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Review

The Effects of Nano-Additives Added to Diesel-Biodiesel Fuel Blends on Combustion and Emission Characteristics of Diesel Engine: A Review

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Abstract: How to improve the combustion efficiency and reduce harmful emissions has been a hot research topic in the engine field and related disciplines. Researchers have found that nano-additives to diesel-biodiesel fuel blends have achieved significant results. Many research results and both current and previous studies on nanoparticles have shown that nano-additives play an essential role in improving the performance of internal combustion engines and reducing the emission of harmful substances. This paper summarizes the recent research progress of nanoparticles as additives for diesel-biodiesel fuel blends. Firstly, the excellent properties of nanoparticles are described in detail, and the preparation methods are summarized and discussed. Secondly, the effects of several commonly used nanoparticles as diesel-biodiesel fuel blends on combustion performance and harmful substances emissions in terms of combustion thermal efficiency, brake specific fuel consumption, CO, UHC and NO_x, are reviewed. Finally, the effects of nano-additives on internal combustion engines, the environment and human health are discussed. The work carried out in this paper can effectively contribute to the application of nanomaterials in the fuel field. Based on our work, the researchers can efficiently select suitable nano-additives that enable internal combustion engines to achieve efficient combustion and low-emission characteristics.

Keywords: biodiesel; diesel; nano-additives; performance; emission

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1. Introduction

As a type of non-renewable resource, fossil fuel is being used excessively by human beings all over the world [1]. In today's world, people are promoting low-carbon living, and the emissions from fossil fuel combustion have a negative impact on plant and animal health and the environment [2–4]. According to the Lancet Countdown [5] on health and climate change, climate change will affect human health over a lifetime due to the greenhouse effect caused by the massive consumption of fossil fuels, with average temperatures today more than four degrees higher relative to the pre-industrial revolution period. Therefore, there is an urgent need for fuels that can replace fossil fuels, and the search for renewable, green alternative fuels with similar performance has become a hot pursuit nowadays.

In the future, internal combustion engines will remain the primary power source for transportation. For this reason, the diesel engine should improve the high combustion efficiency and reduce the lower emission. Moreover, the traditional fuels should be replaced with renewable energy [6–9]. Currently, researchers have studied many alternative fuels for diesel engines and found the biodiesel is considered a very favored alternative fuel [10,11]. The biodiesel is a renewable resource produced in large quantities using various methods. It is mainly produced by the esterification of animal fats, vegetable oils and waste oils in the presence of a catalyst [12–18]. Its main advantage is that it requires essentially no engine modifications when used as an engine fuel. It maintains almost the same engine performance in brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), and brake power. At the same time, emissions such as hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) are significantly reduced in the absence [19]. With the intensive research on biodiesel fuels, it was found that biodiesel such as rapeseed methyl ester [20], jatropha seeds [21], rapeseed methyl ester [22], and sunflower methyl ester can be blended with diesel in different ratios to obtain better emission and combustion performance [23].

In addition, researchers have found several adverse effects in studies of diesel-biodiesel fuel blends [24], such as relatively low cloud and pour points, poor atomization of fuel injection, relatively low calorific value and generally high NO_x emissions [25,26]. Thus, the researchers have tried newer approaches to improve engine performance and reduce exhaust emissions, such as the addition of fuel additives and pretreatment blends [27,28]. The addition of nanoparticles to diesel-biodiesel has emerged as one of the most effective and promising fuels [29,30]. It could be due to the many superior properties of nanoparticles: increased energy content, large surface area to volume ratio, increased number of active centers required for different reactions and processes, faster catalytic reaction rate, high catalytic activity, etc. [31,32]. Elahi et al. [33] found that the addition of added alumina to B20 (20% biodiesel and 80% diesel) resulted in a significant reduction in combustion time (CD) and ignition delay (ID), an increase in peak pressure, and a slight increase in heat release rate (HRR) at maximum load and cylinder pressure. HC and CO missions were reduced by 26.72% and 48.43%, respectively, while NO_x increased by 11.27%. Hosseini et al. [34] conducted experiments on a CI single-cylinder engine by adding carbon nanotubes to diesel-biodiesel fuel blends at 30, 60 and 90 ppm. The results showed compared with diesel fuel, the power, BTE and BSFC of diesel engine fueled with blend fuel was increased by 3.67%, 8.12% and 7.12%, respectively. However, NO_x emissions increased by 27.49%. Meanwhile, Sajith et al. [35] conducted engine tests with different additions (20–80 ppm) of modified biodiesel in compression-ignition engines. They investigated the effect of cerium oxide nanoparticles on engine performance and emission characteristics. The results showed that the brake thermal efficiency of the diesel engine fueled with the addition of cerium oxide nanoparticles increased by 1.5%. In addition, the cerium oxide promoted the HC oxidation, and the NO and HC emissions were reduced by 30% and 40%, respectively. Similarly, adding Cu, Fe, Pt and graphene nanoparticles to diesel-biodiesel fuel blends can improve combustion and reduce emissions to varying degrees [36–46].

