem and minimizes the damage caused by waste spills into the environment. However, the higher viscosity of biodiesel can be reduced by using fuel additives specifically designed to reduce viscosity to reduce fuel injection problems [26]. The viscous biodiesel results in higher fuel spray penetration, narrow injection spray angle, poor fuel atomization, poor fuel vaporization, larger fuel droplets, and wear in fuel pump components [27,28]. As fuel injection systems quantify the fuel to their volume, fuel density affects biodiesel application in diesel engines, and the variation in fuel density during fuel injection directly affects engine power and efficiency [29]. Fuel additives like diethyl ether and nano-additives decrease the viscosity of biodiesel. The diethyl ether acts as a solvent to reduce the viscosity of biodiesel by disrupting intermolecular forces between FAME molecules, while nano-additives modify the molecular structure of biodiesel at the nanoscale, leading to decreased viscosity through various mechanisms such as dispersion and surface modification. Both approaches offer potential solutions for improving the flow properties of biodiesel, particularly in cold weather conditions or for applications where low viscosity is critical [30,31].

Biodiesel has a 12 % lower calorific value than diesel fuel, directly affecting engine efficiency [32]. It is also reported that the oxygenated nature of biodiesel is primarily responsible for higher NOx emissions in the case of biodiesel [33]. The abovementioned issues can be addressed through biodiesel blends with diesel fuel in different proportions and additives [34]. Titration is the most commonly used process to blend the additives into base fuel based on the required concentration (% by volume) [35–37]. The chemical composition of blended fuels depends on the concentration of additives (% by volume) added into blended fuels, which can be determined after the preparation of fuel blends. Chromatography and spectrometry are the most commonly used techniques to determine the chemical composition of blended fuels [38,39]. Homogeneous charge compression ignition (HCCI) [40] can also reduce oxides of nitrogen (NOx) emissions and increase fuel efficiency. The homogeneous combustion control hotspots mainly result in higher NOx emissions. Moreover the lean air–fuel mixture also contributes to lower NOx emissions. Another possible way to reduce NOx emissions is the application of exhaust gas recirculation (EGR). The recirculated exhaust gases like CO_2 and H_2O dilute the fresh intake charge, slowing the combustion process, reducing peak temperatures and suppressing NOx formation [41].

The use of alternative fuels is still in its infancy, as fossil fuels comprised more than 92 % of the total fuel supply to the world's transportation segment in 2018 [42], while alternative fuels formed only around 8 % [43]. The global energy consumption of hydro-treated vegetable oil and fatty acid methyl ester biodiesel 2018 was 50 and 79 Mtoe, respectively. Biodiesel can improve engine efficiency, but NOx and CO_2 emissions also increase, mainly because of their higher oxygen content and cetane rating [44,45]. Moreover, the higher viscosity, lower volatility, poor atomization and density of biofuels may create injection problems [46], deposit formation or higher reactivity of unsaturated hydrocarbon chains in the combustion chamber [47], and early degradation of lubricant oil [48]. Fig. 2 shows the biodiesel characteristics and their impact on engine performance. The application of fuel additives can solve issues linked with biodiesel. Still, many factors like blending properties, additive solubility, toxicity, fuel viscosity, flash point, water solubility, phase separation and economic feasibility influence the choice of fuel additives [49].

Recent advancements indicate that metallic nanoparticles (NPs) are additives in petroleum fuels to achieve desired physical and chemical properties. Nanoparticles speed up ignition and may enhance physical characteristics, including viscosity, diffusivity, and thermal conductivity, improving fuel combustion. Metallic NPs have a higher energy density, which increases the overall calorific value of the fuel, lowers the ignition delay (ID), raises the ignition temperature, and increases the fuel injection velocity, all of which result in better combustion and engine performance. The NPs also have a higher surface area-to-volume ratio, which increases the interaction between the fuel and the oxidizer. Increasing soot oxidation or encouraging the reaction with water molecules to yield hydroxyl radicals and lower oxidation temperature reduces emissions [50]. Therefore, looking for biodiesel chemical additives to improve fuel properties and engine performance is crucial. Alcohol-based additives possess higher latent heat of evaporation and oxygen content, stimulating a cooling effect, clean burning and declining combustion temperature [51,52].

In contrast to lower alcohols, characteristics like superior energy density, cetane number, improved mixing stability, lower hygroscopicity, and longer carbon chains are found in higher alcohols. These characteristics enhance the ignition quality of fusel oil [53]. Fuel oil is a higher alcohol produced during fermentation as a byproduct, and its application in internal combustion engines hastened attention during the last decade [54]. Oxygenated fuels improve cylinder combustion and lower emissions [55,56]. Moreover, they can be produced from renewable bio-based sources such as sugarcane, seed oils, waste oils, and beets, further augmenting their attraction as fuel [57]. Among other alcohol family members, ethanol is widely used in passenger vehicles due to its non-toxic nature and higher producibility from bio sources. A lower carbon-to-hydrogen ratio, higher cetane rating, higher flame propagation speed, lower volatility emissions, and safe storage and distribution features make it a reliable fuel [58,59]. In this regard, higher alcohols are gaining much attention because of their properties and ecofriendly production processes. But methanol and ethanol compete with higher alcohols like propanol and butanol [60,61]. The improvement in engine

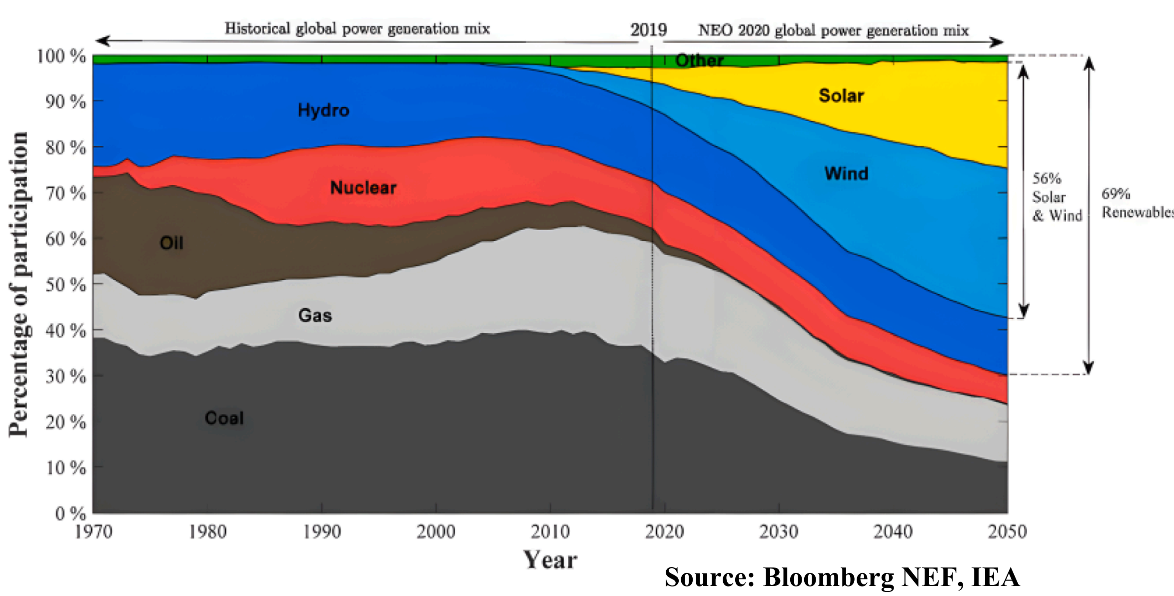

Fig. 1. The worldwide energy consumption trends spanning from 1970 to the projected year 2050 [14].

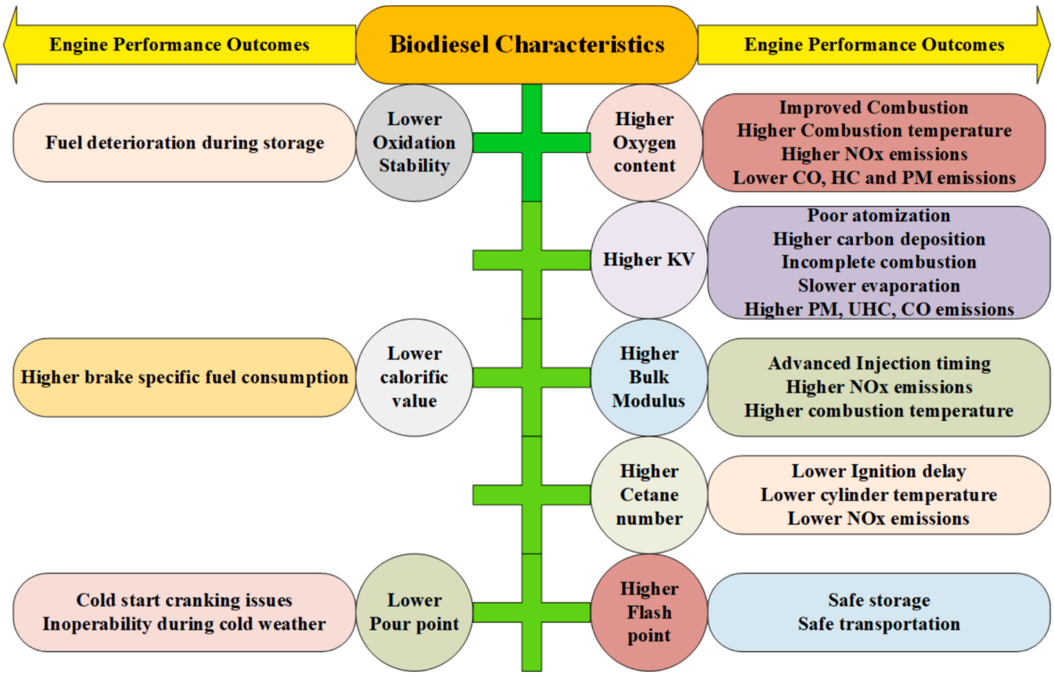

Fig. 2. The characteristics of biodiesel (i.e. lower oxidation stability, higher oxygen content, higher KV, higher bulk modulus, higher cetane number, higher flash point, lower calorific value, and lower pour point) and their influence on engine performance.

Fig. 3. The attributes of a high-quality fuel and its impact on the engine operation.

performance can be reasoned with oxygenated structure and the higher latent heat of isoamyl alcohol, which boosts volumetric efficiency [54].

Bioethanol is a significant contributor to green transport, corresponding to 3 % of the world's energy consumption, and global ethanol production was augmented by 1.85 % in 2019 compared with 2018 [54]. Almost 85 % of global ethanol production through fermentation comes from Brazil and the United States [62]. The addition of nanoparticles to improve fuel properties is an ongoing research field; many advancements have occurred in the relevant field over the past few years. Different nanoparticles with preferred size and dimensions can be created through biological, chemical and physical processes [63]. Some uniquely reported NPs comprised core–shell, polymer-coated magnetite, photo-chromatic, metal oxide, and inorganic nanoparticles [64]. The cetane improver additives are mixed with biodiesel or diesel fuel to surge the cetane number and lower ignition delay (ID). The cold flow property improver additives are blended with biodiesel or diesel fuel to reduce the pour point and resolve the cold start cranking issue.

The antioxidants improve fuel stability, preventing long-term storage deterioration and reducing NOx formation. The characteristics of good-quality fuel are displayed in Fig. 3. Biodiesel, being biodegradable, economically viable, and less toxic, is an attractive alternative to fossil fuel. However, challenges, like poor fuel injection and cold start cranking, are linked with engine biodiesel utilisation. Biodiesel possesses higher viscosity, higher pour point, and lower calorific values, significantly impacting injection characteristics and cold flow properties. In cold climates, biodiesel may result in injector choking, clogging, and filter plugging issues. NOx emissions are also higher for biodiesel fuel because of its oxygenated nature. Fuel additives can be blended with biodiesel blends to enhance engine efficiency. Overall, fuel additives improve engine performance, heat transfer rate, fuel mixture balance, thermo-physical attributes, and lower exhaust emissions.

Lab-scale testing and road transportation are essential in comprehensively investigating blended fuel formulations. It has been reported that there is always some optimum blend composition at which maximum engine performance can be achieved. For instance, Mokhtar et al. [65] conducted both road transportation (up to 50,000 km) and lab scale testing (the batch level at the selected distance covered) to ascertain optimum blend concentration. They used B40 (40 % biodiesel in 60 % diesel) and B30D10 (60 % diesel + 30 % biodiesel + 10 % hydrogenated vegetable oil) and found that the engine operated smoothly for 50,000 km. Both B40 and B30D10 were found to fall within EURO II emission standards. However, B30D10 produced 11.4 % lower CO, 14.7 lower HC and 22.6 % lower PM emissions at the cost of 15 % higher NOx emission in comparison with B40. The deposit test shows that after 50,000 km endurance testing, the deposit at the intake valve and combustion was higher in B40. However, B40 and B30D10 produced similar results in the cold start cranking test. The insoluble content, like pentane and toluene, in engine oil was higher in the case of B30D10. They obtained similar results in terms of metallic particles in engine oil. The fuel blend B30D10 produced almost 2.14 % higher brake power than B40.

The objectives of the current study are as follows:

- Provide a comprehensive overview of the fuel additives available for petroleum fuels, including their chemical compositions, mechanisms of action, and applications.
- Evaluate the effectiveness and performance of various fuel additives in improving fuel quality, engine efficiency, and overall vehicle performance. This includes examining their impact on fuel stability, combustion efficiency, emissions reduction, and engine cleanliness.
- Assess the compatibility of fuel additives with different types of petroleum fuels and engine systems. Discuss any potential safety concerns or risks associated with using certain additives, such as corrosiveness or adverse effects on engine components.
- Analyze the environmental impact of fuel additives, including their potential to reduce harmful emissions such as nitrogen oxides (NOx), particulate matter (PM), and greenhouse gases. Evaluate any claims regarding the eco-friendliness or sustainability of specific additives.
- Identify emerging trends and developments in fuel additives, such as advancements in additive technology, novel formulations, or alternative approaches to fuel enhancement. Discuss potential future directions for research and innovation in this area.

A current study on fuel additives for petroleum fuels can have several potential applications:

- Research and Development: Researchers and scientists in academia and industry can use the review as a basis for further research and development of fuel additives. It can help them identify gaps in knowledge, explore new avenues for experimentation, and design more effective additives to reduce emissions and boost engine performance.
- Engineering and Technology: Engineers and technologists working in the automotive, aerospace, and energy sectors can use the review article to inform their decisions regarding selecting and implementing fuel additives in engines and fuel systems. This can contribute to improving engine efficiency, reducing emissions, and enhancing overall performance.
- Regulatory Compliance: Regulatory agencies and policymakers can utilize the review to understand the current state of knowledge regarding fuel additives and their potential impacts on engine performance, emissions, and environmental quality. This information can inform the development of regulations, standards, and guidelines governing the use of additives in petroleum fuels.
- Industry Practices: Fuel manufacturers, suppliers, and distributors can benefit from the review by gaining insights into the latest trends, technologies, and best practices related to fuel additives. This can help them optimize their product formulations, improve quality control processes, and meet the evolving needs of customers and regulatory requirements.
- Education and Training: Educators and students in academic institutions can use the review as a resource for teaching and learning about fuel chemistry, combustion science, environmental engineering, and related topics. It can serve as a foundational reference for understanding the role of additives in fuel performance and emissions control.

The present study discusses the recent advancements, applications, and technical challenges in fuel additives-assisted engine operations. The fuel additives-assisted engine operations have different practical implications for engine performance. For example, fuel additives help optimize fuel combustion, improving fuel efficiency. Additives can reduce fuel consumption and increase mileage, which is cost-effective for vehicle owners and operators. In addition, many fuel additives are designed to improve combustion efficiency and reduce harmful emissions, which include carbon monoxide (CO), nitrogen oxides (NOx), and particulate matter (PM). Fuel additives can aid in the improvement of air quality and assist vehicles in complying with emission requirements by enabling cleaner combustion. Specific additives are designed to enhance fuel flow and combustion stability in cold temperatures. Additives help alleviate cold weather-related starting and drivability concerns and guarantee reliable engine performance in low temperatures by preventing fuel line freezing, gelling, or waxing. In high-performance or high-compression engines, octane booster additives raise the octane rating of gasoline, which can stop engine knocking. Octane boosters maximize engine performance by enhancing fuel quality and combustion characteristics, enabling more aggressive tuning without running the risk of damaging the engine. Some fuel additives contain corrosion inhibitors that help protect metal surfaces within the fuel system from corrosion and rust formation. Additives can extend the life of fuel system components and save expensive repairs or replacements by protecting vital engine parts from corrosion.

The **novelty** of the current study lies in the comprehensive view of all the significant aspects of fuel additives in petroleum fuels. The review articles typically summarize existing research; the novelty can lie in how the information is synthesized and organized. A novel review may present a fresh perspective on the current state of knowledge, highlighting connections between seemingly disparate studies or identifying overarching themes and trends in literature. Instead of simply summarizing studies, it critically analyzes and evaluates the methodologies, findings, and implications of existing research on fuel additives. By identifying strengths, weaknesses, and gaps in the literature, it is tried to suggest areas for future investigation, as seen in section 15.

2. Diesel fuel additives

Fuel additives are metal-based or biological chemicals that maintain fuel properties without compromising combustion characteristics and efficiency. Fuel additives in minute amounts, ranging from hundreds to thousands of parts per million, can typically blend in base fuel. Fuel additives are categorized into automotive efficiency improvers, distribution system products and refining goods [66–68]. Anti-knocking agents, cetane improvers, antioxidants, and cold flow improvers are all segregated into several groups. A comprehensive list of all the fuel additives that mix with biodiesel or diesel fuel to improve engine performance is shown in Fig. 4.

2.1. Metal-based additives

Metal-based additives act as a catalyst in promoting combustion and ultimately reduce fuel consumption and emissions. Different metal-based additives comprise platinum (Pt), iron (Fe), cerium (Ce), calcium (Ca), barium (Ba), manganese (Mn), aluminium (Al), copper (Cu), magnesium (Mg), gold (Au), silver (Ag), boron (B), silica (Si) graphene, etc. Some other metal-based additives, including nanocupric oxide (CuO), copper chloride ($CuCl_2$), cobalt chloride ($CoCl_2$), ferric chloride ($FeCl_3$), and copper sulphate ($CuSO_4$), are used as fuel-born catalysts. Also, aluminium oxide (Al_2O_3), calcium carbonate ($CaCO_3$), cobalt oxide (Co_3O_4), cerium dioxide (CeO_2), titanium oxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO), and alloys of metals like magnalium (Mg-Al), carbon nanotubes (CNT) and graphene are used as additives. These metal-based additives positively impact exhaust emissions as they act like catalysts with carbon atoms, lower the oxidation temperature, and produce hydroxyl radicals in reaction with water molecules that further improve the soot oxidation [3].

2.2. Oxygenated additives

Combustion requires oxygen or an oxidizing agent in the engine cylinder. Insufficient oxygen results in incomplete combustion, and oxygenated additives improve combustion and reduce exhaust emissions. Therefore, oxygenated additives enhance combustion quality. The prevalent oxygenated additives encompass alcohols (methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, etc.), ethers (ethyl *tert*-butyl ether, di-isopropyl ether, diethyl ether, methyl *tert*-butyl ether, dimethyl ether, etc.), and esters (dicarboxylic acid esters and acetoacetic esters). These additives influence various properties, including oxygen content and ignition temperature reduction, owing to their oxygen content, volatility, viscosity, cetane number, density, and low-temperature behaviours. Despite their advantageous effects, oxygenated additives are associated with drawbacks such as lower heating value, reduced cetane number, inadequate lubricating properties, elevated NOx contents, higher auto-ignition temperature, heat of vaporization, immiscibility, and instability when mixed with pure diesel fuel [69]. By carefully selecting and optimizing the blend ratios of oxygenated additives with traditional fuels, minimising the negative impacts on heating value, cetane number, lubricating properties, and auto-ignition temperature is possible. This can involve fine-tuning the blend composition to achieve the desired balance between performance and drawbacks [30,70].