This paper reviews research progress on different nano-additives for improving combustion and emission characteristics in diesel-biodiesel fuel blends. The main research contents of this paper review are as follows: (1) A comprehensive understanding of the preparation of various nano-additives and their excellent properties; (2) The performance and emission characteristics of combustion and diesel-biodiesel fuel blends combustion engines with different nano-additives, such as increasing engine power, reducing harmful emissions; (3) The researchers selected the most suitable nanoparticles to be added to diesel-biodiesel based on the nature of the nano-additive to achieve efficient combustion and low emissions in diesel engines; (4) To understand the limitations of nano-additives, such as the effect of unburned nanoparticles on engine life, pollution of the atmosphere, and harmful effects on plants and animals.

2. Nano-Additives: A Very Promising Fuel Additive

Nanoscale materials are currently widely used in industry. Their application to diesel-biodiesel fuel blends is an exciting concept and a potential new fuel that has not yet been fully exploited. The reason for the widespread use of nano-additives in diesel-biodiesel is that they exhibit a larger contact surface area, better stability, catalytic properties, rapid oxidation, immense heat of combustion, and large heat and mass transfer rates [47,48]. As shown in Figure 1, nanoparticles are available in different forms (one-dimensional or multi-dimensional), different sizes (1–100 nm) and different surface shapes (cubes, rectangles, cylinders), etc. [49].

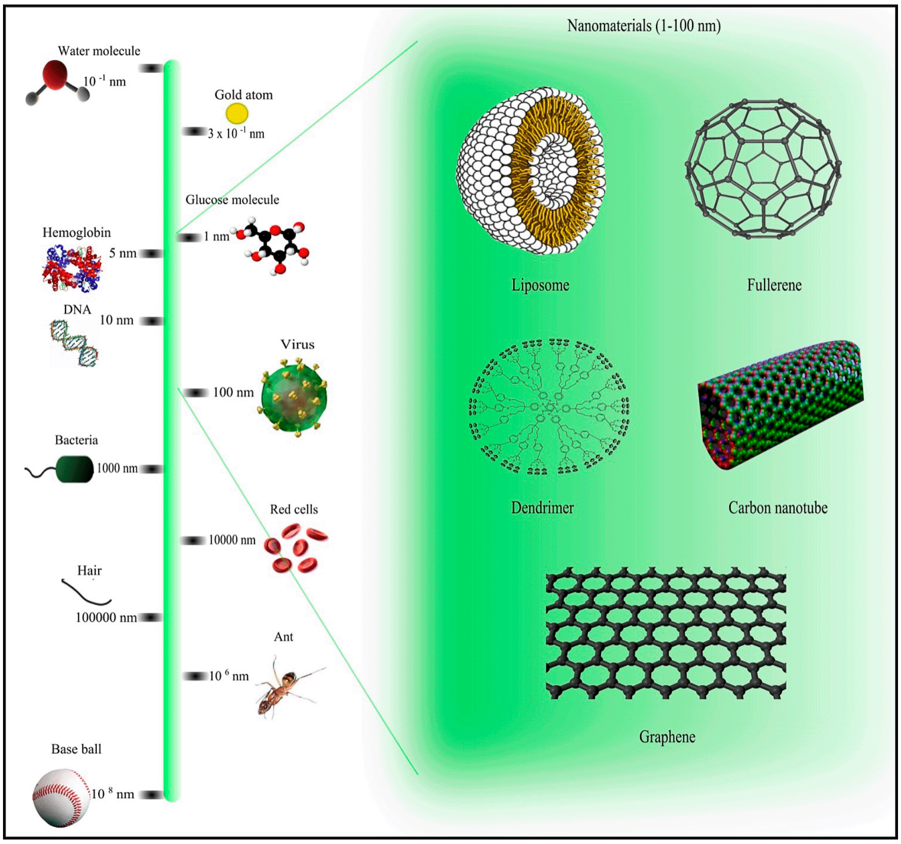

Figure 1. Comparison of the sizes of nanomaterials with those of other common materials [50].

At present, researchers have conducted many experimental studies on the addition of nano-additives to diesel-biodiesel fuel blends and have achieved surprising results. Researchers are currently studying the nano-additives mainly include metals, metal oxides, carbon nanotubes, graphene, organic materials, and hybrid nanomaterials. Among them, the metal oxide nano-additive is one of the more popular nano-additive, which usually has a strong redox reaction because they carry oxygen. It has the advantage of reacting with CO, HC molecules and Carbon atoms in soot and generating large amounts of oxygen, allowing the fuel to burn thoroughly [51,52]. Hao et al. [53] found that aluminium (Al) nano-additives had a strong oxygen extraction ability and could significantly reduce the induction time and energy required for catalytic exothermic reactions. Singh et al. [54] found that carbon-based single-walled nanotubes and multi-walled nanotubes could dramatically increase the ignition rate, ignition delay period, and extend the total combustion time. Therefore, it can be concluded that nano additives are very promising in fuels.

3. Different Preparation Methods to Obtain Stable Nanoparticles

Nanofluid is an extension of nanotechnology and is a fluid obtained by uniformly dispersing nanoparticles into a liquid fluid [55,56]. The flow of nanofluid preparation is shown in Figure 2. Different nanomaterials greatly influence the dispersion and stability of nanofluids, so the preparation and characterization of nanofluids are very important [57,58]. In recent years, researchers have conducted much research on the practice of nanoparticles. They have achieved good results in improving nanoparticles' physical and chemical properties and controlling nanoparticles' size, shape, and porosity. Therefore, selecting a suitable preparation method is very important for nanofluids [59–64]. The synthesis methods of nanofluids are usually in one step, two step and some new techniques have arrisen.

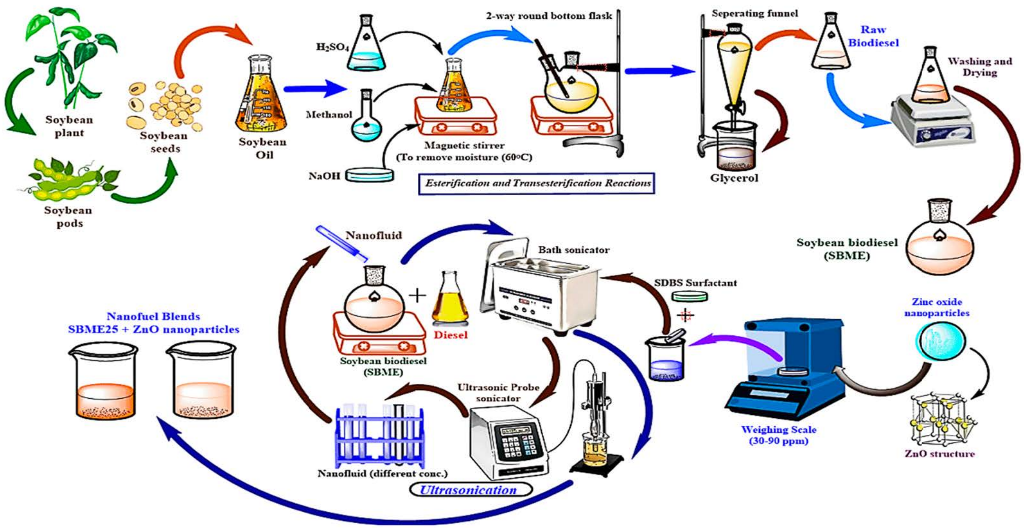

Figure 2. NF of the base fluid with the addition of solid nanoparticles to the base fluid [65].