Moreover, the stabilizers and inhibitors can be added to oxygenated additives to improve their stability and prevent degradation when mixed with pure diesel fuel or other fuels. This can help maintain the integrity of the fuel blend over time and prevent issues such as phase separation or chemical degradation [71]. Engine design and fuel injection systems can be optimized to accommodate the characteristics of oxygenated fuel blends. This can help mitigate issues such as elevated NOx contents and improve overall combustion efficiency, thereby minimizing the negative impacts on engine performance and emissions. Advanced combustion technologies, such as lean-burn engines or exhaust gas recirculation systems, can reduce NOx emissions associated with oxygenated fuel blends [72,73].

2.3. Antioxidant additives

Oxidation may occur in the reaction between fuel molecules and oxygen, leading to fuel deterioration. The fuel deterioration includes sedimentation, fuel darkening organic acid, aldehyde and gum

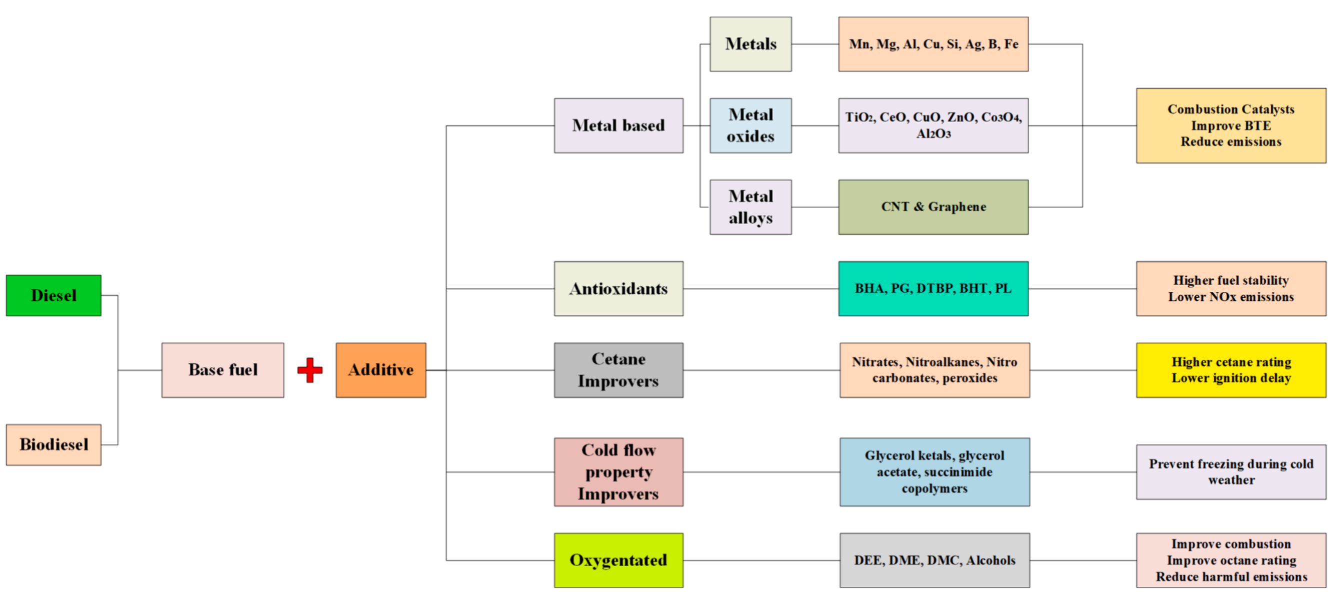

Fig. 4. A list of fuel additives combined with base fuel to improve various engine operation parameters.

formation, and ultimately results in injection problems. Biodiesel is comprised of unsaturated methyl esters, particularly poly-unsaturated methyl esters, which can be readily oxidized like methyl linoleate (C18: 2) and methyl linoleate (C18: 3), which results in acids, aldehydes, esters, ketones, peroxides, and alcohols formation which are decomposed compounds. Biodiesel possesses lower oxidation stability due to its higher unsaturation content. BHA (Butylated hydroxyanisole), DPA (diphenylamine), BHT (Butylated hydroxytoluene), PA (Pyrogallol), TBHQ (Tert-butyl hydroquinone), PG (Propyl gallate) and are antioxidants additives used in diesel–biodiesel blends to avoid auto-oxidation. Antioxidants can also reduce NOx formation and enhance fuel stability by decelerating the pace of the formation of free radicals [74]. The density, acid value, and viscosity of biodiesel and diesel–biodiesel blends may increase after oxidation; however, iodine value decreases as storage time increases [75].

2.4. Cold flow improver additives

The cold flow properties like cold filter plugging point (CFPP), cloud point (CP), and pour point (PP) are related to fuel operation ability at low temperatures. Biodiesel fuels exhibit higher viscosity and increased susceptibility to gelling at lower temperatures than diesel fuel. In colder conditions, the wax content in biodiesel starts to freeze, leading to crystallization that can impact its flow characteristics and cold flow properties. The biodiesel feedstocks significantly impact cold flow properties. Some of the flow improver additives are ethylene vinyl acetate copolymer, glycerol acetates, glycerol ketals, succinimide copolymers, phthalimide, olefin-ester copolymers and dispersants, which may be combined with EVA (Ethylene vinyl acetate) which improve cloud point through preventing the crystal growth [76–78].

2.5. Cetane number improver additives

Ignition delay is the time between the commencement of fuel injection and the start of combustion. Cetane numbers possess an inverse relationship with ignition delay. The cetane number ranges from 48 to 67 in high-speed compression ignition (CI) engines, as a higher cetane rating is required for operations at higher engine speeds. The lower cetane rating results in cold-start issues, lower power, higher fuel consumption, engine noise, and higher exhaust emissions. However, the higher cetane rating decreases the ignition temperature and reduces NOx emissions. Various additives, including nitrates (such as 2-ethylhexyl nitrate, isopropyl nitrate, octyl nitrate, amyl nitrate), nitro alkanes, nitro carbonates, tetra-azoles, peroxides, aldehydes, etc., are utilized to enhance the cetane rating. Among these additives, tertiary butyl peroxide and 2-ethylhexyl nitrate (2-EHN) are the most commonly employed cetane improvers [79,80].

3. Fuel additives characteristics

In this section, the physicochemical properties of all five fuel additives, including oxygenated, metal-based, antioxidants, cetane improver, and cold flow property improver additives, are discussed in detail.

3.1. Oxygenated additives

Compared to conventional petroleum fuels, oxygenated fuels carry economic and environmental advantages as can be used as additive or base fuel in diesel engines without any significant modification at the cost of lower exhaust emissions [81]. However, some complications need to be eradicated regarding their utilization as a blend with diesel fuel in terms of lower lubricity, poor vaporization, and higher auto-ignition temperature. These issues can be overcome by applying them as fuel additives or increasing the intake air temperature [82]. The blending of alcohols in diesel fuel requires emulsifiers or cosolvents as they are immiscible with each other. Blending is expensive due to the separation, splashing, heating, and mixing steps [83]. Although alcohols are immiscible with diesel fuel, they are miscible with biodiesel fuel blends. Therefore, ternary fuel blends (diesel-alcohol-biodiesel) can be used as the same mixture without major miscibility issues [84].

Alcohols as additives can significantly reduce the density and viscosity of biodiesel fuels as they possess lower density and viscosity than diesel/biodiesel fuels. Combustion efficiency can be improved at the cost of lower exhaust emissions for oxygenated additives. There are multiple applications of alcohol in diesel engines, such as direct injection, emulsification, blending, and port injection (fumigation) [85]. The poor miscibility, lower heating value, and higher auto-ignition temperature restrict the limit of alcohol from being exceeded by 20 % in the direct injection method. Therefore, it would be difficult to apply the direct injection method in the case of oxygenated fuels in the engine. Many studies investigate the impact of alcohol usage in engines through the port injection technique as a fumigated additive. In the port injection technique, alcohol is injected into the intake ports while diesel fuel is directly injected. The blending technique ensures the homogeneity of the mixture as additives, while the emulsion method mixes the fuel blend to prevent phase separation, which can displace up to 25 % diesel fuel [82]. The port injection method permits the use of higher alcohol concentration in diesel engines than other methods [86].

The first four members of the alcohol family, i.e., methanol, ethanol, propanol, and butanol, are extensively used in diesel engines by considering the favourable fuel characteristics that allow them to produce optimum results. The higher oxygen content in alcohols transforms carbon-rich particles to CO_2 and significantly decreases PM emissions [87]. Methanol is marked as the first member of the alcohol family with a chemical structure of CH_3OH. Methanol provides better combustion and is extensively available around the globe. Diesel fuel and methanol are not completely miscible because a minuscule amount of water can cause the methanol/diesel mixture to separate into diesel and water-methanol phases [88]. Ethanol is the second member of the alcohol family, and it is a biodegradable, transparent, colourless liquid produced from sugar by yeast, corn, barley and vegetable materials [89]. Ethanol is the most common alternative fuel used worldwide. Brazil is the leading country to consume ethanol as fuel and export sugarcane worldwide [90]. Ethanol is a polar molecule, and its solubility in diesel fuel is influenced by blending ratio, water content and temperature. A higher percentage of ethanol in diesel fuel is difficult, especially at lower temperatures ($<10\,^{\circ}C$) [91]. Ethanol has a lower cetane rating, which is further reduced when mixed with diesel fuel [92]. The higher water content in the ethanol causes phase separation, similar to methanol [93]. Another issue is the ethanol fumigation at the intake manifold [94]. Propanol is the third member of the alcoholic family with three carbon structures, which exist in the form of two isomers, n-propanol and isopropanol/isopropyl alcohol [95]. Both isomers are potential alternatives to lighter alcohols (methanol and ethanol) as blending components with diesel fuel. It is a colourless and flammable liquid [96]. Propanol is majorly produced by oxo-synthesis of a petrochemical process, which is currently the most economical process [97].

There is limited literature on the investigation of the impact of propanol on diesel engine performance and emissions. Butanol can be produced through biomass fermentation, including algae, corn, and plant materials that contain cellulose [98]. Both butanol and propanol are less volatile and toxic than methanol [90]. Despite being of the same family, butanol has distinct physicochemical properties from other members. The physicochemical properties depend on the molecular structure of that particular alcohol type [99]. The significant alcohol fuel characteristics of methanol, ethanol, propanol and butanol are explained below. Moreover, the physicochemical properties of oxygenated fuels are compared in Table 1.

(i) Butanol possesses a higher boiling point; thus, it requires a higher temperature for evaporation. However, butanol easily ignited

Table 1
A comparative assessment between oxygenated fuel additives and diesel fuel based on physicochemical characteristics.

Properties	Laminar flame speed	Boiling point	Cetane number	Density	(A/F)$_s$	Flash point	Calorific value	Auto-ignition temperature	Oxygen content	Latent heat of evaporation	Kinematic viscosity
Diesel fuel [108–113]	0.3 m/s	180–360 °C	51	840 kg/m^3	14.5	≥55 °C	42.5 MJ/kg	256.85 °C	15 %	250 kJ/kg	3.5 mm^2/s
Methanol [11,111,114]	0.52 m/s	64 °C	05	729 kg/m^3	6.5	11–12 °C	20 MJ/kg	470 °C	50 %	1178 kJ/kg	0.54 cSt
Ethanol [53,83,111]	0.39 m/s	78 °C	07	792 kg/m^3	9	17 °C	27 MJ/kg	434 °C	34 %	840 kJ/kg	1.04 cSt
Propanol [111,115]	0.44 m/s	97 °C	12	804 kg/m^3	6.45	11.7 °C	30.6 MJ/kg	350 °C	26.6 %	728 kJ/kg	1.74 cSt
Butanol [111,116]	0.38 m/s	118 °C	25	810 kg/m^3	11.2	35–37 °C	33 MJ/kg	385 °C	22 %	585 kJ/kg	2.20 cSt
Pentanol [111,117]	0.42 m/s	138 °C	20	814 kg/m^3	12.5	49 °C	34.7 MJ/kg	300 °C	18.2 %	308 kJ/kg	2.89 cSt
Hexanol [107,111]	–	157 °C	23	822 kg/m^3	15.5	59 °C	39.1 MJ/kg	285 °C	15.7 %	486 kJ/kg	5.32 cSt
Octanol [107,111]	–	195 °C	39	827 kg/m^3	17	76 °C	52.9 MJ/kg	270 °C	12.3 %	538 kJ/kg	5.8 mm^2/s
DEE [118]	–	34.6 °C	125	710 kg/m^3	–	–	35.6 MJ/kg	160 °C	21 %wt	33.9 kJ/kg	1.21 mm^2/s
DME [118]	–	−25 °C	61	667 kg/m^3	–	–	–	239 °C	35 %wt	21 kJ/kg	–
DMC [119]	–	90 °C	52	847 kg/m^3	–	95 °C	38.7 MJ/kg	–	–	–	3.3 mm^2/s

under atmospheric conditions due to the lowest autoignition temperature [100].

(ii) Both butanol and propanol are suitable for diesel engines, while other alcohol family members are suitable for gasoline engines [101].

(iii) Both butanol and propanol possess a higher calorific value and flash point than methanol and ethanol, offering better engine performance and safer storage [102,103].

(iv) Methanol and ethanol possess higher heat of vaporization; thus, both fuels experience longer ignition delay (ID) during combustion in contrast to butanol [90].

Table 1 displays the physicochemical properties of oxygenated additives. Alcohol additives possess lower density and viscosity than diesel/biodiesel fuel and are responsible for stable and soluble fuel blends, making fuel blend pumping easy. The lower boiling point plays a significant role in the atomization, vaporization and burning of fuel additives, resulting in uniform combustion. Both oxygen content and cetane rating of alcohol additives are desirable to reduce knocking and ignition delay and improve combustion [104]. Fuel additives with lower latent heat of evaporation let the combustion process take place more appropriately, but primarily, oxygenated additives possess higher latent heat than diesel fuel. Fuel consumption and fuel efficiency should be considered when selecting fuel additives, and it is recommended to use fuel additives with higher calorific values for optimum engine performance.

Moreover, the auto-ignition temperature should be lowered for appropriate combustion. The combustion quality can be improved due to higher oxygen content in the case of alcohols. The improved combustion results from lower ignition delay, lower ignition temperature and lower heat losses [105]. It is evident from Table 1 that lower alcohols possess higher oxygen content and lower calorific value than higher alcohols. Furthermore, the calorific value of oxygenated additives is lower than that of biodiesel fuels, which is mainly responsible for more fuel consumption [106]. The alcohols with higher carbon chains (5–20), higher cetane number, and higher density closely resemble diesel fuel.

Moreover, the higher alcohols exhibit a calorific value more significant than that of lower alcohols. Due to its lower water solubility than n-butanol, hexanol can be seamlessly blended with diesel fuel using the splash method. Additionally, hexanol is considered safer than n-butanol due to its lower volatility. When mixed with diesel fuel, hexanol contributes to combustion promotion, as evidenced by its oxygen content of approximately 15.7 % [107]. The main disadvantage of higher alcohols is their higher viscosity. Hence, evaluating and investigating the optimal blending ratio of long-carbon alcohols with diesel fuel is imperative, potentially up to 20 %. Fig. 5 indicates the variation in physicochemical properties for increasing alcohols from methanol to octanol.

3.2. Metal-based additives

Nanotechnology is an emerging scientific area that deals with changes in matter at the atomic or molecular level [63]. A nanoparticle (NP) is an ultrafine particle with a length dimension of 1 to 1000 nm and a diameter range of 1 to 100 nm [120]. NPs are classified by form, structure, occurrence, size, material, and origin. Nanomaterials are generally classified into the following ways: carbon, metals (Cu, Ce, Pt, Fe, B, CO, and Al), metal oxides, and carbon-based materials [99]. The NPs are available in a variety of configurations (one-dimensional or multidimensional), shapes (cube, sphere, rectangle, and cylinder), sizes (1–100 nm), and different materials [99]. The application of NPs in

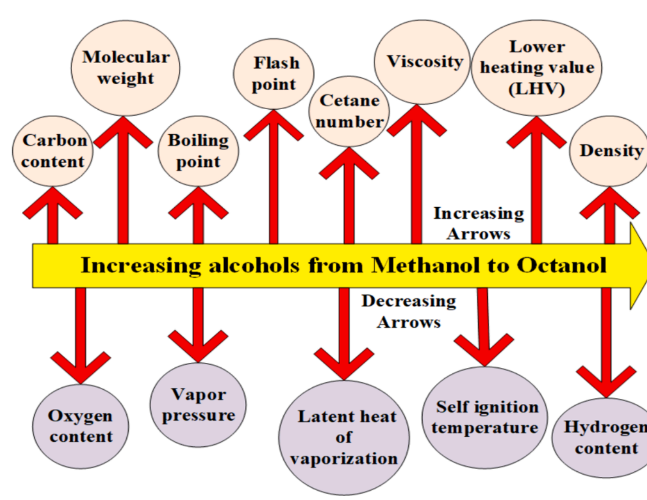

Fig. 5. The change of physicochemical properties of alcohol with increasing chain length from methanol to octanol.

biofuel production processes is thriving due to its exceptional impact on chemical reactions. Nanomaterials like nanofibers, nano-metals, nanotubes, and metallic mixtures have been used as additive chemicals in biofuel production to improve the physicochemical properties of the fuel. Thus increasing combustion efficiency and performance properties and reducing hazardous emissions [45].

NPs can be proven effective and efficient sources in improving fuel properties of diesel/biodiesel without any significant modification in diesel engines. The distinctive physicochemical properties of NPs are mainly responsible for their prevalent usage as fuel catalysts to improve engine efficiency and minimize fuel consumption, ID, smoke, and toxic emissions [121]. An exceptional NP additive should be competent to mitigate exhaust emissions, improve oxygen concentration and particulate filter ability, enhance fuel stability, and decrease ID and FP. Nanotechnology has led to the development of nano-scale particulate matters (PMs) with physicochemical attributes that vary because of micron-scale elements of similar source materials like the wider surface contact area, lower melting point, increased stability, quick oxidation, lower heat of fusion rate, higher heat of combustion, and higher heat and mass transfer rates [122–124].

NPs can improve biofuel synthesis, portraying incredible catalytic potentials for bio-feedstock transesterification [2]. Baskar et al. [125] determined the optimal reaction conditions for maximizing biodiesel yield using zinc oxide as a nano-catalyst. They employed a central composite design (CCD) within the response surface methodology (RSM) framework to manipulate key reaction parameters, including the alcohol-to-oil ratio, reaction temperature, reaction time, and catalyst dosage. The highest biodiesel yield, reaching 95.2 %, was achieved under the following conditions: a reaction temperature of 55 °C, a methanol-to-oil ratio of 8 mol, and a catalyst dosage of 11.07 %, with a reaction time of 60 min. Hebbar et al. [126] investigated the optimum reaction conditions for Bombax Ceiba oil biodiesel processing using CaO. The CCD in RSM achieved a biodiesel yield of 96.2 %. The best-predicted reaction conditions were at 600 rpm, catalyst amount of 1.5 wt%, alcohol: oil ratio of 10.37:1, and temperature of 65 °C, at 60 min reaction period. A nano-catalyst can be recycled for around five reaction cycles to achieve a higher yield rate. The carbon-based nanoparticles can be used as catalysts in *trans*-esterifying vegetable oils for optimum yield rate.

3.2.1. Nanoparticle combustion stages

Combustion of nanoparticles additive fuel occurred in five stages: (i) Preheating and ignition stage, (ii) Classical droplet combustion stage, (iii) Micro explosion stage, (iv) Surfactant flame stage, (v) Nanoparticle droplet flame stage. In the preheating and ignition stage, base fuel evaporated on the droplet surface, and a vapour cloud formed adjacent to the fuel droplet [127]. The droplet combustion stage is like the standard burning behaviour of single-component droplets. A distinct flame envelope is formed around the primary droplet in this stage. Few nanoparticles are ignited, and burning nanoparticles rose rapidly to include multiple flares, leading to flame disruption. Small bubbles are included within the main fuel droplets during the flame disruption. These bubbles grow and merge into a single bubble. The formation of bubbles within primary droplets builds up powerful pressure inside the primary drop. Because of the building up of intense pressure, primary fuel droplets swell and eventually explode into smaller droplets and nanoparticle aggregates, which ignite and burn, forming narrow flames. This phenomenon of rapid fragmentation of primary fuel droplets into smaller droplets is known as micro explosion.

During the surfactant flame stage, the cover diffusion flame went off. Soon after that, a second flame was initiated about the big agglomerate. It lasted for a short period, about 0.1 s before it was extinguished. The flame looks like an envelope diffusion flame. In this stage, combustion of the surfactant or its pyrolysis products takes place. During the nanoparticle droplet flame stage, the flame is characterized by a halo and smoke. The smoke tail is due to a diffusion of the aluminium oxide outwardly and upwardly. The aluminium droplet flame lasted about 0.4 s, comparable to the classical combustion stage [128]. Table 2 depicts the physicochemical properties of metal-based additives.

3.3. Properties of antioxidants

The antioxidants can be used as additives in diesel fuel/biodiesel blends to improve fuel stability. The most common antioxidant additives are butylated hydroxyl anisole (BHA), diphenylamine (DPA), butylated hydroxyl toluene (BHT), pyrogallol (PL), propyl-gallate (PG), *tert*-butyl hydroxyquinone (TBHQ), Di-tert butyl peroxide (DTBP) and others which their physicochemical properties as displayed in Table 3. Antioxidant additives have higher boiling points. This property ensures the additives remain stable at high temperatures in the diesel engine's combustion chamber. The higher boiling point helps prevent the antioxidants from vaporizing or breaking down under operating conditions, allowing them to perform their intended function effectively. Flashpoint refers to the minimum temperature when a substance gives off enough vapour to form an ignitable mixture with air. Antioxidant fuel additives typically have higher flash points, reducing the risk of ignition or combustion at lower temperatures. This property helps enhance the safety of the fuel and reduces the chances of uncontrolled combustion or fire hazards. The melting point of antioxidant additives is not a critical factor in diesel engines. However, these additives should have low melting points.

A lower melting point ensures that the additives can easily mix with the diesel fuel and distribute evenly throughout the system, improving their effectiveness in inhibiting oxidation reactions. Autoignition is the minimum temperature required to ignite a substance spontaneously without an external ignition source. Antioxidant fuel additives can help in increasing the autoignition temperature of diesel fuel. Raising this temperature reduces the risk of premature ignition or knocking in the engine, allowing for more controlled combustion and improved overall engine performance. The density of antioxidant fuel additives is typically like that of diesel fuel. Having a similar density ensures that the additives can blend effortlessly with the fuel without causing any significant changes in the overall density of the mixture. This property is essential to maintain accurate fuel metering and consistent combustion performance in the engine. Overall, the favourable properties of antioxidant fuel additives in terms of boiling point, flash point, melting point, and autoignition temperature contribute to increased stability, enhanced safety, and improved combustion characteristics in diesel engine.

3.4. Properties of cetane improver additives

The core purpose of applying cetane improver fuel additives is to improve the fuel's cetane rating to reduce ignition lag so that combustion may occur appropriately. Therefore, cetane improvers possess a higher boiling point as they ensure that additives do not evaporate quickly during fuel storage and combustion. Moreover, higher boiling points also provide a wide range of operability. The higher flash point reduces the risk of accidental fire and unintended ignition during handling, storage, and fuel transportation. A lower melting point facilitates the blending process and improves the overall stability of the fuel-additive mixture. Cetane improver additives aim to lower the autoignition temperature of diesel fuel, making it easier for the fuel to ignite during the combustion process. This property helps ensure reliable ignition and smooth engine operation. Density is desirable as it enables the additive to mix uniformly with the fuel without causing phase separation or sedimentation issues. Matching densities between the additive and fuel ensures homogeneous combustion and avoids potential engine problems. Table 4 presents the physicochemical characteristics of cetane improver additives.

Table 2
The physicochemical properties of blends comprise base fuel and nanoparticle additives, explicitly focusing on metal-based additives.

Authors	Base fuel	Nanoparticle additives	concentration	Fuel properties				
				Density (kg/ m^3)	Viscosity (cSt)	Flash point (°C)	Calorific value (MJ/kg)	Cetane Number
Sajin et al. [129]	Mango seed biodiesel	ZnO	40 ppm	790	3.6	171	38.75	59
Ang et al. [130]	Diesel fuel	CNT	50 ppm	846	3.86	–	50.18	54.8
		SiO_2	50 ppm	835	3.98	–	47.78	55.2
		Al_2O_3	50 ppm	856	3.81	–	49.32	55.3
Hoang et al. [131]	Diesel fuel	CuO	50 ppm	833–834	3.3–5.8	60	42–45	48–57
Feroskhan et al [132]	Diesel fuel	CeO_2	25 ppm	825–848	3.3–5.8	49–62	40.9–45.1	47
Devarjin et al. [133]	Palm stearin biodiesel	AgO	10 ppm	797	3.71	132	38.54	–
Nanthagopal et al. [134]	Calophyllum inophyllum biodiesel	ZnO	50 ppm	871.1	4.76	123	37.02	54
		TiO_2	50 ppm	869.2	4.73	123	37.12	53
Anchupogu et al. [135]	Calophyllum inophyllum biodiesel	Al_2O_3	40 ppm	858	3.64	64	41.44	54.58
Najafi [136]	Diesel-Biodiesel blend	Ag	40 ppm	854.7	4.36		46.44	47
		CNT	40 ppm	879.9	4.74		47.12	57
Hoang et al. [131]	Diesel-Biodiesel blend (B20)	Fe_2O_3	100 ppm	843–859	3.4–3.5	76–81	41.6	49–51
Hoang et al. [131]	Biodiesel (B100)	MgO	30–50 ppm	874–896	3.23–5.09	150–180	25.8–42	51–55
Mehta et al. [137]	Diesel fuel	B_2O_3	0.5 %wt	825–855	1.3–4.1	60–80	42–45	48–57
Mehregan et al. [138]	Biodiesel (B20)	Mn_2O_3	50 ppm	830	3.1	140	41.6	50
Karthikeyan et al. [139]	Biodiesel (B20)	CO_3O_4	50–100 ppm	830–841	3.1–5.72	39–140	37–41.6	46–50
Zaharin et al. [60]	Biodiesel-diesel blend	Graphene oxide	20,40, and 60 ppm	834.6–836.5	3.1–3.65	132.3–132.8	40.8–41.08	53.8–54.36
Arunprasad et al. [140]	Algae-based biodiesel (B20)	MgO	50 ppm	891	6.19	126	40.23	–
Celik [141]	cottonseed biodiesel	Manganese	16 ppm	851	2.65	46	39.56	–

3.5. *Properties of cold flow improver additive*

The primary purpose of a cold flow improver fuel additive is to reduce cloud point (CP), pour point (PP), and cold filter plugging point (CFPP) so that fuel burns appropriately even at lower temperatures. Pour point testing identifies where a liquid sample ceases to flow. It is the temperature at which fuel forms a wax cloud. This condition is detrimental to any engine as solidified wax thickens the fuel and clogs the fuel filters and injectors. A lower cloud point is advantageous because it allows the diesel fuel to remain fluid and free-flowing at lower temperatures. This ensures that the fuel can be readily pumped, atomized, and efficiently combusted in the engine, even in cold weather conditions. It helps prevent the formation of wax crystals and the associated issues of filter plugging, fuel line blockages, and impaired fuel delivery.

The CFPP method determines the low-temperature operability of diesel fuel, biodiesel, blends, and gas oils. The CFPP is a critical property used to forecast the lowest temperature at which fuel will freely flow through filters in a diesel engine system. CFPP should be lower for better engine operations. The pour point is the temperature at which the fuel loses its flow characteristics and becomes too viscous to pour. It measures the fuel's ability to flow at low temperatures. A higher pour point means the fuel will become denser and more challenging to wash at lower temperatures. This can result in fuel line blockages and insufficient fuel supply, leading to starting difficulties and poor engine performance in cold weather. Therefore, a lower pour point is desired to ensure proper fuel flow and prevent operational issues during cold starts. Table 5 represents the physicochemical properties of the cold flow improver additive.

4. Literature review

Table 6 contains all the relevant literature regarding fuel additives affecting engine performance, exhaust emissions, combustion behavior, and fuel properties for the distinct proportion of additives, operating conditions, and diesel engine specifications. Nano particles depict promising potential in energy applications, but only their scope in alternative fuels is discussed to converge the current study to alternative fuel additives. Lai et al. [163] used nanoparticles to optimise diesel engine performance as an additive in tyre pyrolysis biodiesel. They ascertained the coefficient of friction (COF), surface roughness (Ra), wear scar diameter (WSD) by varying load from 20 to 60 kg, engine speed from 1000 to 1400 rpm and nanoparticles concentration from 0 to 0.2 wt%. The optimal speed, load, and concentration values for the MgO nano fuel model were 1000 rpm, 26.99 kg, and 0.0531 %wt.; for the graphene nano fuel model, the values were 1161.73 rpm, 21.83 kg, and 0.105 %wt., and for the Al_2O_3 nano fuel model, the values were 1109.3 rpm, 30.37 kg, and 0.0107 %wt., in that order. The investigation showed that the tribological behavior of the Al2O3, graphene, and magnesium oxide nanofuels had improved. The optimized Al_2O_3 nano fuel showed the best tribological performance with the lowest concentration, price, load, and speed, in contrast to MgO and graphene nano fuel. Table 6 shows that many researchers used cerium oxide (CeO) [164,165], copper oxide (CuO) [166,167], magnesium additive [168], alumina additive [169–173], graphene additive [174 175], silica additive [176], titanium dioxide additive (TiO_2) [177], zinc oxide (ZnO) [178], carbon nanotubes (CNT) [179], cobalt oxide [180], silver additive [181], manganese additive [182]. The results show that emissions like NOx and HC decrease, BTE and flash point increase, but viscosity decreases for higher concentrations and increases for lower concentrations of cerium oxide.

Emissions like CO, HC, and CO2 decrease for CuO particles, but NOx decreases and increases for higher concentrations. The performance parameters like BTE and EGT usually increase, but BSFC increases for lower concentrations and decreases for higher concentrations. The physicochemical properties like density and KV increase, but calorific value (CV) decreases for lower concentrations and increases for higher concentrations. The flash point (FP) increases for lower concentrations and decreases for higher concentrations. The in-cylinder pressure and heat release rate increase and the ignition delay for CuO particles decreases. For magnesium (Mg) particles, the BTE increases, BSFC decreases, CO decreases, NOx increases, ignition delay increases and

Table 3
The summary of the physicochemical properties of antioxidants fuel additives.

Properties	Antioxidant											
	BHA [142,143]	BHT [144]	PL [145]	PG [146]	GE [145]	TBHQ [142,147]	NPPD [142,148,149]	PPDA [150]	AT [150]	LA [150]	DPPD [142,151]	DTBP [152,153]
Chemical formula	$C_{11}H_{16}O_2$	$C_{15}H_{24}N$	C_6H_6O	$C_{10}H_{12}O_5$	$C_{10}H_{18}O$	$C_{10}H_{14}O_2$	$C_{12}H_{12}N_{12}$	$C_6H_8N_2$	$C_{31}H_{52}O_2$	$C_6H_8O_6$	$C_{18}H_{16}N_2$	$C_8H_{18}O_2$
Molecular weight (g/mol)	180.25	220.4	126.11	212.20	154.25	166.2	184.24	108.14	430.71	176.13	260.3	146.23
Flash point (°C)	112	127	–	–	–	–	193	154	–	–	87.6	95
Boiling point (°C)	264–270	265	309	–	230	273	276	267	200–220	553	220–225	111
Melting point (°C)	48–55	72	–	150	–	127–129	68	145–147	2.5–3.5	190	143–145 °C	−40
Auto-ignition temperature (°C)	315	470	–	–	–	–	–	–	–	–	–	165
Density (g/cm^3)	1.06	–	1.45	–	0.889	1.050	1.36	1	0.95	1.69	1.2	0.750

Table 4
The comprehensive assessment of physicochemical properties of cetane improver additives.

Properties	Cetane Improver Additives	
	DTBP [152,154–156]	2-EHN [156–159]
Chemical formula	$C_8H_{18}O_2$	$C_8H_{17}NO_3$
Molecular weight (g/mol)	146.34	175.23
Flash point (°C)	18	76
Boiling point (°C)	109	307
Melting point (°C)	−40	–
Cetane number	104	≥76
Auto ignition temperature (°C)	165	215
Density (kg/m^3)	0.79	0.963

Table 5
The comprehensive assessment of physicochemical properties of cold flow improver additives.

Fuel Additives	Flash point (°C)	viscosity mm^2/s	Freezing point (°C)
Diesel + PMA [160 161]	74	3.86 at 40 °C	−3
Diesel + PMA + GO [160]	77	3.86 at 40 °C	–
OECP [161]	–	18.64 at 100 °C	−5
EACP [161]	–	15.58 at 100 °C	−7
1,4-Dioxane [162]	95	3.76 at 40 °C	−10

cylinder peak pressure increases. For alumina additive, brake power increases, BTE increases, BSFC decreases, BSEC decreases, HC decreases, CO decreases, NOx increases, combustion pressure increases, and heat release rate (HRR) increases. However, the ignition delay increases for lower concentrations and decreases for higher concentrations. However, a research gap exists in the comprehensive analysis of the impact of alumina additives on physicochemical properties.

For graphene additives, performance parameters like BTE increases and BSFC decreases, and emissions like CO, HC and NOx decrease. The combustion parameters like ignition delay decrease, HRR increase, and cylinder peak pressure increase. For silica additives, the performance parameters like BTE and BSFC increase, CO and HC emissions decrease, but NOx emissions increase. The physicochemical properties like KV and CV increase, but FP and density decrease. For TiO_2 additive, the engine performance parameters like torque, BP, BTE, and EGT increase and BSFC decrease. Exhaust emissions such as CO, CO2, and NOx decrease. The properties like flash point, calorific value and cetane rating increase, but KV decreases for lower concentrations and increases for higher concentrations. For ZnO, the performance parameters like BP, EGT, and BTE increase and BSFC decreases. The emissions like CO and HC decrease. The properties like KV, FP, cetane number, and calorific value increase. For CNT, the engine efficiency, flash point, calorific value, CO and HC emissions decrease. However, the NOx, KV and density increase. For cobalt oxide additives, emissions like CO, NOx, and HC decrease, along with an increasing trend in BTE. Silver fuel consumption and emissions like CO, HC and NO_X are declining. However, the brake power and CO_2 emission increase. The BSFC, CO, HC, ICP, ID and KV decrease for the manganese additive. However, the NOx emission increases. The above-stated behaviour of NPs is due to their higher surface and improved reactivity, leading to improved combustion, lower emissions and higher fuel efficiency [183–185]. Moreover, thermal stability prevents fuel degradation [186,187].

Table 6 summarizes the impact of oxygenated additives (Methanol, Ethanol, Propanol, Butanol, Pentanol, Hexanol, Octanol. Decanol, DEE, and DME) on engine performance and emission along with variation in physicochemical properties of blended fuel [4,11,13,112,188–195]. The brake power and torque in the case of oxygenation sometimes show mixed trends, either increasing or decreasing. The brake power and torque increase due to higher flame speed and oxygen content [196,197]. However, the lower calorific value contributes to lower

Table 6
A detailed representation of published research articles detailing the authors' affiliations, the variety of additives utilized across different operating conditions and engine types, and the significant findings regarding engine performance, emissions, combustion behaviour, and variation in physicochemical properties.

Authors with reference, year	Additives	Operating Conditions	Engine specifications	Findings Engine performance	Emissions	Combustion behaviour	Properties
Sajeevan and Sajith [164]	Cerium oxide (5–40 ppm) in diesel fuel	A standard ultrasonic shaker (Power Sonics 405) has been used to mix the nanoparticles to obtain a stable nanofluid. Experiments were conducted at a constant 1500 rpm.	A water-cooled single-cylinder diesel engine of 5.5 kW rated power.	BTE 6 %	HC 40–45 % NOx 30 %	–	FP Viscosity
Sajith et al. [165]	Cerium oxide (20–80 ppm and 10–20 nm size) in jatropha biodiesel diesel fuel	A standard ultrasonic shaker (Power Sonics 405) has been used to mix the nanoparticles to obtain a stable nanofluid. Experiments were conducted at a constant 1500 rpm.	A water-cooled single-cylinder diesel engine of 5.5 kW rated power.	BTE 1.5 %	HC 25–40 % NOx 30 % CO (unchanged)	–	Viscosity Volatility FP
Perumal and Ilangkumaran [166]	CuO nanoparticles (100 ppm) in Pongamia biodiesel	All experiments were conducted at constant load and speed (1500 rpm)	A diesel engine of 562 cc and rated power of 3.7 kW.	BTE 4.01 % BSFC 1.01 %	HC 7.9 % NOx 9.8 % CO 29 %	ICP HRR ID	Calorific value Density KV FP Ash
Rastogi et al. [167]	CuO nanoparticles (25, 50, and 75 ppm) in Jojoba biodiesel	All experiments were conducted at variable loads (0,25,50,75 and 100) at constant speed (1500 rpm).	A water-cooled single-cylinder diesel engine of 5.2 kW rated power.	BTE 1–2 % BSFC 16–24 % EGT 5–12 %	CO 2–3 % HC 4–7 % CO_2 2–5 % NOx 0.4–1.8 % Smoke opacity 5–8 %	ICP 1–1.6 % HRR 4–5 % ID	Calorific value Density KV FP
Guru et al. [168]	Magnesium additive (12 micro-mol) in chicken fat biodiesel (B10)	Engine tests were conducted at full load operating conditions and speeds from 1800 to 3000 rpm.	A single-cylinder 395 cc diesel engine.	BSFC 5.2 % BTE 4.8 %	CO 13 % Smoke 9 % NOx 5 %	ID Cylinder peak pressure	–
Gurusala and Selvan [169]	Alumina (25 and 50 ppm) in waste chicken fat biodiesel (B20 and B40)	Experiments were conducted at fixed 1500 rpm with a variable compression ratio between 5 and 20.	A single-cylinder diesel engine of 3.7 kW.	BSFC BTE	HC 40 % NOx CO 18 % Smoke 65 %	ID Cylinder peak pressure	–
Soudagar et al. [174]	Graphene (20, 40 and 60 ppm) in dairy scum oil	All experiments were conducted at 80 and 100 % load.	A single-cylinder diesel engine of 638 cc and 17.5 CR	BTE 11.56 % BSFC 8.34 %	CO 38.62 % NOx 5.62 % HC 21.68 %	ID Cylinder peak pressure HRR	KV 14.3 % CV 0.7 % FP 0.4 % CN 3.3 % Density 0.6 %
EL-Seesy and Hassan [175]	Graphene oxide (50 mg/l, 1.2 nm thick and 7 µm wide) in jatropha biodiesel	All experiments were conducted at 2000 rpm and loading conditions (0, 3, 6, 9, 12, 13.5 Nm).	A single-cylinder diesel engine of 347 cc and 21.5 CR.	BTE 25 % BSFC 35 %	CO 55 % NOx 45 % HC 50 %	ID Cylinder peak pressure HRR	–
Gavhane et al. [176]	SiO_2 nano additive (25,50,75 ppm) in soybean biodiesel through ultrasonicator	All experiments were conducted at 1800 rpm and loading conditions (0, 3, 6, 9, 12 kg).	A single-cylinder diesel engine of variable CR from 12 to 21.5.	BTE 3.48–6.39 % BSFC 5.81–9.88 %	CO 1.9–17.5 % NOx 7.6–10.25 % HC 20.56–27.5 % Smoke 10.16–23.54 %	–	KV 12.28 % CV 3.92 % FP 10.26 % Density 3.67 %
Fangsuwannarak and Triratanasirichai [177]	0.2 % TiO_2 in 99.80 % palm oil biodiesel	The required quantity of the additives was measured using a precision electronic balance. Each required additive was mixed with the tested fuel using an ultrasonic shaker for 15 min to produce the uniform suspension.	A four-cylinder diesel engine of 2982 cc and 17.9 CR.	BSFC 13.22 % BP 7.78 % Torque 1.01 %	CO CO_2 NOx		KV 1.88 % FP 4.41 % Specific gravity 0.61 % Carbon residue 20 %
Karthikeyan et al. [178]	ZnO (50 and 100 ppm, size being less than 100 nm) in Promolin Stearin waxbiodiesel	Experiments were conducted at 0, 25, 50,75 and 100 % load at 1500 rpm and 220 bar injection pressure.	A single-cylinder diesel engine of 17.5 CR.	BSFC BTE BP EGT	CO HC Smoke NOx (unchanged)		KV 6.45 % FP 2.17 % Cetane number 1.75 % Calorific value 0.5 %