3.1. One-Step Preparation Method

The one-step method is prepared by mixing nanoparticles and the base solution together at the same time. The main advantages of the one-step method are: (1) The production cost is low compared with other methods because the production is simple and does not require drying, storage or dispersion. (2) The nanofluid produced by the one-step process can maintain stability for a long time due to the low aggregation of nanoparticles. The current main methods for one-step synthesis of nanofluids include direct evaporation, vapour deposition, laser ablation, and submerged arc welding nanoparticle synthesis systems. The one-step method was first proposed by Akoh et al. [66], using vacuum evaporation to obtain 0.25 nm ferromagnetic metal super-particles. Tran et al. [67] produced well-dispersed nanoparticles with a size of 9–21 nm by laser ablation without the use of dispersants or surface reagents. Lo et al. [68] developed a submerged arc nano synthesis system based on the gas coalescence principle, where copper aerosols had immediately coalesced into nanoparticles in the presence of a dielectric liquid. The nanoparticles were then dissolved in the dielectric liquid to form metallic nanofluids. This method is mainly used to prepare copper, copper oxide, cuprous oxide and copper phase nanoparticles, and then dissolve them in dielectric liquid to become metal nanofluid.

3.2. Two-Step Preparation Method

The two-step method is a method in which nanoparticles are first fabricated and then mixed into the base fluid using different techniques. Nanofluids prepared by two-step method have good dispersion efficiency and stability; this is the most widely used nanofluid synthesis method [69,70]. The main techniques for synthesizing nanomaterials are currently divided into bottom-up and top-down processes (Figure 3).

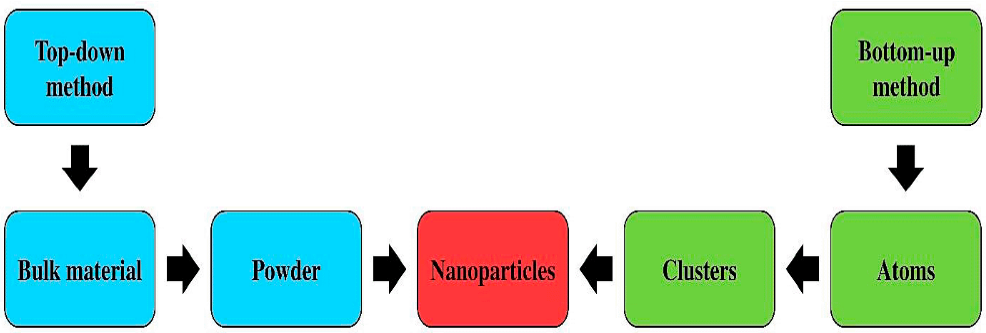

Figure 3. Synthesis process [71].

The bottom-up method is the accumulation of materials from atoms to agglomerates to nanoparticles. The commonly used methods are sol-gel, chemical vapor deposition, pyrolysis and biosynthesis. The sol-gel method has the advantages of simple synthesis, scalability and controllability, and is the preferred method of researchers today. Singh and PalSingh [72] used zinc acetate ($Zn(CH_3COO)_{22}H_2O$) as the precursor, ethanol (CH_2COOH) as the solvent, sodium hydroxide and distilled water as medium and successfully Zinc Oxide(ZnO) nanoparticles with nanometer size of 81.28–84.98 nm were prepared by sol-gel method. Similarly, Alagiri et al. [73] prepared nickel oxide(NiO) nanoparticles using the sol-gel method. Bhaviripudi et al. [74] synthesized single-walled carbon nanotubes using gold nanoparticle catalyst by thermochemical vapor deposition. Biosynthesis is a green method for producing non-toxic and biodegradable nanoparticles using bacteria, plant extracts, fungi, and precursors [60].