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Table 6 (*continued*)

Authors with reference, year	Additives	Operating Conditions	Engine specifications	Findings Engine performance	Emissions	Combustion behaviour	Properties
Tewari et al. [179]	Carbon nanotubes (25 and 50 ppm, average particle size of 10–30 nm) in Honge oil methyl ester	During the experiment, compression ratio, injection opening pressure and injectionThe timing was kept at 17.5, 205 bar and 23 bTDC for diesel operation and 17.5, 230 bar and 17.5 bTDC for HOME-MWCNT.	A single-cylinder diesel engine of 17.5 CR.	BTE 3 %	Smoke HC 29.2 % CO 40 % NOx 3.44 %	–	Density 2.05 % FP 2.35 % KV 1.79 % Calorific value 4.04 %
Ganesh and Gowrishankar [180]	Particle size of 38–70 nm cobalt oxide in Jatropha biodiesel	Experiments were conducted against brake mean adequate pressure (BMEP) of 1.3, 2.6, 3.9 and 5.2 bar, corresponding to 25, 50, 75 and 100 % load of the test engine.	A single-cylinder diesel engine of 661 cc and 17.5 CR.	BSEC 2 % BTE 0.6 %	HC 60 % NOx 46 % CO 3 %	–	–
Saraee et al. [181]	Silver (30–50 nm and 10, 20, 40 ppm)	All experiments were conducted under 8 mode tests.	A multi-cylinder diesel engine of 16 CR.	BSFC BP	CO CO_2 NO_X HC	–	–
Uyaroğlu et al. [182]	5 mμMol/L organic manganese additive in crambe orientalis biodiesel	All experiments were conducted at 2200 rpm, 3.75, 7.5, 11.25, and 15 Nm.	A single-cylinder diesel engine of 395 cc and 18 CR.	BSFC 3–4 % ITE	CO 12–15 % HC 4–31 % NOx	ICP 1.2 % ID	KV
Bitire et al. [170]	Al_2O_3 (10, 20, and 30 ppm) in lemongrass biodiesel blend	All experiments were conducted at 1500 rpm, varying loads from 0 to 100 %.	A single-cylinder diesel engine of 17.5 CR.	BSEC BP 2.71 %	HC 5.98 % NOx 2.25 % CO 15.15 %	Combustion pressure 4.75 % HRR 20.4 % ID	–
Attia et al. [171]	Al_2O_3 (10–50, and 100 ppm) in jojoba biodiesel blend through ultrasonicator.	All experiments were conducted at 1300 and 1500 rpm and varying loads from 0 to 75 % with a gap of 25 %.	A single-cylinder diesel engine of 824 cc.	BSFC 6 % BTE 2.71 %	HC 55 % NOx 70 % CO 75 %	Combustion pressure 4.75 % HRR 20.4 % ID	
Soudagar et al. [172]	Al_2O_3 (20, 40 and 60 ppm) in Honge biodiesel blend through ultrasonicator	All experiments were conducted at 1500 rpm, varying loads from 80 to 100 %.	A single-cylinder diesel engine of 638 cc and 17.5 CR.	BSFC 11.6 % BTE 10.57 %	HC 26.72 % NOx 11.27 % CO 48.43 % Smoke 22.84 %	Combustion pressure HRR ID	–
BALAJI and CHERALATHAN [173]	Al_2O_3 (100–300 ppm) in Neem oil biodiesel blend	All experiments were conducted at 1500 rpm, and the brake mean effective pressure was reduced from 1.3 to 5.2.	A single-cylinder diesel engine of 661 cc and 17.5 CR.	BSFC 11.6 % BTE	HC 10.37 % NOx 7.81 % CO 16.56 %	Combustion pressure HRR ID	
Shafii et al. [219]	0.4 and 0.8 % volumetric proportions of ferrofluid in diesel fuel	Experiments were conducted at a constant speed (2200 rpm) with load varied from 40 to 170 kPa.	A multi-cylinder diesel engine of 1800 cc and 17 CR.	BSFC 10.85 % BTE 12.17 %	CO 42 ppm NOx 24 ppm	–	–
Ramachandran [220]	Ferrofluid of 10 nm size and 4,8 and 12 % in diesel fuel	Experiments were conducted at a constant speed (1500 rpm) with no load, 50, 75 and 100 % load conditions.	A single-cylinder diesel engine of 5 HP rated power.	BSFC 18.18 % BTE 21.43 %	NOx 30 ppm CO 43 ppm	–	–
Sarıkoç et al. [188]	Butanol (5,10,20 %v) mixed in biodiesel blend (20 % biodiesel in 80 % diesel)	The experiments were performed with maximum engine torque (1400 rpm) and maximum engine power (2800 rpm) with full throttle and engine load conditions.	A single-cylinder diesel engine of 510 cc.	Torque SFC Energy efficiency	CO NOx CO_2	–	LHV H/C O/C
Zhang et al [189]	Methanol (10 %, 20 %, 30 %, and 40 %) in diesel fuel	All experiments were conducted by varying engine speeds from 1000 to 4000 rpm.	A multi-cylinder diesel engine of 14 CR.	BP 1.07–15.45 % Torque 1.08–15.45 % BSFC 3.77–17.61 % BTE 19.51 %	Soot 0.25–25.28 % NOx 1.65–4.90 % for DM20-40 NOx 1.18 % for DM10 CO 56.59 % HC 14.24 %	ID ICP 0.89–3.17 % ICT 0.27–0.87 %	LHV Calorific value KV

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Table 6 (*continued*)

Authors with reference, year	Additives	Operating Conditions	Engine specifications	Findings Engine performance	Emissions	Combustion behaviour	Properties
Huang et al. [190]	Methanol (10 and 20 %v) blended in soybean biodiesel fuel	All experiments were conducted at 10 %, 30 %, 50 %, 70 %, and 90 % at 1800 rpm	A multi-cylinder diesel engine of 2982 cc.	EGT	CO HC NOx 1,3 butadiene Benzene Acetaldehyde	ICP ID for DM20 ID for DM10 HRR CD	LHV Calorific value KV Density FP
Ashok et al. [4]	Hexanol (30–40 %v) in Calophyllum Inophyllum biodiesel (10–20 %v)	All experiments were conducted at 1500 rpm, and engine load varied from no load to 25 %, 50 %, 75 %, and 100 % maximum load.	A single-cylinder diesel engine of 661 cc and 17.5 CR.	BTE 4.7–9.5 % BSFC 22.5–33.8 %	CO HC NOx 3.5—5.56 %	ICP 1.68–1.82 % HRR 0.26–1.04 % ID 5.92–9.88 %	–
	Octanol (30–40 %v) in Calophyllum Inophyllum biodiesel (10–20 %v)			BTE 10.5–11.5 % BSFC 36.5–39.1 %	CO HC NOx 13.07–14.95 %	ICP 1.82–1.96 % HRR 0.39–0.78 % ID 0.79—1.19 %	–
Imtenan et al. [191]	Butanol (5 to10 %v) in biodiesel blend (10 to 20 % in diesel fuel)	Engine tests were conducted at variable speeds, ranging from 1000 to 3000 rpm at a constant 80 N-m torque.	A multi-cylinder diesel engine of 2477 cc.	BSFC 2.3–3.9 % BSEC 3.9 % BTE 2.8–5.3 %	NOx 5.05 % For 5 % blend NOx 8.83 % for 10 % blend CO 23–30.7 % HC 28–48 % Smoke 17–27 %	ICP HRR	LHV Calorific value KV Density FP Cetane number
	Di-ethyl ether (5 to10 % v) in biodiesel blend (10 to 20 % in diesel fuel)			BSFC 5.5–6.8 % BSEC 7 % BTE 6.6–8.8 %	NOx For 5 % blend NOx 12 % For 10 % blend CO 11–20.6 % HC 32–52 % Smoke 30–38 %	ICP HRR	LHV Calorific value KV Density FP Cetane number
Mujtaba et al. [13]	Ethanol (10 %v) in palm oil biodiesel (20 % in 70 % diesel fuel)	All experiments were conducted under full loading conditions in the speed range from 1000-2400 rpm with intervals of 200 rpm	A single-cylinder diesel engine of 638 cc.	BSFC 3.02 % BTE 1.55 % EGT	NOx 33.74 % CO 27.46 % HC 56.51 % Smoke		Density 0.87 % KV 20.89 % PP CV 3.74 %
	Propanol (10 %v) in palm oil biodiesel (20 % in 70 % diesel fuel)			BSFC 3.2 % BTE 1.57 % EGT	NOx 7.56 % CO 49.13 % HC 19.53 % Smoke		Density 0.99 % KV 17.66 % PP CV 3.56 %
	Butanol (10 %v) in palm oil biodiesel (20 % in 70 % diesel fuel)			BSFC 1.66 % BTE 0.87 % EGT	NOx 17.74 % CO 8.38 % HC 8.6 % Smoke		Density 0.75 % KV 12.44 % PP CV 2.86 %
	Pentanol (10 %v) in palm oil biodiesel (20 % in 70 % diesel fuel)			BSFC 3.38 % BTE 1.24 % EGT	NOx 27.79 % CO 30.34 % HC 66.96 % Smoke		Density 0.56 % KV 10.95 % PP CV 2.48 %
	Hexanol (10 %v) in palm oil biodiesel (20 % in 70 % diesel fuel)			BSFC 0.12 % BTE 0.39 % EGT	NOx 26.17 % CO 18.21 % HC 44.12 % Smoke		Density 0.41 % KV 24.19 % PP CV 2.18 %
Nour et al. [192]	Pentanol (10 %v) in biodiesel (10 %)	For each tested fuel, the engine speed and load were adjusted to the tested four operating points of 0 % load/ 1500 rpm, 25 % load/ 1500 rpm, 50 % load/ 1500 rpm and 75 % load /1500 rpm.	A single-cylinder diesel engine of 824 cc and 17 CR.	BP BTE 3.4 % BSFC 3.4 %	NOx 16.3 % Smoke 9 % CO 80.8 % CO_2 56 %	HRR 11.7 % ICP ID	CV 6.39 % LHV 26.5 % KV 4.4 %
	Octanol (10 %v) in biodiesel (10 %)			BP BTE 4.5 % BSFC 3.2 % BSEC 7.5 %	NOx 18.4 % Smoke 70.4 % CO 41 % CO_2 33.3 %	HRR 9.7 % ICP ID	CV4.58 % LHV 26.78 % KV 17.5 %
Tamilvanan et al [112]	5 % DEE in biodiesel-diesel blend (10 % to 20 % biodiesel and 75 % to 80 % diesel fuel)	All experiments were conducted at 0 %, 25 %, 50 %, 75 %, and 100 % at 1500 rpm.	A single-cylinder diesel engine of 661.45 cc and 17.5 CR.	BTE 2.7–3.4 % BSFC 3.5–3.7 %	HC 20–22 % NOx 0.4–2 % CO 2–4 % CO_2 1.5–6.1 %	ICP 0.45–2.8 % HRR 3.2–9.5 % ID	LHV Calorific value KV Density FP

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Table 6 (*continued*)

Authors with reference, year	Additives	Operating Conditions	Engine specifications	Findings Engine performance	Emissions	Combustion behaviour	Properties
	5 % ethanol in biodiesel-diesel blend (10 % to 20 % biodiesel and 75 % to 80 % diesel fuel)			BTE 6.1–6.2 % BSFC 3.7–3.8 %	HC 20–22 % NOx 3.3–5.1 % CO 6–12 % CO_2 1.5–6.1 %	ICP 0.8–2.8 % HRR 2–10.4 % ID	LHV Calorific value KV Density FP
Atmanli [193]	Propanol (20 %v) blend in biodiesel blend (40 % diesel fuel + 40 % biodiesel) through splash blending	All tests were conducted at a fixed engine speed of 1800 rpm and four loads, 1, 3, 6 and 9 kW.	A four-cylinder diesel engine of 19 CR.	BSFC 5.28 % BTE 0.95 % EGT 30.54	HC 34.47 % CO 39.95 % NOx 15.05 %	–	Density 3.04 % LHV 0.84 % KV 27.35 % FP 30.4 %
	Butanol (20 %v) blend in biodiesel blend (40 % diesel + 40 %biodiesel) through splash blending			BSFC 0.89 % BTE 5.58 % EGT 31.58 %	HC 17.37 % CO 38.83 % NOx 19.27 %	–	Density 2.81 % LHV 0.64 % KV 26.26 % FP 29.84 %
	Pentnol (20 %v) blend in biodiesel blend (40 % diesel fuel + 40 % biodiesel) through splash blending			BSFC 0.95 % BTE 4.94 % EGT 27.23 %	HC 17.50 % CO 12.60 % NOx 27.44 %	–	Density 2.69 % LHV 1.50 % KV 23.41 % FP 28.49 %
Mujtaba et al. [11]	Palm-sesame biodiesel blend (B30) + 10 % (V/V) Dimethyl carbonate	All experiments were conducted at 1050–2300 rpm with a step of 250 rpm under full load (100 %) conditions.	A single-cylinder diesel engine of 638 cc and 17.7 CR.	Torque 0.22 % BP 0.33 % BSFC 0.87 % BTE 9.88 %	CO 29.90 % HC 21.4 % NOx 7.49 %	–	Density 2.31 % KV 26.59 % Calorific value 7.79 %
	Palm-sesame biodiesel blend (B30) + 5 % (V/V) Diethyl Ether			Torque 0.04 % BP 0.15 % BSFC 2.22 % BTE 5.03 %	CO 21.9 % HC 15.17 % NOx 4.90 %	–	Density 0.31 % KV 11.65 % Calorific value 1.95 %
	Palm-sesame biodiesel blend (B30) + (100 ppm) Carbon Nano Tubes			Torque 0.88 % BP 1.04 % BSFC 3.5 % BTE 5.17 %	CO 8.5 % HC 54.54 % NOx 3.92 %	–	Density 0.13 % KV 0.74 % Calorific value 0.6 %
	Palm-sesame biodiesel blend (B30) + (100 ppm) TiO_2			Torque 1.28 % BP 1.47 % BSFC 4.1 % BTE 5.49 %	CO 12.46 % HC 8.63 % NOx 1.84 %	–	Density 0.16 % KV 0.59 % Calorific value 0.5 %
Balan et al [194]	Decanol (10–20 %v) in jatropha biodiesel (10–20 %v in diesel fuel)	All experiments were conducted at a constant 1800 rpm speed under variable loading conditions.	A single-cylinder diesel engine of 620 cc and 18 CR.	–	NOx 7.4 % Smoke 4.4 % CO 5.7 % HC 5.9 %	–	Density 1.1—4.2 % KV 9.4–15.6 % Calorific value 1.01–2.43 % CI 0–3.8 %
Jeyakumar and Narayanasamy [195]	Decanol (10–20 %v) in karanja biodiesel (10–20 %v in diesel fuel)	All experiments were conducted at constant speed under variable loading conditions (0, 25, 50 and 100 %).	A single-cylinder diesel engine of 17.5 CR.	BTE 4.6–6.8 % BSFC 14.7–17.6 %	NOx 5.8–13.9 % Smoke 7.3–17.5 % CO 10.8–17.4 % HC 7.5–11.8 % CO_2 3.5–5.2 %		Density 2.15—3.40 % KV 32.45–48.93 % Calorific value 4.67–7.85 % CI 1.92–3.85 % FP 11.1–19.2 %
Mehta et al. [137]	Aluminum (30–60 nm size) in diesel fuel with 0.5 and 1 wt% Iron (5–150 nm size) in diesel fuel with 0.5 and 1 wt%	All the experiments were carried out by varying the loads at a constant speed of 1500 rpm.	A single-cylinder diesel engine of 661 cc and 17.5 CR.	BSFC 7 % EGT 9 % BTE 9 % EGT 7 % BTE 4 %	Soot 8 % CO 30 % NOx 54 % Soot 12 % CO 25–40 % NOx 23 %	Cylinder pressure 20.3 % Cylinder pressure 13.04 %	

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Table 6 (*continued*)