The top-down approach is to reduce the larger size materials into nanoscale particles. Commonly used methods include mechanical grinding, nanolithography, laser ablation, and thermal decomposition. Mechanical grinding is a physical method for preparing nanoparticles, which works by plastic deformation of large-sized materials into particle shapes [75]. Nanolithography uses advanced photolithography to reduce large-sized materials from microns to less than 10 nm. There are many processes for nanolithography such as electron beam, optical, nanoimprinting, multiphoton and scanning probe lithography [76]. Laser solution ablation is a reliable top-down method and the synthetic preparation of precious metal nanoparticles using laser solution ablation is usually more trustworthy than conventional chemical reduction methods [77]. Table 1 shows various nanoparticles synthesized in different ways [71].

Table 1. Category of the nanoparticles synthesized from the various methods [71].

Category	Method	Nanoparticles
Bottom-up	Sol-gel	Carbon metal and metal oxide based
	Spinning	Organic polymers
	Chemical Vapour Deposition	Carbon and metal based
	Pyrolysis	Carbon and metal oxide based
	Biosynthesis	Organic polymers and metal-based
Top-down	Mechanical milling	Metal, oxide and polymer-based
	Nanolithography	Metalbased
	Laser ablation	Carbon based and metal oxide based
	Sputtering	Metal-based
	Thermal decomposition	Carbon and metal oxide based

3.3. Some New Techniques

In addition, researchers have achieved remarkable results using two or more nanoparticles to prepare nanofluids. Hybrid nanofluids have received much attention due to their ability to improve the chemical and thermophysical properties of single-phase nanofluids [78,79]. Arul Mozhi Selvan et al. [80] investigated the effect of incorporating cerium oxide nanoparticles and carbon nanotubes into diesel-biodiesel-ethanol blends on engine performance and emissions. It was found that cerium oxide nanoparticles acted as oxygen supply catalysts to oxidize CO and reduce nitrogen oxides. The activation of cerium oxide removes carbon deposits in the cylinder, resulting in a significant reduction in HC and smoke emissions. The combined use of both nanoparticles can contribute to clean combustion and further reduce emissions.

4. Nano-Additives in the Diesel-Biodiesel Fuel Blends

Biodiesel has been used in various countries or around the world, and the benefits it brings are undeniable [81,82]. Compared with diesel fuel, biodiesel is a renewable energy source, very friendly to the environment, degradable and non-toxic [20,83]. Many scientific studies have shown that mixing biodiesel with diesel in different ratios as a diesel engine fuel can improve diesel engines' combustion performance, service life, and reduce emissions. However, biodiesel also has disadvantages, such as poor flowability in the cold state and increased NO_x and CO_2 emissions due to the increased oxygen content of the blended fuel. Researchers have found that nanoparticles can compensate for the drawbacks of biodiesel. Wang et al. [84] incorporated different mass fractions (0.05–5%) of cerium oxide nanoparticles into nanofluid fuels, investigated the evaporation characteristics at 673 K and 873 K and compared with diesel. The results showed that the promotion of fuel droplet evaporation by cerium oxide nanoparticles was very obvious. In particular, the addition of nano-additives at 873 K can prolong the droplet life due to their ability to promote secondary atomization of fuel during diesel injection and combustion, as well as strong micro-explosion phenomena that can occur during evaporation (Figure 4). In-depth research studies have found that the base fuel's thermophysical properties and the nanoparticles' stability and the nanofluid's density, porosity, and structure affect the intensity of secondary atomization [85]. The effects of the most commonly used nanoadditives such as copper oxide(CuO), aluminium oxide(Al_2O_3), cerium oxide, Graphene Oxide(GO), carbon nano-tubes(CNT)and titanium dioxide(TiO_2) added to diesel-biodiesel fuel blends on the combustion performance and emissions of the engine are summarized as shown in Table 2. These nanoparticles have the advantages of high thermal conductivity, strong catalytic function, high oxygen content, more free radicals and fast combustion rate, which are conducive to reducing fuel consumption, improving thermal efficiency and further improving emission pollution.