Authors with reference, year	Additives	Operating Conditions	Engine specifications	Findings Engine performance	Emissions	Combustion behaviour	Properties
Rashedul et al. [210]	2,6-di-*tert*-butyl-4-methyl phenol (BHT) (1 %v) mixed in biodiesel (30 % moringa biodiesel with 70 % diesel fuel)	All experiments were performed under a constant load of 20 Nm condition with varying speeds ranging from 1000 to 1800 rpm with an interval of 200 rpm.	A single-cylinder diesel engine of 638 cc and 17.7 CR.	BTE 0.52 %	NOx 4.35 % CO 36.81 % HC 14.88 %	ICP 0.29 % HRR 2.04 %	Density 0.02 % KV 4.66 % FP 1.60 % CV 0.24 %
	2,2′-methylenebis(4-methyl-6-tertbutylphenol) (MBEBP) mixed in biodiesel (30 % moringa biodiesel with 70 % diesel fuel)			BTE 0.7 %	NOx 4.23 % CO 20.36 % HC 11.92 %	ICP 0.10 % HRR 1.15 %	Density 0.018 % KV1.99 % FP 2.14 % CV 0.11 %
Sathiyamoorthi and Sankaranarayanan [211]	Butylated hydroxyanisole (BHA) (500, 1000, 2000 ppm by weight) mixed in LGO25 blend (75 % diesel + 25 % neat lemongrass oil by % volume).	All experiments were conducted at constant speeds of 1500 rpm and variable loads.	A single-cylinder diesel engine of 17.5 CR.	BSFC 0.24–1.66 % BTE 0.47–1.29 % EGT 2.54–7.1 %	CO 5.8–14.8 % HC 2.2–10.2 % NOx 2.2–11 % Smoke 2.3–11.8 %	–	KV0.28–2.01 % FP 1.89–11.3 % CV 1.75—1.05 %
	Butylated hydroxytoluene (BHT) (500, 1000, 2000 ppm by weight) mixed in LGO25 blend (75 % diesel + 25 % neat lemongrass oil by % volume).			BSFC 0.01–0.96 % BTE 0.14–0.82 % EGT 1.8–5.32 %	CO 8.5–16.5 % HC 4.3–11.1 % NOx 2.1–9.1 % Smoke 5.1–17.5 %	–	KV 0.57–3.74 % FP 3.77–13.21 % CV 1.15–1.80 %
Karthikeyan et al. [145]	Geraniol (GE) with Pistacia khinjuk oil methyl ester (PB20 blend)	All experiments were conducted at 1500 rpm at various loads (20,40,60,80 and 100 %).	A single-cylinder diesel engine of 17.5 CR.	BTE 0.19 % BSFC 0.99 %	CO 6.52 % HC 33.3 % NOx 5.04 % Smoke 7.89 %	ICP 2.05 % HRR 12.24 %	Density 0.11 % KV0.88 % FP 1.61 % CV 0.21 %
	Pyrogallol (PY) with Pistacia khinjuk oil methyl ester (PB20 blend)			BTE 0.42 % BSFC 1.99 %	CO 2.17 % HC 11.67 % NOx 8.77 % Smoke 14.47 %	ICP 0.54 % HRR 3.25 %	Density 0.095 % KV1.46 % FP 1.61 % CV 0.45 %
	Di-tetra-butyl-phenol (DTBP) at 10 % volume is mixed with the karanja biodiesel blend (45 % of diesel fuel and 45 % of biodiesel)			BTE 0.4 % BSFC 60 %	NOx 1.8 % Smoke 3.2 % CO 7.6 % HC 4.9 %	ICP 5.12 % HRR 6.36 %	Density 1.28 % KV 5.88 % FP 4.55 % CV 0.72 % Cetane number 9.2 %
Devarajan et al. [152]	1-Pentadecanol (1-DEC) at 10 % volume is mixed with the karanja biodiesel blend (45 % of diesel fuel and 45 % of biodiesel)	An experiment was conducted in a diesel engine by varying the load at a constant speed of 1500 rpm, while the fuel injection was retained at 23° before TDC.	A single-cylinder diesel engine of 661 cc and 17.5 CR.	BTE 0.6 % BSFC 40 %	NOx 3.1 % Smoke 4.9 % CO 4.9 % HC 3.3 %	ICP 3.80 % HRR 3.02 %	Density 3.85 % KV8.82 % FP 7.95 % CV 0.36 % Cetane number 5.56 %
Kumar and Raj [214]	Di-Tetra-Butyl-Phenol (DTBP) at 0.4 % volume is mixed with the cotton seed biodiesel blend (90–95 % of diesel fuel and 5–10 % of biodiesel.	All experiments were conducted at 100 % loading conditions at speeds of 1250 to 3500 rpm.	A single-cylinder diesel engine of 325 cc and 18 CR.	BTE BSFC Torque BP	NOx CO HC	ICP ID HRR	
Mishra et al. [155]	Di-Tetra-Butyl-Phenol (DTBP) of 0 to 1.4 %v blended in waste cooking oil biodiesel (0 to 88.6 % v)	An experiment was conducted in a diesel engine by varying the load at a constant speed of 1600 rpm.	A single-cylinder diesel engine of 661 cc and 18 CR.	BTE 1.5 % BSFC 1.6 % Torque BP	NOx 11 % HC 46–53 % CO 56 %	–	Density 23.81 % FP 96.8 % CV 5.79 %
Adam et al. [142]	2(3)-test-butyl-4-methoxy phenol (BHA) was added at concentrations of 1000 and 2000 ppm to 20 % RB (RB20)	All experiments were conducted at full load and in a speed range of 1500–3500 rpm with 500 rpm intervals.	A multi-cylinder diesel engine of 1998 cc and 22.4 CR.	BSFC 1.55 % EGT 5.89 %	CO 12.35 % HC 20.19 % NOx 2.11 %	ICP 2.19 % HRR 10.13 %	Density 0.3 % KV 0 % FP 1.48 % CV 0.05 %
	N, N′-diphenyl-1,4-phenylenediamine			BSFC 0.91 % EGT 12.36 %	CO 12.80 % HC 27.13 %	ICP 3.97 % HRR 14.74 %	Density 0.94 % KV0.30 %

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Table 6 (*continued*)

Authors with reference, year	Additives	Operating Conditions	Engine specifications	Findings			
				Engine performance	Emissions	Combustion behaviour	Properties
	(DPPD) was added at concentrations of 1000 and 2000 ppm to 20 % RB (RB20)				NOx 4.12 %		FP 1.48 % CV 0.03 %
	2-test butylbenzene-1,4-diol (TBHQ) was added at concentrations of 1000 and 2000 ppm to 20 % RB (RB20)			BSFC 3.14 % EGT 3.28 %	CO 15.25 % HC 25.44 % NOx 0.85 %	ICP 1.77 % HRR 5.78 %	Density 0.71 % KV 0 % FP 1.48 % CV 0.05 %
	N-phenyl-1,4-phenylenediamine (NPPD) was added at concentrations of 1000 and 2000 ppm to 20 % RB (RB20)			BSFC 1.77 % EGT 8.05 %	CO 10.17 % HC 20.65 % NOx 2.68 %	ICP 1.93 % HRR 11.24 %	Density 0.3 % KV 0.30 % FP 1.48 % CV 0.025 %
Paneerselvam et al. [80]	2 % of DTBP was added with peppermint biodiesel blend (P20)	Engine speed is maintained at 1500 rpm during the experiments. Readings are taken for different load values from 0 % load condition to 100 % load condition in 25 % increments.	A single-cylinder diesel engine of 17.5 CR.	BSFC BTE	NOx 10.4 % CO HC	ID ICP HRR 7.9 % Smoke	Density 0.36 % KV 2.34 % FP 3.26 % CV 0.20 % CN 17.78 %
Chacko et al [215]	2-Ethylhexyl nitrate (EHN) in 2000 ppm in Karanja biodiesel (B20)	All experiments were conducted at 2, 4.1, 6.2 and 8.3 bar.	A multi-cylinder diesel engine of 909 cc and 18.5 CR.	BTE 1 % BSFC	NOx 11.4 % HC 14 % CO 5.36 %	ID 11.5 % ICP HRR 11.2 %	–
Vellaiyan et al. [216]	2-Ethylhexyl nitrate (EHN) of 0.5 %v in Karanja biodiesel (B20)	Measurements were performed at 2000 rpm and three different loads: 25, 50 and 75 %.	A multi-cylinder diesel engine of 134 kW rated power.	BTE BSFC6.2 % EGT9.7 %	NOx 25 % HC 9.2 % CO 8.4 % Smoke 18.5–22.2 %	ID ICP 10.5 % HRR 19.9 %	–
Gurusamy et al. [156]	5 % 2-EHN in algae-based biodiesel (B20)	All experiments were conducted at 20, 40, 60, 80 and 100 % loading conditions and 1500 rpm speed.	A single-cylinder diesel engine of 17.5 CR.	BSEC 4 % BTE 3 %	CO 28.57 % NOx 1.2 % Smoke 33.83 % HC 11.32 %	–	–
	5 % DTBP in algae-based biodiesel (B20)			BSEC 1.7 % BTE 4.5 %	CO 46.42 % NOx 12 % Smoke 45 % HC 24.52 %	–	–
Islam et al. [217]	PMA was added to the 30 % (B30), 20 % (B20) and 10 % (B10) biodiesel blends at 0.02 %, 0.03 %, 0.06 % and 0.09 % by weight.	–	–	–	–		–
Arya et al. [221]	1,4-Dioxane in karanja biodiesel	–	–	–	HC 25.3 % CO 25.5 %		–
Monirul et al. [218]	PMA (0.03 %wt) in coconut biodiesel (B20)	The experiment was conducted with varying speeds from 1200 rpm to 2400 rpm with an interval of 300 rpm at full throttle conditions.	A single-cylinder diesel engine of 638 cc.	BSFC 3.24 % BTE 2.16 %	NOx 2.15 % HC 19.81 % CO 13.35 % Smoke 3.93 %		–
Zhao et al. [160]	poly (tetradecyl methyl-acrylate)-graphene oxide (0.03 %, 0.05 %, 0.07 %, 0.1 %, 0.15 %, 0.2 %, and 0.25 %wt)	All experiments were conducted from 1000 to 2200 rpm.	A 2.5 L turbocharged four-cylinder indirect injection (IDI) diesel engine was used to evaluate the emission performances.	–	NOx 1.28–5.74 % HC 7.72–12.5 % CO 10.38—19.74 % CO_2 1.4–21.77 %	–	–
Boshui et al. [161]	olefin-ester copolymers (OECP) of 0,0.01, 0.03 and 0.05 % in soybean biodiesel.	Determinations of PP and CFPP by this method well correspond to ASTM D-97 and EN 116, respectively).	–	–	–	–	–
	ethylene vinyl acetate copolymer (EACP) of 0,0.01, 0.03 and 0.05 % in soybean biodiesel.		–	–	–	–	–
	Polymethyl acrylate (PMA) of 0,0.01, 0.03 and 0.05 % in soybean biodiesel.		–	–	–	–	–

brake power and torque. Moreover, the higher oxygen content helps improve combustion, reflecting lower exhaust emissions [198–201]. The BTE in the case of oxygenated fuels increases due to higher laminar flame speed, which results in combustion completion before any significant heat losses [202,203]. Moreover, the higher LHV also play a role in increasing volumetric efficiency [204]. The octane rating of oxygenated fuels is higher, but the cetane rating is lower [205,206]. The brake-specific fuel consumption is higher in the case of oxygenated additives due to lower calorific values [207,208]. The flash point, density and kinematic viscosity are lower in the case of oxygenated additives [209]. The ignition delay in the case of oxygenated additives is higher due to a lower cetane rating [143].

Table 6 shows the impact of anti-oxidants like BHT [210 211], BHA [142,211], GE [145], PY [145], MBEBP [210], DPPD [142], TBHQ [142], and NPPD [142] on engine performance, exhaust emissions and physicochemical properties of blended fuel. For BHT, engine performance parameters like BTE increases, BSFC decreases, and EGT decreases. The exhaust emissions like CO and HC increase, and NOx decreases. The density and KV increase; however, the flash point and calorific values decrease. For BHA, engine performance parameters like BTE increases, BSFC decreases, and EGT decreases. The exhaust emissions like CO and HC increase and NOx decreases. The density, flash point, and KV increase, however, the calorific values decrease. For GE, PY, and MBEBP the similar results can be observed from Table. The performance parameters like BTE increases and BSFC decrease. The emissions like CO and HC are increased and NOx is decreased. The combustion parameters like HRR and ICP are decreased. The physicochemical properties like density and flash point are increased. However, the KV and CV are decreased. The anti-oxidant additives like DPPD, TBHQ and NPPD produced similar results (see Table 6)—the performance parameters like EGT and BSFC decreased. The emissions like CO are increased, and HC and NOx are decreased. The combustion parameters like HRR and ICP are decreased. The physicochemical properties like density, KV and flash point are increased. However, the CV is decreased. The emissions like CO and HC are increased, and NOx is decreased; this behaviour can be credited to anti-oxidation behaviour [212]. The lack of oxygen results in a lower conversion of CO to CO_2 and inhibits NOx formation. The improvement in BTE can be credited to improved combustion as they prevent the formation of oxidative biproducts [213].

The impact of cetane improver additives like DTBP [80,152,155,156,214] and EHN [156,215,216] on engine performance, exhaust emissions and physicochemical properties of blended fuel has been displayed in Table 6. For DTBP, the performance parameters like BTE increase, BSFC decreases, and BSEC increases. The emissions of CO, HC, NOx, and smoke have decreased. The combustion parameters like ID, ICP and HRR are decreased. The physicochemical properties like density, KV, FP, and CV decrease and cetane rating increases. For EHN, the performance parameters like BTE increase, BSFC decreases, and BSEC increases. The emissions of CO, HC, NOx, and smoke have decreased. However, a gap exists in the literature in ascertaining the impact of EHN on combustion parameters and physicochemical properties of blended fuel.

Table 6 represents the impact of cold flow improver additives like PMA [161,217,218], OECP [161], EACP [161] and olefin [161] on engine performance, exhaust emissions and physicochemical properties of blended fuel. For PMA, the performance parameters like BTE increase and BSFC decrease. The emissions of CO, HC, NOx, and smoke have decreased. The physicochemical properties like pour point (PP), cloud point (CP), and cold filter plugging point (CFPP) are reduced. However, additives like OECP, EACP and olefin also show a decline in PP, CP and CFPP.

5. Effect of nanoparticles on engine performance

The inclusion of nanoparticles (NPs) significantly improves brake thermal efficiency (BTE) due to improved atomization, which decreases brake-specific energy consumption (BSEC) and results in improved fuel combustion. The higher oxygen content improves fuel combustion characteristics, which is ultimately reflected through reduced exhaust gas emissions (CO, HC, NOx and PM) [122]. The improved combustion in the case of NPs is due to a higher surface-volume ratio, which acts as a catalyst for combustion, resulting in higher fuel oxidation and better fuel efficiency. NPs function as oxygen buffers, producing higher air–fuel mixing rates and fuel combustion. NPs additives in diesel/biodiesel fuel reduce their evaporation time and result in lower ignition delay (ID). These NP attributes increase BTE and heat release rate (HRR) during combustion [222]. Three factors, including in-cylinder pressure, latent heat of vaporization, specific heat, ignition delay, and heat release rate, significantly affect the combustion process.

Quality fuel possesses higher in-cylinder temperature (ICT), lower latent heat of vaporization (LHV), lower specific heat, higher reaction heat, and lower ID [223]. NPs in biodiesel positively impact the oxidation reaction, leading to higher peak pressure [224]. The parameters like latent heat of fuels, density, viscosity, calorific value, fuel burning velocity and combustion temperature significantly influence HRR [225]. NPs in biodiesel blends result in faster ignition and higher net heat release than biodiesel fuel at premixed combustion [123,124]. NPs possess a higher surface-to-volume ratio, contributing to improved combustion and lower ID [226]. The higher HRR of biodiesel and additives is because of the higher combustion rate. It can be concluded that NPs improve both combustion reactions and oxidation. Copper oxide (CuO) is a transition metal oxide that helps heat transfer from the engine and lowers NOx [2]. CuO serves as a combustion catalyst for hydrocarbon fuels, contributing to the elevation of both the flash point (FP) temperature and the cetane rating of biodiesel [227]. Gurusala and Selvan [169] found lower CO, HC and smoke emissions along with higher NOx emissions for alumina–biodiesel blend compared to neat diesel because of higher cetane rating and oxygen content—the uniform dispersion of NPs, which subsequently reacts with available air to accomplish improved combustion. The higher NOx emissions may be due to oxidation of nitrogen at elevated temperatures.

Bitire et al. [170] found that the optimum addition of NPs enhanced the occurrence of more O_2 molecules that rise in cylinder combustion. This is achieved by a higher area-to-volume ratio, fast evaporation, improved atomization, and higher air–fuel mixing with alumina nanoparticles. Alumina prevents carbon particle deposition by the usage of alumina nanoparticles. Due to the addition of alumina nanoparticles, oxygen availability rises, and the easy conversion of carbon monoxide to carbon dioxide takes place, reducing CO emissions. Adding alumina nanoparticles lowers the NOx emission since the particle is a reducing agent. The particle also acts as an oxygen buffer to decrease the NOx emission. The diffusive combustion phase is shortened because alumina nanoparticles are added, reducing ID and resulting in quicker combustion. The combustion duration is inversely proportional to ID. A higher peak pressure is created, enhancing faster combustion in the pre-mixed combustion phase. The rise in peak pressure is mostly because of O_2 liberating capability of aluminum oxide (Al_2O_3) nanoparticles. Higher HRR may be because the presence of more oxygen molecules promotes oxidation to the motion of the fuel particles.

The ignition delay (ID) is significantly influenced by biodiesel feedstock, cetane rating, air–fuel ratio, engine speed, intake air temperature, fuel atomization, viscosity, oxygen content and engine load [228]. However, cetane rating has the maximum influence on ignition delay. As biodiesel has a higher cetane rating, it has a shorter ID. Also, the evaporation and atomization are prompted by viscosity, while the higher oxygen level results in an improved combustion process. Additionally, the engine load increases the gas temperature and decreases the ID [2]. The introduction of NPs in biodiesel blends leads to a shorter igniting delay. Higher HRR can be achieved due to a shorter ID and better combustion capabilities of NPs added in fuel blends [229]. The emissions content depends on engine operating conditions, fuel quality, and engine nature. Insufficient air–fuel mixing, influenced by factors such as fuel injection parameters, biodiesel properties, fuel operating conditions, vaporization heat, and oxygen concentration, leads to an increase in hydrocarbon (HC) emissions. HC emissions decline with the increase in load as the combustion temperature increases and reduces ignition delay [121]. It can further be credited to the oxygenated nature of biodiesel fuel with lower carbon content, which results in a complete combustion process, reduces the fuel-rich zone and lowers HC emissions [226]. The main reasons for HC emissions are the engine misfiring in a fuel-rich zone, lubricant oil desorption, and flame quenching [230]. Moreover, NP addition in biodiesel can further reduce HC emissions because NPs act as an oxidizing catalyst, leading to complete combustion [124].

Three factors responsible for oxides of nitrogen (NOx) emissions include cylinder temperature, combustion duration, and oxygen content. The engine speed, load, cetane number (CN), and oxygen concentration significantly influence NOx emissions in the case of diesel/biodiesel blends [231]. NOx emissions are particularly higher in the case of biodiesel blends than diesel fuels because biodiesel fuel possesses higher unsaturated fatty acids and higher adiabatic flame temperature [232]. Additionally, the reduction in nitrogen oxide (NOx) emissions is attributed to a diminished premixed phase, characterized by a lower heat release rate (HRR), resulting in a lower cylinder temperature [224].

Carbon monoxide (CO) emission is a result of inefficient fuel combustion. The air-to-duel ratio decreases as the engine load increases, resulting in lower CO emissions [231]. CO emissions depend on air–fuel ratio, engine speed, load, fuel injection timing, pressure, and fuel type (cetane rating and oxygen content) [233]. Adding NPs into biodiesel increases oxygen content and lets the carbon molecule burn more effectively, leading to better fuel combustion and lower CO emissions [234]. Moreover, the CO emissions would be higher due to higher specific gravity and viscosity possessed by fuel [46]. The larger surface-to-volume ratio in the case of NPs results in higher catalytic activity, which improves the air–fuel mixing rate [2]. Biodiesel possesses higher oxygen content, lower nitrogen, lower carbon content, and lower aromatics than diesel fuel. Particulate matter (PM) emissions in the case of biodiesel are mostly lower, but exceptions may also exist, especially at higher loads [235]. It can be credited to poor fuel atomization, higher viscosity, and bulky fuel molecules. The engine load and engine speed have less influence on PM emission in the case of biodiesel–diesel blends. The NPs addition in biodiesel helps in reducing PM emissions because they produce better combustion because of their characteristics, as explained above. Fig. 6 indicates the impact of nanoparticle characteristics on fuel combustion.

6. Impact of antioxidants on engine performance

Fuel instability and degradation significantly depend on fuel oxidation, affecting fuel combustion quality. Biodiesel degradation is four times quicker than neat diesel fuel. For longer storage time, biodiesel degrades due to oxidation and forms jelly-like crystals [236]. In this regard, antioxidants can improve fuel stability by preventing free radical formation [237]. It is reported that NOx emissions may increase for biodiesel blends due to their oxygenated nature. Antioxidants can absorb excess oxygen during fuel combustion; consequently, biodiesel degradation may slow down, and NOx formation may turn down [143]. NOx results from higher combustion temperature and free radical formation; however, antioxidants possess aromatic ring-like structures, which may neutralize free radicals through electrons to eradicate unpaired radical states [238].