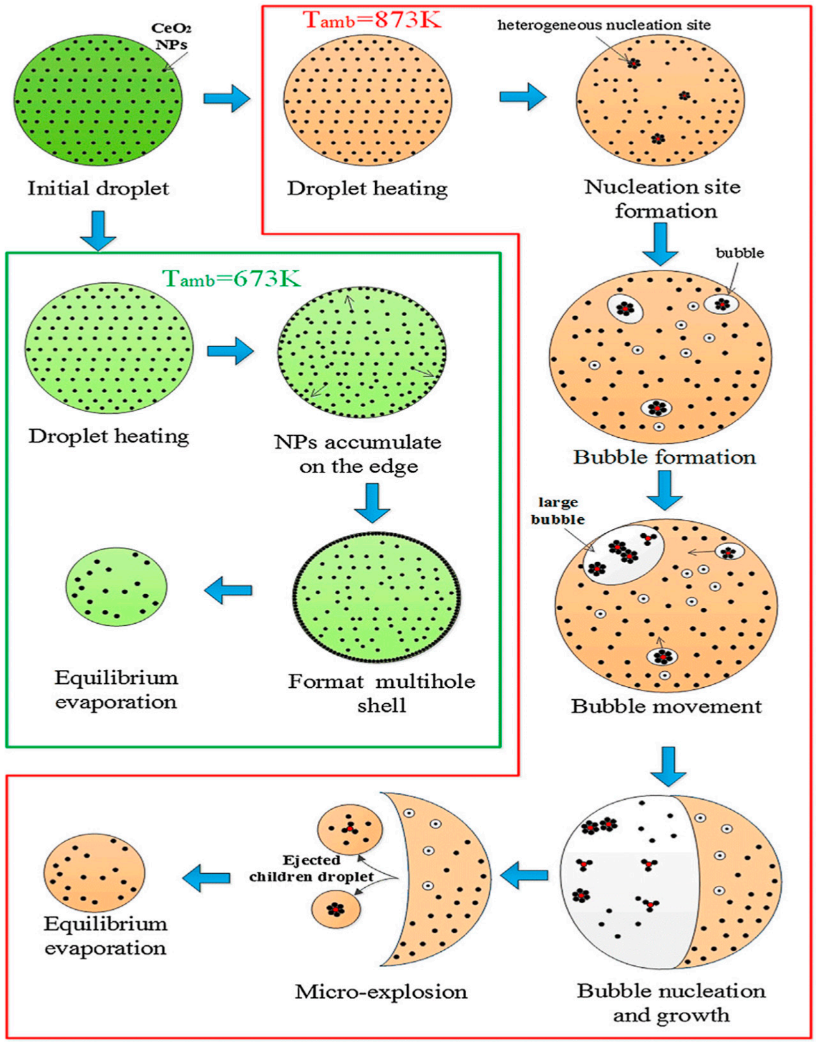

Figure 4. Evaporation diagram of nano fuel droplets [84].

In addition, many researchers have found the micro-explosion phenomenon in diesel-biodiesel fuel blends with the addition of nano-additives, which was an interesting phenomenon. Micro-explosion is caused by heterogeneous nucleation, where nucleation occurs at the droplet surface [86]. It enables secondary atomization or further fragmentation of the fuel droplets to produce very fine droplets that can mix well with air to achieve fast combustion [87–89]. As shown in Figure 5, Jong Boon et al. [90] compared the micro-explosions of three different nano-additives (GNPs, Al_2O_3, and CeO_2). The results showed that GNPs had higher micro-explosion frequencies than Al_2O_3 and CeO_2. This was because GNPs have a weaker van der Waals force constraint, leading to easier thermal decomposition and accelerated combustion processes. Thus, the fuel conversion efficiency of the diesel engine is improved and the output work is increased.