The antioxidant additives in the diesel/biodiesel blend positively impact BTE, brake-specific fuel consumption (BSFC), and NOx emissions. Therefore, the antioxidants are accounted as stable radicals that react with the free radical of fatty acid to gain oxidation stability. Rashedul et al. [210] blended MBEBP (4-methyl-6-tert- butyl phenol) and BHT (2,6-di-*tert*-butyl-4- methyl phenol) in Moringa oleifera biodiesel (B30D70). They found an increase in BTE, CO, HC and smoke emissions and a decrease in BSFC, EGT and NOx emissions. They reasoned this trend with a reduction in hydrogen peroxide (H_2O_2) and peroxyl (HO_2) radicals' formation during oxidation, and an increase in consumption of hydroxyl (OH) radicals reduce carbon oxidation. However, NOx is reduced because of lower free radical formation. Fattah et al. [239] evaluated the impact of Butylated hydroxytoluene (BHT) and butylated hydroxyl anisole (BHA) antioxidant additives for the concentration of 1000 ppm in palm biodiesel (B20). The findings revealed that both additives increase the BSFC, CO and HC emissions. However, the BTE and NOx decreased in comparison with the biodiesel blend.

Nagappan et al. [240] compared the performance of BHT and BHA in a 10 % concentration of biodiesel/diesel fuel blend. They found an increase in BTE and HRR for both antioxidant additives. However, BSFC, HRR, NOx, CO, HC, and smoke are significantly reduced. They obtained much better results in the case of BHA than BHT. Both BHA and BHT in biodiesel blend provide surplus oxygen to minimize HC and CO emissions and improve fuel conversion efficiency. Moreover, the lower viscosity and higher fuel vapour pressure in the case of both BHT and BHA significantly improve air–fuel mixing capacity and fuel vaporization. The catalytic behaviour of BHA and BHT supports the combustion reaction time and lowers combustion temperature and NOx emissions.

Dhahad et al. [241], compared the performance of distinct BHA, DPPD, BHT, and PPD additives at distinct concentrations of 250, 500, 750, 1000, 1250, and 1500 ppm in 20 % biodiesel (B20) proportion in diesel engines. They achieved higher NOx emissions for B20 fuel. With an increase in the concentration of antioxidants from 250 to 1000 ppm, the NOx emission decreased, and with a further rise in antioxidant concentration, NOx emissions started increasing. The minimum NOx emissions were achieved at 1000 ppm antioxidant concentration, which is considered the optimum concentration. The lower oxidation stability is a significant challenge for long-term biodiesel storage; therefore, applying antioxidants is fruitful in improving fuel stability. When selecting antioxidants, their impact on performance, as well as their exhaust and combustion characteristics, must be considered. TBHQ proves to be a better antioxidant than others, improving fuel stability without compromising fuel characteristics.

Rajendran [150] examined the impact of p-phenylenediamine (PPDA), L-ascorbic acid (LA), and A-tocopherol acetate (AT) additives in Annona biodiesel-diesel fuel blend (A20) on the NOx emission. They observed lower NOx emission in the case of PPDA, LA, and AT by 24.7, 23.8, and 22 %, respectively, compared to the A20 blend without additives. The PPDA produces maximum NOx reduction compared to other additives because it donates hydrogen atoms or electrons to trap free radicals. The L-ascorbic acid antioxidant additive can also be a practical choice in reducing HC and NOx emissions. Prabu et al. [242] studied the impact of BHT and n-butanol in 2000 concentration and 20 % volume, respectively, blended in a palm oil biodiesel (B20) blend. The findings depicted that the BHT additive surpasses the n-butanol and biodiesel blend in terms of achieving higher BTE and lower BSFC. However, the BHT produced slightly higher HC, NOx, smoke and CO emissions. They also observed that advancement in injection timing reduces BTE, CO, smoke, and HC emissions. However, they achieved more decline in NOx emissions for retarded ignition timing.

Karthickeyan et al. [145] studied Geraniol (GE) and Pyrogallol (PY) antioxidant additives in Pistacia khinjuk oil methyl ester (PKME) biodiesel (B20). The results showed higher BTE, CO, HC, and NOx while lower smoke and BSFC in the case of antioxidant additives. PY outperformed GE in all aspects. Nevertheless, the oxidation stability is significantly enhanced by N-diphenyl-1,4-phenylenediamine (DPPD), N-phenyl-1,4-phenylenediamine (NPPD), and 2-Ethylhexyl nitrate (EHN) [243]. DPPD exhibits the highest oxidation stability, followed by NPPD, with EHN being the least stable. They observed lower BTE for B20 than diesel fuel, which is the opposite of the general results. However, DPPD, NPPD, and EHN augment BTE, lower BSFC, NOx and Smoke emissions,

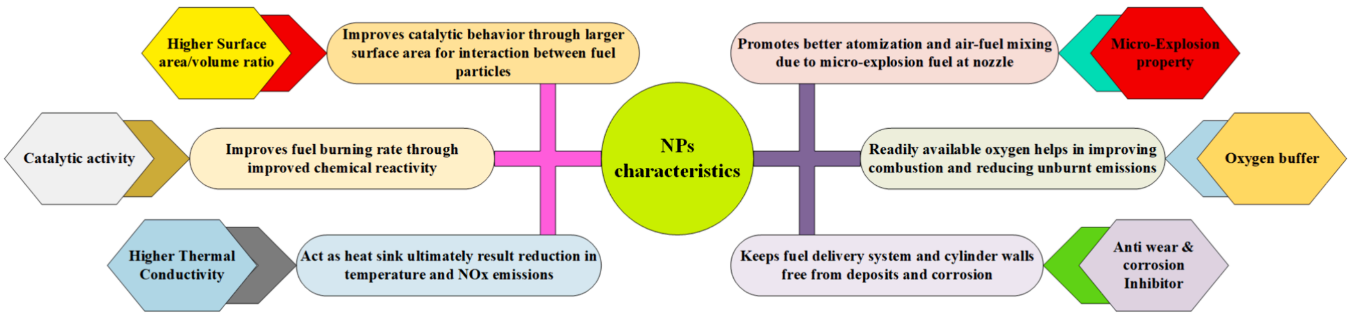

Fig. 6. The effect of blending nanoparticles with biodiesel in improving the combustion efficiency.

and higher HC and CO emissions than B20 without an antioxidant. NPPD demonstrated lower levels of CO and HC emissions compared to both DPPD and EHN. Additionally, DPPD exhibited lower NOx emissions than NPPD and EHN. Furthermore, DPPD showed higher Brake TBTE) and lower Brake Specific Fuel Consumption (BSFC) than NPPD and EHN. Similarly, the inclusion of EHN as an additive in biodiesel-alcohol blends led to a reduction in ignition delay (ID) through an increase in cetane rating, consequently enhancing diffusion rates and improving combustion [244]. Consequently, the BSFC and NOx were reduced, while HC and CO emissions increased marginally.

Adam et al. [142] found that 2-*tert*-butylbenzene-1,4- diol (TBHQ) antioxidants exhibit the highest capability in enhancing the stability of Rape seed methyl ester. It is succeeded by NPPD, BHA, and DPPD, respectively. Importantly, these improvements in stability were achieved without inducing significant alterations in physical properties. Antioxidant additives usually reduce the NOx and HRR and increase in-cylinder pressure (ICP), CO and HC emissions. Combustion results in the production of hydrogen peroxide (H_2O_2) and peroxyl (HO_2), which are further transformed into hydroxyl radical (OH) and also responsible for the transformation of CO to CO_2. However, the combustion of antioxidant additives slows the formation of hydrogen peroxide and peroxyl radicals, resulting in lower combustion efficiency and oxidation processes between hydrogen, oxygen, and carbon molecules—moreover, the CO, smoke, and HC emissions increase. The optimum dosage of antioxidant additives in biodiesel has not been found in the literature. Still, different scientists have used 1000 ppm as an average concentration to improve oxidation stability and are responsible for significant reductions in NOx emissions.

7. Impact of cetane improver additives on engine performance

Cetane rating is an indicator of the ignition delay (ID) period and ignition quality of fuel. ID significantly influences the cylinder combustion process, engine performance and exhaust emissions [245]. ID is inverse to the cetane rating, as it is lower for a higher cetane rating [246]. Higher cetane rating fuel can reduce ID and lower combustion temperature, NOx, and pressures [143]. 2-Ethyl Hexyl Nitrate (EHN) with a chemical formula of $C_8H_{17}NO_3$) and Di Tertiary Butyl Peroxide (DTBP) with a chemical formula of $C_8H_{18}O_2$ are the most common cetane improver additives [154]. Aromatics and alcoholic fuels are very common these days due to their production from natural sources and lower exhaust emissions, but they possess lower cetane ratings. Therefore, cetane improvers are essential for such fuels with lower NOx emissions [247]. It is stated that a cetane number (CN) greater than 60 results in immediate fuel combustion and leads to engine damage and a decline in engine performance. Adding 0.1 to 0.25 % in cetane number improvers may increment the cetane rating by 6 on average [248].

7.1. Di tertiary butyl peroxide (DTBP)

DTBP is a commonly used cetane improver additive that significantly reduces ID. The DTBP additive contains a weak O–O bond within its chemical structure, accompanied by two *tert*-butyl groups attached to the O–O bond for symmetry. This configuration enhances the stability of the molecule. Oxy-radical results from thermal homolysis and organic peroxides initiating oxy-radical formation, increasing active oxygen percentage and lowering CO and HC emissions [155]. Kumar & Raj [214] investigated the impact of 0.4 % DTBP in cotton seed biodiesel (5 % bioethanol and 10 % bioethanol). They noticed a considerable reduction in BSFC, NOx, CO, and HC emissions and an increment in BTE for DTBP blended additives. Ors et al. [249] examined the impact of 1, 2, and 3 % DTBP (cetane improver) in waste cooking oil/ethanol blend on the diesel engine performance. The results indicate that BSFC, CO and HC emissions were increased, but EGT, NOx, smoke and BTE were reduced in the case of ethanol blended waste cooking oil biodiesel. However, CO, HC, and BSFC are reduced when DTBP is added to blended fuel. Subsequently, the EGT, NOx and BTE were increased. Adding cetane improver modifies physicochemical characteristics, increasing cetane's rating and heating value. Ranganathan et al. [80] compared DTBP and DEE additives in diesel/biodiesel blends and examined their impact on emission and performance characteristics. In every aspect, DTBP demonstrated superior performance compared to DEE and the neat diesel–biodiesel blend. DTBP results in a decline in ID, ultimately reflecting a reduction of HRR, ICT and NOx emissions in comparison with diesel fuel.7.2. 2-Ethyl Hexyl Nitrate (EHN).

EHN is an ignition booster or cetane improver which further reduces NOx emission. Atmanli [250] studied 2-ethylhexyl nitrate impact in biodiesel/pentanol and biodiesel/butanol microemulsion blends. They observed lower BSFC, NOx and HC emissions and higher CO emissions. H. Kumar et al. [251] compared the impact of 1000 and 2000 ppm EHN concentrations in diesel/bioethanol blends (E20). They achieved lower emissions except for HC emissions for blended additives. In a different study [252], lower NOx emissions and higher BTE were noticed for the EHN-added biodiesel blend due to free radical formation, accelerating the oxidation process and reducing ignition delay (ID), ultimately resulting in improved combustion. However, NOx emissions were increased in the case of EHN because of nitrogen content. Cetane improver additives find predominant application in alcohol fuel additives due to their inherently lower cetane rating [253]. EHN additives on biodiesel-diesel fuel blends result in higher HC, CO, brake power, and BTE and lower NOx, smoke, and BSFC [254–256]. Ramalingam and Rajendran [257] used EHN (antioxidant additive) to reduce NOx emission, but CO emissions were increased. Krishnasamy et al. [258] declared that EHN can improve cetane rating better than DTBP. Rahman et al. [259], observed that the EHN can enhance the cetane rating by 24 % and shorten the ID time by 10 %.

8. Impact of oxygenated additives on engine performance

Adding oxygenated additives in ternary and quaternary fuel blends significantly affects fuel properties and combustion characteristics. The in-cylinder temperature (ICT) reduces homologous saturating alcohols in diesel biodiesel fuel blends. Datta and Mandal [260] stated that alcohols possess higher latent heat of vaporization (LHV) than neat biodiesel and diesel fuel. It produced a cooling impact on entering the air–fuel mixture followed by ICT reduction—the higher LHV results in maximum pressure drop. Additionally, the higher ignition delay (ID) and a slower combustion initiation can result from blends with lower cetane rating [261,262]; for alcoholic blend concentrations beyond 30 %, in-cylinder pressure (ICP) drops, and an abrupt combustion process takes place. However, peak pressure remains unchanged for ethanol-blended diesel fuel, so combustion quality remains stable for higher ethanol concentrations. The higher ID, rate of pressure rise (ROPR) and HRR can be achieved for higher alcoholic fuel concentration. The pressure rise ratio exceeds 10 bar per degree, along with alarming vibration and noise levels of the engine. The pressure increase per degree for DM15 (15 % methanol in 85 % diesel), DM20 (20 % methanol in 80 % diesel), and DM25 (25 % methanol in 75 % diesel), surpasses 10 bar, whereas DE20 (20 % ethanol in 80 % diesel), has registered 12 bar/degree, exceeding the permissible limit [263]. It results in a higher knocking effect for ethanol addition.

Alcohol possesses higher LHV and cooling effects, responsible for prolonged ID and lower ignition temperature. Furthermore, alcoholic fuel contains a lower cetane number, and its concentration is higher than 30–40 %, which results in unstable engine operations [264]. Higher alcoholic fuel blends result in longer ID, shorter combustion duration, higher HRR and higher ICP. The HRR for ternary and quaternary fuel blends is higher than that for pure diesel fuel. The unsaturated fatty acids adversely contribute to evaporation, leading to higher vaporization time and ID. Ethanol and n-butanol exhibit higher LHV and autoignition compared to diesel fuel, accompanied by a lower cetane rating, leading to increased ignition delay (ID). However, alcohols possess lower density and viscosity, resulting in better fuel atomization and molecule mixing, higher HRR and quicker combustion. The interpretation of HRR for alcoholic fuels is also consistent with findings stated by authors [265,266].

Higher alcohols (octanol, hexanol and pentanol) possess higher oxygen content and cetane number, producing improved engine performance in comparison with lower alcohols. The ternary fuel blends with waste plastic oil, diesel fuel and n-hexanol are blended as D50-W40-*H*10 (50 % diesel + 40 % waste plastic oil + 10 % hexanol), D50-W30-H20 (50 % diesel + 30 % waste plastic oil + 20 % hexanol), and D50-W20-H30 (50 % diesel + 20 % waste plastic oil + 30 % hexanol), under different loading conditions and fixed engine speed (1500 rpm). The investigation in the direct injection compression ignition (DICI) engine from [267] explores the potential utilization of waste plastic oil combined with n-hexanol and diesel fuel, examining blends such as D50-W40-*H*10, D50-W30-H20, and D50-W20-H30 under various load modes of brake means adequate pressure (BMEP) while maintaining a constant speed of 1500 rpm. The BTE in the case of D50-W40-*H*10 was maximum, around 13.1 % higher than BTE in the case of waste plastic oil (WPO); however, it is still lower than neat diesel fuel by 2.7 %. The higher LHV by n-hexanol is responsible for the cooling effect and reduction in cetane rating. The least BTE is produced in the case of D50-W20-H30, but it is still 7.6 % higher than WPO. In a comparative analysis of biodiesel-diesel fuel-n-hexanol and biodiesel-diesel-ethanol blends, it was found that the B90-D5-H5 (90 % biodiesel + 5 % diesel + 5 % hexanol) blend exhibits excellent BSFC [268]. More precisely, the BSFC of B90-D5-H5 is 5 % lower than that of pure diesel, 10 % lower than B80-D5-E15 (80 % biodiesel + 5 % diesel + 15 % ethanol), and 12 % lower than B100. It is concluded that ethanol-blended fuel produced lower BTE than n-hexanol-blended fuel.

Propanol also produces better combustion results with ternary diesel and biodiesel fuel blends. A study on ternary fuel blends (WCO biodiesel, propanol and diesel fuel) is examined on diesel engines to assess their impact on fuel physicochemical properties, BTE, BSFC, and exhaust gas temperature (EGT) [269]. The D80B5Pro15 (80 % diesel + 5 % biodiesel + 15 % propanol) blend exhibits the highest average EGT, whereas the lowest is observed for D80Pro20 (20 % propanol in 80 % diesel). The percentage reduction in EGT for D80B5Pro15, D80B10Pro10, D80B15Pro5 (80 % diesel + 15 % biodiesel + 5 % propanol), and D80Pro20 in comparison to D100 is 0.78 %, 13.39 %, 19.5 %, and 53.93 %, respectively. The higher LHV in the case of propanol is responsible for the decrease in EGT. The results show an increase in BSFC of D80B15Pro5, D80B10Pro10, D80B5Pro15, and D80Pro20 in comparison with D100 by 4.95 %, 8.07 %, 8.33 %, and 11.65 % respectively. The primary reasons for higher brake-specific fuel consumption (BSFC) are biodiesel's higher density and viscosity and lower calorific value in comparison with D100. These factors are responsible for larger injected fuel particle diameter and result in difficulty in evaporation. Moreover, propanol possesses a lower calorific value and higher oxygen content than B100 and D100. Therefore, injecting more fuel inside the cylinder for the same power output is essential.

A study by [270] on a direct injection diesel engine fueled with diesel fuel, Rice bran biodiesel (R100), and blends of R100 with 10 and 20 % vol. propanol. The higher oxygen content, lower viscosity and higher cetane rating of R90P10 (10 % propanol in 90 % rice bran biodiesel) and R80P20 (20 % propanol in 80 % rice bran biodiesel) promote oxidation, higher EGT, and lower ID and combustion duration. The propanol with lower viscosity and volatility is responsible for higher BTE compared to biodiesel with higher viscosity and fuel consumption. Compared to R100, the BTE of R90P10 and R80P20 is boosted by increasing the concentration of propanol. In another study, propanol improves the fuel properties of the waste plastic pyrolysis oil blends, which reflect on improved engine performance [271]. Around 5 to 15 % propanol addition gradually increased BTE, with BTE of D70-WPO20-P15 (70 % diesel + 20 % waste plastic oil + 15 % propanol) observed to be higher in comparison to pure diesel fuel at higher loading conditions. Propanol with lower cetane rating and viscosity results in higher ignition delay time and promotes air–fuel mixture uniformity, improving BTE.

Additionally, the higher oxygen content results in complete oxidation, leading to lower BSFC in the case of propanol blended waste plastic oil (WPO). However, the BSFC of WPO-diesel blends is found to be higher than neat diesel fuel due to the lower heating value. A study by [272] was conducted on 10, 15 and 20 % vol. pentanol in biodiesel. The higher fuel-to-air ratio in the premixed combustion phase of pentanol is due to its higher volatility and lower viscosity, and it results in higher peak pressure in the cylinder along with delay in the start of combustion for pentanol blended fuel.

The combustion characteristics are improved with increased pentanol concentration in blended fuels. The improvement in combustion characteristics is mainly responsible for optimization in engine performance, reduction in exhaust emissions, rise in engine mileage, improvement in combustion rate, prevent oxidation, ecosystem balance, etc. [261]. The improved combustion characteristics reflect better engine performance (BTE, BSFC, etc.) and reduced exhaust emissions [273]. At low and medium engine loads, the rate of heat release (ROHR) at the premixed combustion zone is improved for neat diesel fuel (D100) compared to Oc10E10D80 (10 % octanol + 10 % ethanol + 80 % diesel) and Pe10E10D80 (10 % pentanol + 10 % ethanol + 80 % diesel). This returns to poor fuel atomization and poor mixing with air. Also, the fuel injection pressure does not provide enough energy to break the fuel droplets into smaller droplets, particularly for highly viscous fuel such as OC10E10D80, which produces high output power; therefore, the Pe10E10D80 has higher fuel consumption compared to Oc10E10D80 which also results in higher fuel consumption compared to D100. This is due to the low calorific value of Pe10E10D80 and Oc10E10D80, which leads to more fuel consumption.

On the other hand, the high viscosity of octanol and, consequently, Oc10E10D80, as compared to D100 and Pe10E10D80, will lead to poor fuel atomization with larger fuel droplets that take longer to vaporize. Therefore, when the time is insufficient, the fuel and air mixing will be inadequate, leading to incomplete combustion and lower heat release. Thus, more fuel must be consumed to generate the same output power, increasing BSFC [192].

9. Factors affecting regulated diesel engine emissions

Biodiesel fuel combustion is responsible for higher CO_2 emissions due to its oxygenated nature. It is observed that more CO_2 emissions are usually produced at higher engine loads. The higher oxygen content, along with lower density and kinematic viscosity (KV) and improved fuel vaporization in the case of oxygenated fuels, are responsible for enhanced combustion and result in higher CO_2 emissions. The higher catalytic activity in the case of metal-based additives improves the oxidation process of hydrocarbon fuels, resulting in higher CO_2 emissions. Due to their properties, such as length or saturation level, HC emissions are reduced for biodiesel blends. Higher exhaust gas, in-cylinder gas temperatures, and lower oxygen availability are the critical parameters for significantly lower HC emissions at higher engine loading conditions. However, HC emissions would be higher if the abrupt oxidation took place for injected fuel. The injection timing (IT) and exhaust gas recirculation (EGR) significantly affect HC emissions. The lower oxidative free radical formation in the case of antioxidants led to higher HC emissions. Alcoholic fuels exhibit a mixed trend in HC emissions. The higher oxygen content enhances combustion, leading to reduced HC emissions. Conversely, the higher latent heat of vaporization and cooling within the combustion chamber contributes to increased HC emissions. However, the metal-based additives function as oxygen buffers, improving combustion and lowering HC emissions.

Biodiesel fuels produce lower CO emissions due to their higher oxygen nature and lower C/H ratio than diesel fuels. As the biodiesel concentration increases, the CO emissions further decrease. The biodiesel feedstock and cetane rating are responsible for lower CO emissions. Engine speeds and loads positively influence CO emissions. The lower oxidation capability of antioxidants in diesel fuel/biodiesel blend increases lower CO emissions. The improved oxidation of CO to CO_2 in the case of metal-based additives results in lower CO emissions. The higher air-to-fuel ratio of oxygenated additives results in improved combustion.

Moreover, the cold flow improvers boost the combustion process, resulting in lower CO emissions. However, CO emissions in the case of cetane number improvers are higher due to lower mixing time. The higher NOx emissions in the case of biodiesel are due to higher cetane rating, oxygen content, and injection characteristics. Cetane improvers reduce ID and premixed combustion, lower in-cylinder temperature and pressure and result in lower NOx emissions. Moreover, the oxygenated additives produced lower NOx emissions due to reduced premixed combustion and higher LHV, as these two factors contribute to lower in-cylinder temperature (ICT). The unsaturation in biodiesel feedstock plays a significant role in NOx emissions. Higher unsaturated compounds result in higher NOx emissions. In most cases, the higher engine loads during biodiesel combustion are also linked with higher NOx emissions. Applying EGR can significantly reduce NOx emissions in the case of biodiesel, but engine power may be compromised. Antioxidants mitigate NOx emissions by inhibiting the formation of free radicals in both the combustion process and during fuel storage.

PM emissions in the case of biodiesel blends are lower compared to diesel fuel. It can be credited to lower sulphur compounds, higher oxygen content, higher cetane numbers and lower aromatic contents. There is a consensus among scientists that PM emissions possess a direct relation with engine loads and an inverse relation with engine speeds. Although the EGR technique helps reduce carbon and NOx emissions, PM emissions slightly increase. Oxygenated additives reduce the viscosity and density of biodiesel/diesel fuel blends and increase fuel blends' oxygen content, resulting in lower PM emissions. Antioxidant additives also boost combustion efficiency and subsequently reduce PM emissions.

10. Impact of fuel additives on human health

The possibility of unburnt Nanoparticles from the exhaust affects human health and the global environment [274]. The most considerable apprehension is that free nanoparticles or nanotubes could be inhaled, absorbed through the skin, or swallowed. Many works indicate that nanoparticles are more venomous when incorporated into the human body than larger particles of the same materials.

Inhaled particles can have two significant effects on the human body: their primary toxic effect is to induce inflammation in the respiratory tract, causing tissue damage and subsequent systemic effects [275]. Passage through the bloodstream to other vital organs or nerves of the body. This may result in cardiovascular effects.

The study of the effect of nanoparticles on the environment is only at an initial stage. Among the research needs are issues like the effect of nanoparticles on species other than humans, how they behave in the air, water, or soil, or their ability to collect in food chains. Considering the high number of parametersfor NPs (size, chemical composition, shape, and specific surface treatment), substantial research efforts are needed to fill the knowledge gaps. Critical examinations are also being done to capture the possible unburnt NPs from the discharged emissions. However, the alcohol family can have varying impacts on the environment and human health. Here is an overview of their effects:

Methanol is highly toxic and can cause serious health issues if ingested, inhaled, or absorbed through the skin. It can lead to blindness, organ damage, and even death [276]. Ethanol in moderate amounts may have some health benefits, but excessive intake can lead to alcohol-related diseases such as liver damage, cardiovascular issues, and addiction [277]. Propanol, particularly isopropyl alcohol (isopropanol), is commonly used as a disinfectant and cleaning agent. While it can cause skin and eye irritation, it is generally considered safe when used as directed [278]. Butanol can irritate the eyes, skin, and respiratory system. Prolonged exposure to high concentrations may lead to headaches, dizziness, and nausea [279]. Limited specific health information is available for these higher alcohols (Pentanol, Hexanol, Octanol). In general, excessive exposure to any alcohol can be harmful, causing similar health effects as ethanol or other alcohol. It is important to note that the impacts mentioned above are general observations, and the specific effects can vary depending on factors such as concentration, exposure duration, and individual susceptibility.

PM emissions are responsible for heart or lung diseases, aggravated asthma, and increased respiratory symptoms like difficulty breathing, irritation in airways, and coughing [280]. It is reported that antioxidant and cetane number improvers significantly decrease the adverse impact on human health damage in the category of biodiesel combustion by neutralizing the antagonistic effect of biodiesel on emissions like NOx [3]. Polycyclic hydrocarbons (PAHs) pose serious health threats linked to their environmental and human exposure [281]. It is observed that n-butanol in diesel fuel/biodiesel results in a decline in adverse health impacts of PAH emissions [282].

11. Lifecycle assessment (LCA)

LCA has been acknowledged as a keen approach to address the potential challenges linked with environmental impacts from synthesis to burning of fuel additives. Consequently, the current study is designed to comprehensively review the effects of different diesel fuel/biodiesel additives (cold flow improver, metal-based, cetane number improver additives, oxygenated, lubricity improver, and antioxidant) along with engine operating parameters (engine load, engine speed, EGR, and IT) on both regulated and non-regulated emissions. All emission indexes under the LCA approach for all fuel additives can be consolidated (climate change, human health, resource damage and ecosystem quality). They assist in the facilitation of multi-objective optimization and interpreting emissions data by reducing the environmental impacts of fuel additives. LCA has been consistently employed to evaluate and contrast the environmental, economic, and energy dimensions of biodiesel synthesis from distinct global feedstocks. Nevertheless, there have been no endeavours to examine the environmental repercussions of diesel/biodiesel fuel additives using LCA. Hence, the primary objective of this review is to thoroughly explore the environmental impacts of various fuel additives employed in diesel/biodiesel fuel blends concerning engine emissions.

Life cycle assessment (LCA) is a valuable technique to assess and evaluate the environmental impacts of a product or process from its resource extraction to final disposal. Regarding its advantages, LCA provides a comprehensive perspective of a process or product's environmental effects by considering every stage of its life cycle. For instance, the case of the LCA of fuel additives provides a complete scenario of ecological impact, including the extraction of raw material, manufacturing, refinement, transportation, fuel blending, usage, recycling, and disposal. In addition, LCA identifies the most significant stage of a product or process's life cycle. For example, it identifies which stage of LCA significantly contributes to its environmental impact, which consequently helps reduce the environmental burden with targeted efforts. The results from LCAs can help to inform policy, process optimization, and product design decisions that minimize adverse environmental effects and advance sustainability.

Using LCA data, eco-labels and certifications can be created, assisting customers in making eco-friendly purchases and encouraging manufacturers to enhance the environmental performance of their goods. As LCA results are based on scientific methods and data, they help to communicate environmental performance to the stakeholders. However, obtaining accurate and meaningful data for all the stages of a product or process's life cycle is challenging, which leads to uncertainties and limitations in the assessment. Conducting LCA is a complex process, especially for large and complex systems, and it requires expertise in different disciplines such as environmental science, engineering, and data analysis. Furthermore, defining the scope and boundaries of LCA is subjective, and it could affect the outcomes. For example, different assumptions and methods can produce different results, which can impact the validity and consistency of evaluations. Despite its limitations, LCA is a valuable tool for encouraging sustainable development and directing well-informed decision-making towards more environmentally responsible practices.

In the case of conventional fuels, the life cycle begins with the extraction and processing of crude oil. Activities such as drilling, oil exploration and raw material transportation to refineries are part of this stage. In the refinery, several operations, like distillation and cracking, etc., are conducted, and the LCA considers the energy inputs and emissions related to these activities. After refinement, the fuel is delivered to distribution centres and final consumers. Additional energy use and emissions are involved, such as transportation by trucks, ships, pipelines, etc. In the consumer stage, the combustion of conventional fuels is done to produce energy. In this stage, the emissions from burning fuel are considered. These emissions include particulate matter, Sulphur dioxide, nitrogen oxides, and greenhouse gases like carbon dioxide. After use, waste management processes such as disposal or recycling treat conventional fuel residues. Table 7 describes the different steps to consider in analyzing the LCA for additives-based fuels.

For oxygenated-based fuel additives, for instance, oxygenated fuels derived from bio-based feedstocks like agricultural residues, natural gas, and biomass are major raw material sources. The LCA considers the environmental effects of agricultural practices, such as energy use in farming and biodiversity impacts. In the next phase, the production of oxygenated fuel additives through processes such as fermentation, dehydration, gas-reforming or chemical synthesis is considered, and the environmental effects at this stage include energy consumption and greenhouse emissions. Similarly, the refineries or other blending facilities combine oxygenated fuel additives with conventional fuels, and LCA considers the effect of the blending process on emissions. At the end of their life cycle, oxygenated fuel additives may undergo several disposal or recycling procedures. The waste management practices and their potential effects on soil and water quality are evaluated.

LCA of metal-based fuel additives involves the environmental impact and its evaluation of different extraction stages, production, transportation, usage and disposal. In the extraction phase, metals such as iron, copper, and manganese are produced, and their environmental impact is considered. The extracted metals are transformed into a usable form in the next stage. Energy inputs, production-related emissions, and possible chemical waste produced during additive manufacturing are considered. Then, metal-based fuel additives are transported from production centres to blending centres. Refineries or other blending facilities blend conventional fuels with metal-based fuel additives. The LCA considers the effects of the blending process, such as energy usage, emissions, and any modifications to the fuel's properties that could influence combustion efficiency, emission during engine operation, and effects on engine performance. At the end of their life cycle, the disposal or recycling procedures are carried out, and their environmental impacts are quantitatively evaluated.

LCA of antioxidant-based fuel involves the environmental impact of different phases of its life cycle, i.e. raw material extractions such as phenols, amines, Sulphur compounds and metal, etc., production of antioxidants by polymerization, nitration, chelation reactions, thiolation reactions, phosphorylation, alkylation etc., transportation to blending facility, antioxidant mixing with the conventional fuel and usage, recycling and disposal of antioxidant-based fuels.

LCA of cold improver-based fuel additive considers the various stages involved in the additive's production, distribution, and use. It feels the environmental impact of extracting and processing raw material such as polymeric compounds, surfactants, alcohol derivatives, i.e., polyethylene glycol (PEG) or polypropylene glycol (PPG), esters, alkylphenols etc., needed to produce cold flow improver-based fuel additives. It also includes energy consumption, emissions, and waste generated during production processes such as polymerization and esterification. It also considers energy and emissions associated with transporting, blending, using, recycling, and disposal of cold flow improvers and provides insights into the additive's overall impact on sustainability.

Similarly, the LCA of cetane number improver-based fuel additive aims to identify environmental hotspots and assess the overall sustainability of the fuels. In the first phase, the energy consumption and the environmental impact of producing and transporting the raw materials, such as Alkyl nitrate compounds, peroxides, ethers, alcohols, esters, amides, etc., to production and refining processes such as nitration, hydrogenation, amination, and carbonylation are generally evaluated. In the next stage, the environmental cost of producing the cetane number improvers additives such as DTBP and 2-EHN and transporting them to the blending facility is estimated. At the blending facility, the cetane number improver additive combines with the conventional fuel, and LCA considers the effect of the blending process on emissions. In the final stage, the environmental footprint of the usage, recycling, or disposal of cetane number improver-based fuel additive is evaluated.

12. Pros/Cons of fuel additives

Fuel additives are advantageous to both refiners and end-users. The refiners can benefit from fuel additives in terms of prolonged life of production setup, minimal process losses, and maintenance cost so that operations may take place at optimal rates with maximum efficiency. The end-users can benefit from fuel additives for better fuel economy because of lower engine emissions, higher power output, smooth engine operations with improved engine life, and lower maintenance costs. Fig. 7 depicts the benefits of fuel additives to end-users and refiners. The detailed features of each fuel additive are shown in Fig. 8. Cetane improver additives accelerate ignition in the combustion chamber, resulting in reduced ignition delay time (IDT), lower NOx emission, engine stability, improved combustion efficiency, reduced exhaust emission, improved fuel viscosity, reduction in cold start cranking issue, lower combustion noise, prolonged engine life and cost-effective increment in cetane quality.

On the other hand, the cooling effect inside the engine cylinder may

Table 7
The illustration of the distinct stages of the life cycle for various fuel types, encompassing raw material extraction, transportation, refinement, fuel blending, utilization, recycling, and disposal processes.

Fuel Type	Raw material extraction 	Transportation of raw material 	Production and refinement 	Transportation of fuel 	Fuel blending 	Usage, recycling, and disposal 
Conventional Fuel	Gasoline and diesel fuel derived from crude oil	Transportation to the production facility	Distillation and cracking, etc.	Transportation to distribution points	–	Usage, disposal, or recycling of conventional fuel residues
Oxygenated-based fuel additives	Oxygenated fuels derived from bio-based feedstocks like agricultural residues, natural gas, and biomass	Transportation to the production facility	Fermentation, Dehydration, gas reforming or chemical synthesis	Manufacturing facilities to blending facilities	Oxygenated fuel blending with conventional fuels	Usage, disposal, or recycling
Metal-based fuel additives	Extraction of Iron, copper, and manganese through mining	Transportation to the production facility	Synthesis of additives	Production centres to blending centres	Metal-based fuel additives blended with conventional fuel	Usage, disposal, or recycling
Antioxidant-based fuel additives	Phenols, amines, Sulphur compounds, metal deactivators, stabilizers	Transportation to the production facility	Polymerization, Nitration, Chelation reactions, Thiolation Reactions, Phosphorylation, Alkylation	Production centres to blending centres	Antioxidant blending with conventional fuel	Usage, disposal, or recycling
Cold flow improver-based fuel additives	Polymeric compounds, Surfactants, Alcohol derivatives, i.e., polyethylene glycol (PEG) or polypropylene glycol (PPG), Esters, Alkylphenols etc.	Transportation to the production facility	Polymerization and Esterification	Production centres to blending centres	Cold flow improver blending with the conventional fuels	Usage, disposal, or recycling
Cetane number improver-based fuel additive	Alkyl nitrate compounds, peroxides, ethers, alcohols, esters, amides, etc.	Transportation to the production facility	Nitration, Hydrogenation, Amination, and Carbonylation	Production centres to blending centres	Cetane number improver blending with conventional fuels	Usage, disposal, or recycling

be compromised, HC emissions may rise, and increased diffusion in combustion, especially under rich fuel–air regions, may result in higher CO emissions. Antioxidants are responsible for increased stability and storability, suppressing peroxyl free radical formation on reaction with aromatic amines; lower NOx, prevents oxidation, increases in flash point and cetane number, higher density, and kinematic viscosity, resulting in a large mass of fuel injection for same fuel volume inside the engine. On the contrary, the HC emission would be higher due to lower oxidative free radicals' formation, lower calorific value, lower heat energy content, and higher CO emission as antioxidants inhibit oxidation. Cold flow property improver prevents crystal growth, reduces pour point temperature, and prevents fuel line heating systems. However, the paraffin crystal precipitation due to higher density values concerning the liquid portion and crystals settling during storage may lead to the formation of a paraffin-rich layer at the fuel tank bottom. Oxygenated additives improve combustion, reduce emissions, improve brake thermal efficiency, improve fuel viscosity and shorter ignition delay. However, oxygenated additives are carcinogenic, have lower calorific value, deposit formation, sludge and oxide formation, and less stability as emulsifiers and surfactants required to prevent phase separation. Metal-based additives may have lower viscosity and flash point, lower oxidation temperature and PM, lower oxidation energy, efficient combustion, increased engine power, lower fuel consumption, reduced exhaust emissions, lower ignition temperature, lower pour point and cloud point, improved cold cranking characteristics, shorter ignition delay, higher heat release rate. However, they may have lower mixability with fuels and higher NOx emissions owing to the catalyst effect of metal additives in the combustion process.

13. Strength, Weaknesses, opportunities and threats (SWOT)

The fuel additives may face issues like conglomeration, sedimentation, and non-uniform size distribution. Such problems can be solved for smaller particles than 100 nm [283]. SWOT is an acronym for strengths, weaknesses, opportunities, and threats. SWOT analysis linked with fuel additives is displayed in Fig. 9. The strengths related to fuel additives are improved engine performance, enhanced thermophysical properties, fuel stability, combustion behavior, mechanical properties, tribological characteristics and reduction in exhaust emissions. The weaknesses are limited effectiveness, higher cost, dependency on base fuel, lack of awareness, limited Standardization, and cost competitiveness. New business avenues, global market expansion, novel research areas, technological advancements, stringent emission regulations, and environmental awareness are opportunities. The threats are health risks, environmental degradation, market competition, compatibility issues, regulatory restrictions, and extreme competition.

14. Challenges and perspectives

Fuel additives-assisted engine operations offer many advantages, but they also have different challenges and perspectives. Here, some key challenges and perspectives associated with fuel additives-assisted engine operations have been highlighted.

14.1. Challenges

- Fuel additive manufacturers have to adhere to strict regulations on performance, safety, and environmental impact. Manufacturers may have difficulties in terms of formulation, testing, and certification to comply with these regulations.
- Certain fuel additives have the potential to cause compatibility problems, corrosion, or other harm when they unexpectedly contact engine parts or fuel system materials. Ensuring compatibility with a

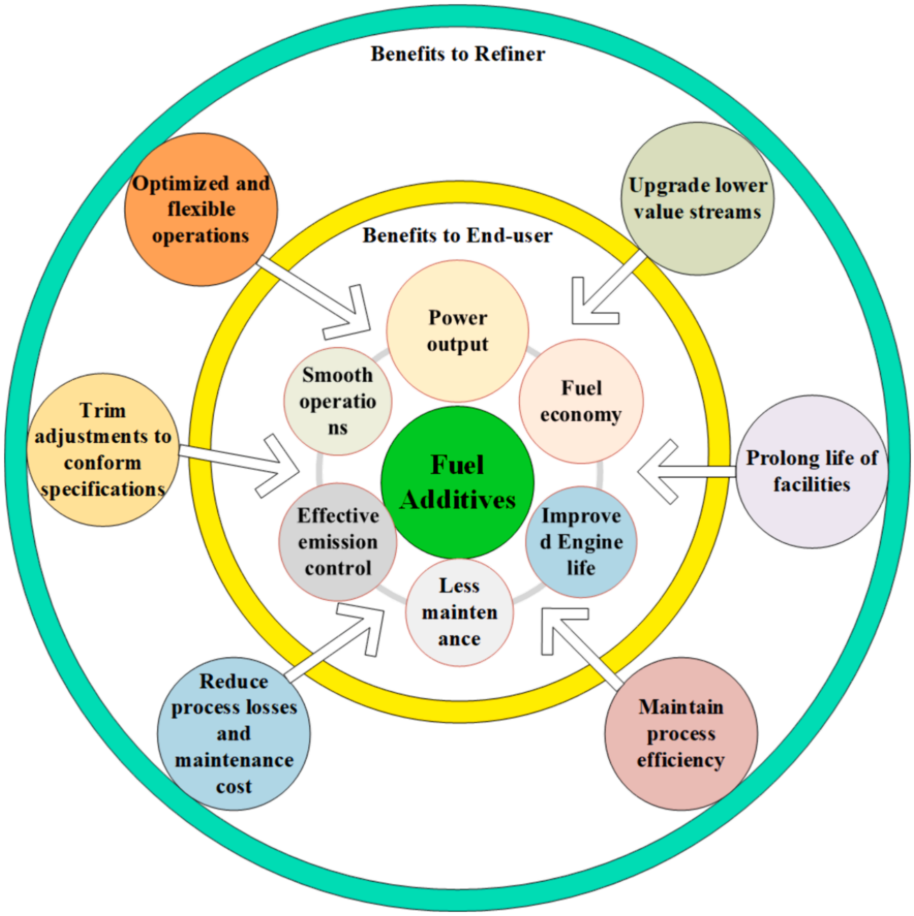

Fig. 7. A brief illustration of the benefits of fuel additives to refiners and end users.

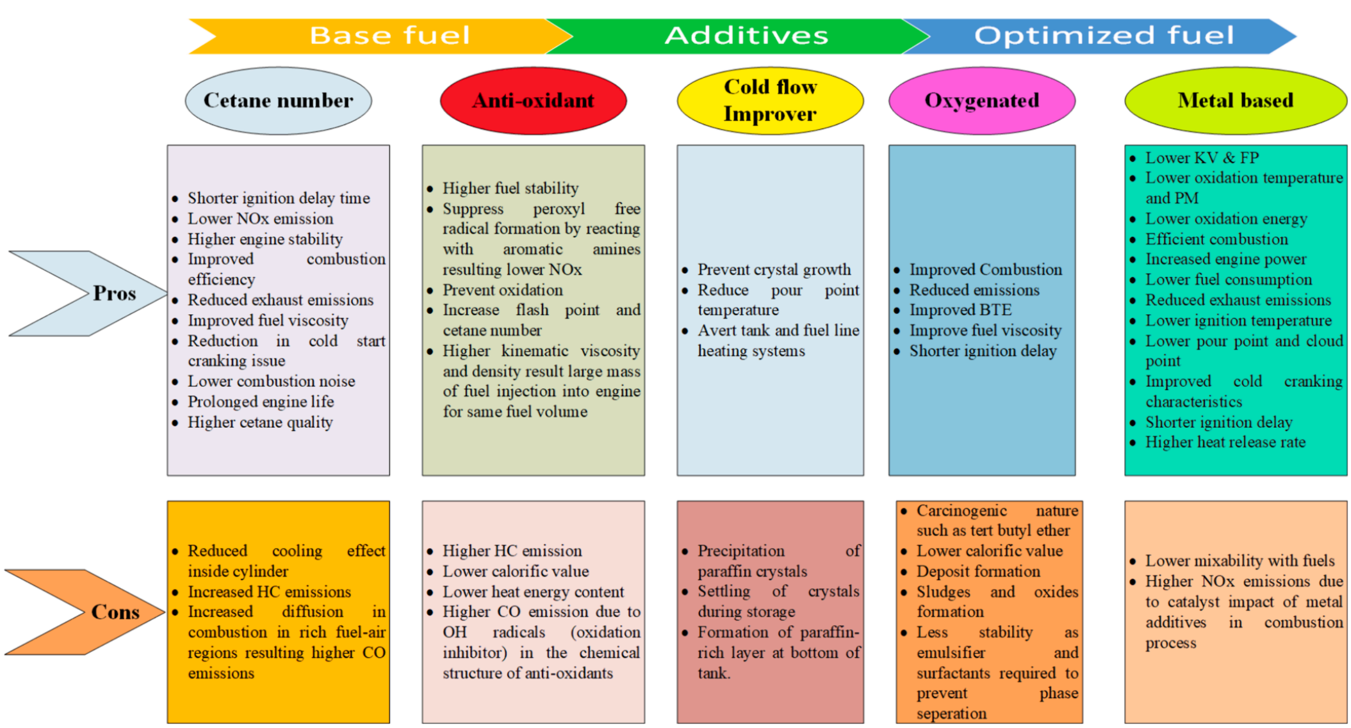

Fig. 8. An outline of the merits and demerits of blending fuel additives into base fuel to achieve an optimized fuel mixture.

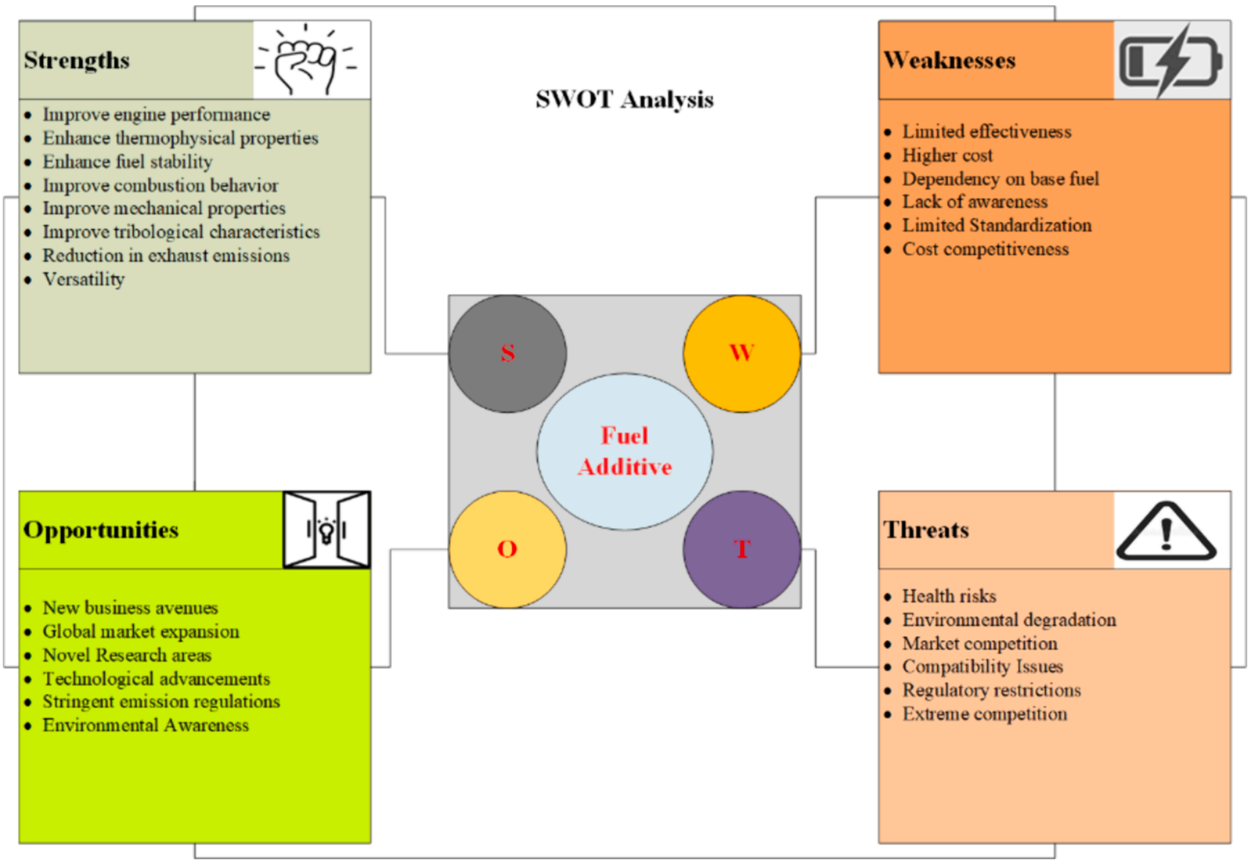

Fig. 9. SWOT analysis of engine operations assisted by fuel additives, considering their social, economic, and environmental impacts.

wide range of engine types and materials can be challenging for additive manufacturers.

- The effectiveness of fuel additives can vary depending on factors such as fuel quality, operating conditions, and engine design. Achieving consistent and reliable performance across different applications and environments is challenging for additive manufacturers.
- The advantages fuel additives offer in terms of engine performance, pollution reduction, fuel efficiency, and maintenance savings must outweigh their cost. Securing a cost-performance equilibrium is crucial for guaranteeing the extensive implementation of fuel additives.

14.2. Perspectives

- From an environmental perspective, fuel additives contribute to environmental sustainability by improving fuel efficiency, reducing emissions, and extending the lifespan of engine components.
- From a performance perspective, fuel additives can enhance engine performance by improving fuel combustion, preventing deposits, and reducing engine wear and tear, which in turn help optimize engine operations, increase power output, and prolong engine life.
- From a perspective of flexibility and customization, fuel additives offer versatility and adaptability to diverse engine and operating conditions.
- From a perspective of innovation and research, fuel additives represent a dynamic and evolving area of study with the potential to unlock new solutions for improving engine performance and environmental sustainability.
- From a perspective of integration with alternative fuels, fuel additives can facilitate the transition to cleaner and more sustainable energy sources for transportation.

15. Conclusions and recommendations

The conclusions and future recommendations have been presented in the current study as follows;

- In the context of biodiesel, exhaust emissions are generally lower than those of pure diesel fuel, except for NOx emissions. This discrepancy is attributed to biodiesel's reduced aromatic compounds and higher oxygen content. The introduction of metal-based additives has the potential to diminish NOx emissions linked to the combustion of biodiesel and its blends through cetane rating improvement. The reduction in smoke opacity, as well as HC and CO emissions reduction, can be achieved by augmenting the fuel evaporation rate and catalyzing oxidation reactions.
- Oxygenated additives decrease smoke opacity and CO and HC emissions because of lowered cylinder temperature. These additives may elevate CO_2 emissions through enhancement of the fuel vaporization rate, thereby impacting the combustion process accordingly. Antioxidant additives demonstrate effectiveness in managing NOx emissions by inhibiting the generation of free radicals throughout both fuel storage and combustion phases. These additives can improve combustion efficiency and decrease PM emissions. In the presence of antioxidants, there is a reduction in the oxidation potential of CO emissions. HC emission can be increased when free radical formation is suppressed. The cetane number improver aids in mitigating NOx and smoke emissions by diminishing ignition delay and shortening the premixed combustion phase. Additionally, the cold flow improver enhances ignition temperature, thereby reducing exhaust emissions.
- The nano-fuel's stability relies on the concentration and size of nanoparticles. The higher concentrations are usually constrained due to poor atomization, sedimentation, large-size fuel droplets, higher

viscosity, and poor combustion efficiency. Improved durability and uniform dispersion of nanoparticles in nano-enhanced fuels contribute to enhanced heat and mass transfer, fostering uniform combustion processes. Nano additives, specifically those based on metal–organic framework (MOF) nanoparticles, offer a promising avenue by combining the advantages of organic and inorganic materials, making them potential candidates for future fuel additives. The catalytic activity, high porosity, significant surface area, consistent pore size, structural tunability, and versatile topological/ compositional characteristics of these hybrid porous crystalline nanoparticles, MOFs, are harnessed for this purpose. The substantial surface area and a high concentration of chemically bonded oxygen in MOF nanoparticles, when introduced into the fuel, increase the combustion chamber pressure. More precisely, the employed MOF nanoparticles actively participate in hydrogen synthesis reactions at elevated temperatures, facilitating combustion and contributing to heightened pressure within the chamber.

- For CI engines, fuel simultaneously reduces NOx and soot emissions due to water content and oxygenated structure. Alcoholic fuels are a proper alternative for homogeneous charged combustion (HCCI) engines. The less reactive nature helps control the beginning and combustion phases, especially for HCCI combustion. The performance of the fuel oil in HCCI mode can be further improved through a variable compression ratio.
- The phase separation issue in the case of alcoholic fuels can be reduced by mixing propanol/isopropanol in methanol/diesel and ethanol/diesel fuel blends. Mixed literature exists for NOx production from alcoholic fuel blends, higher NOx emissions due to their oxygenated nature, and lower NOx emissions due to higher LHV. Other exhaust emissions like PM, soot, CO, and HC are reduced due to lower aromatic components in fuel oils.
- Cetane improvers are essential for improving ignition quality and decreasing the fuel ID period. Alcohol has a lower cetane rating; therefore, cetane improver additives benefit alcoholic fuels for better engine performance and reduced exhaust emissions. Mostly, the exhaust emissions decrease for cetane improver additives except for CO emissions. It is reported that adding EHN reduces NOx emission and increases BTE due to free radical formation, lower ID, and improved combustion. The optimal concentration of antioxidants should be determined by balancing oxidation stability and engine performance, ensuring a practical tradeoff that enhances oxidation stability without detrimentally impacting engine performance. Metal-based additives are mixed to decrease viscosity, minimize PP, and increase FP in biodiesel, yielding superior outcomes compared to alternative additives. The catalytic impact of these fuel additives leads to a reduction in BSFC, HC and smoke emissions.
- Oxygenated additives are beneficial for reducing the density and viscosity of diesel/biodiesel fuel and increasing the oxygen content. The oxygenated additives (DEE, ethanol, DMC) result in lower BSFC and emissions (CO, HC, CO_2, and smoke) when added to diesel/ biodiesel fuel. The cetane improver additives significantly decrease the ignition delay timing in diesel engines. The EHN fuel additive is the most common commercially available in the market and results in an improved combustion process. The NOx emissions are substantially reduced with the use of antioxidant additives in diesel/ biodiesel fuel, along with higher flash points and cetane numbers but lower calorific values. The most common antioxidant additives are BHA and BHT, and result in higher brake thermal efficiency. The ignition temperature and BTE of the engine increase at the cost of lower exhaust emissions for cold flow enhancer additives. The lubricity enhancer additives benefit improved combustion and lower ignition delay, CO, and NOx emissions. The cetane number improver additives produce results similar to lubricity improver additives due to lower ignition delay.
- Although fuel additives are responsible for reducing harmful emissions, the overall environmental impact cannot be accurately evaluated from the emissions trends only. The life cycle assessment is mandatory for the comprehensive environmental effects of fuel additives. Generally, the current review article concludes that the additives in diesel/ biodiesel fuel can result in optimized C.I. engine performance along with lower exhaust emissions. However, non-edible biodiesel like rapeseed, argemone, pongamia, linseed, Mexicana, and sterculia foetida need to be investigated comprehensively for optimized results.
- It is reported that for NPs, the BTE generally increases from 1 to 25 %, with some exceptions, like magnesium and carbon nanotube additives, which are responsible for the reduction in BTE by up to 4.8 %. However, the hydrocarbon emissions generally decrease from 4 to 60 %. The NOx emissions decline typically from 4 to 45 %, with some exceptions like manganese, aluminium oxide, silicon dioxide, and carbon nanotubes. For oxygenated additives, the HC emissions generally decrease up to 34.47 %, with the exceptions of diethyl ether and hexanol. The BTE increases up to 9.88 %. The NOx emissions typically decrease from 1.65 to 33.74 % except for pentanol and hexanol. For anti-oxidants, the BTE generally increases from 0.4 to 1.5 %, hydrocarbon emissions decrease up to 53 %, and NOx decreases up to 11 %. For cetane improver additives, BTE increases up to 4.5 %, NOx decreases up to 25 %, and HC decreases up to 24.52 %. For cold flow property improvers, no significant literature is found on their impact on engine performance and emissions. However, properties like the cold filter plugging point decrease up to 14 °C. The pour point decreases up to 9 °C. But the flash point increases up to 8.83 %. The current study comprehensively portrays all the aspects of fuel additives for their potential applications in automotive so that it would be easier for researchers and manufacturers to select any fuel additives for particular purposes.
- The impact of fuel additives on performance parameters like variable injection timing, variable injection pressure and variable compression ratios (CR), along with the direct effects on combustion inside the engine, has not yet been investigated. Therefore, extensive research is required to account for the emission and combustion characteristics of biodiesel fuel additives with varying volume fractions and operating parameters like CR, injection timing (IT), and injection pressure (IP).
- Both aggregation and sedimentation result in changes in the thermophysical of NPs added to biodiesel. Less literature exists on fuel injection parameters like atomization, dispersion, and penetration of NPs additives. The injection parameters usually vary when NPs are blended in the base fluid. The injection properties may vary for NPs added base fuel. Therefore, to establish the feasibility of using NPs additives, the fuel injection properties need to be analyzed.
- Exceeding the optimal nanoparticle concentration could result in abnormal combustion and knocking. Hence, additional experimental investigations are necessary to establish the ideal nanoparticle concentration in the base fuel for enhancing performance and minimizing emissions. For the NPs production, diverse plant extracts, algae, fungi, bacteria, and novel biological entities like oleic acid alginate, gelatin, starch, and ovalbumin need to be explored in the future.
- The carbonyl investigation in the diesel engine combustion exhaust should be extended to oxygenate and alcohol-based fuel to produce a clear picture and gather comprehensive data about oxygenated HCs produced in a CI engine. Particulate matter (PM) and unregulated emissions from diesel fuel combustion should not be neglected. More studies should be conducted to understand PM, unregulated emissions, and chemical composition and help clarify the formation of unidentified chemical species.
- The formation of a two-phase composition is the main problem in alcohol additives at specific temperatures. However, this issue can be avoided through alcohol additives with a number of carbon atoms higher than four. However, the pros of higher alcohol additives need to be explored in future. Moreover, the technologies for alcoholic

fuel production from microalgae and lignocellulosic biomass need to be adopted in biorefineries.

- The potential future research focus lies in optimizing the performance and emission characteristics of ternary blends comprising additives, biodiesel, and diesel fuel. This area offers promising opportunities since there has been relatively limited research on maximizing performance and minimizing emissions in such blends. Modifications in injection pressure, injection timing, and compression ratio can also be investigated for better combustion optimization. Limited research exists regarding the impact of cetane improver and cold flow properties improver additives on engine performance. In the future, their tribological implications and effect on engine combustion and performance must be comprehensively ascertained.
- Government policies encourage biofuels to extract maximum energy from natural and dumped sources. The increasing biofuel ratio in base fuel (diesel fuel) significantly varies fuel properties, and the additives in fuel ensure expected specifications in terms of fuel economy, engine performance, lower emissions, storage stability, prevention from corrosion and contamination, operation ability at lower and higher temperature along with a reduction in wear and prolonged engine cycle. Applying additives in fuel is inevitable to meet the expectations of refiners and end-users. Therefore, future research on additives will increase because of stringent emission regulations and efforts to improve engine efficiency.
- In the future, additives that reduce NOx and BSFC need to be developed without compromising engine power and fuel economy. Moreover, lifecycle assessment (LCA), which is linked to the ecosystem and human health, must be done. It is also important to investigate after-treatment technologies and advanced combustion technologies by considering the sustainability index and LCA approach.

CRediT authorship contribution statement

Muhammad Ali Ijaz Malik: Writing – original draft, Methodology, Formal analysis, Data curation. **M.A. Kalam:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Muhammad Mujtaba Abbas:** Writing – review & editing, Software, Resources. **Arridina Susan Silitonga:** Writing – review & editing, Supervision. **Adeel Ikram:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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