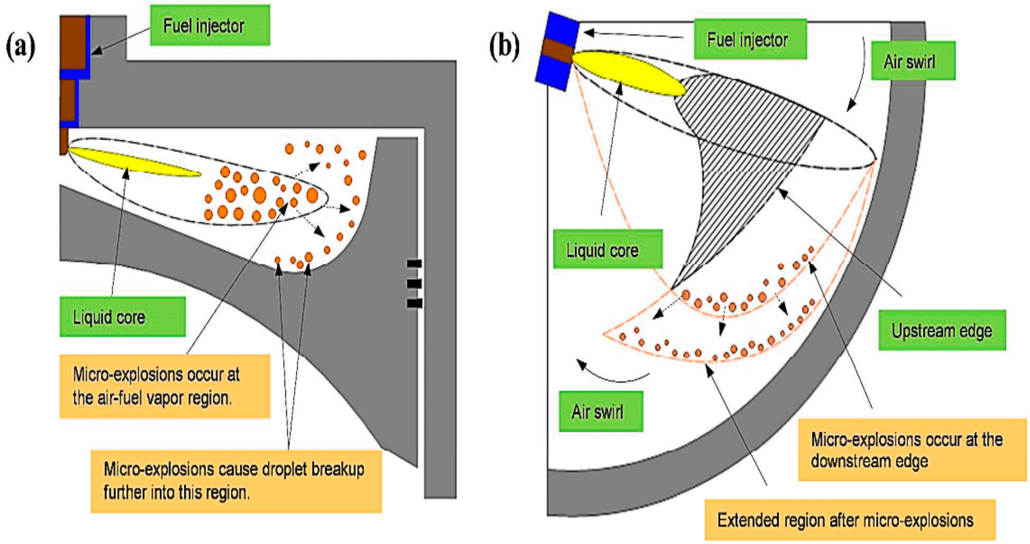

Figure 5. Droplet distribution of micro-explosion in diesel combustion chamber, (**a**) cross-sectional view and (**b**) top surface view [90].

Table 2. The main role of nano-additives in diesel/biodiesel mixed fuel.

Diesel Blended with	Blended Percentage	Nanoparticle	NPs Dosage and Size	Main Effect	Refs.
Neochloris oleoabundans methyl ester	5–15%	CuO_2	60 ppm <50 nm	Nanoparticle-added fuel has higher BTE, EGT and lower BSFC, showing higher peak cylinder pressure	[38]
Garcinia gummi-gutta	20%	CeO_2, ZrO_2 and TiO_2	25 ppm	CO, UBHC and smog emissions are reduced NO_x and CO_2 emissions increase sharply at peak loads.	[62]
biodiesel–ethanol	30%	CeO_2 nd CNT	25–100 ppm	CO emission increased to 22.2%, while HC and smog emissions decreased to 7.2% and 47.6%, respectively.	[80]
Jatropha biodiesel	20% 10%	Al_2O_3	10–30 ppm 28–30 nm	BSFC decreased by 4.93%, BTE increased by 7.8% and emissions of HC, CO, flue gas decreased and nitrogen oxides by 5.69%, 11.24%, 6.48% and 9.39%. Respectively.	[91]
Oenothera Lamarckian biodiesel	20%	GO	30–90 ppm	Power and EGT increased significantly, and CO and UHC emissions were significantly reduced. However, carbon dioxide emission and nitrogen oxide emission increased slightly.	[92]

Table 2. *Cont.*

Diesel Blended with	Blended Percentage	Nanoparticle	NPs Dosage and Size	Main Effect	Refs.
Botryococcus braunii algae oil methyl ester	20%	CuO_2	150 nm 50 ppm 50–100 nm	Shows higher BTE, lower BSFC and EGT, and increases the fuel mixture in the combustion chamber	[93]
Dairy scum oil methyl ester	20%	GO	20–60 23–27 mm	BSFC was decreased by 8.34%, BTE was increased by 11.56%, unburned HC decreased by 21.68%, and smoke decreased by 24.88%, which was significantly improved.	[94]
tamanu biodiesel	0–30%	TiO_2	25–100 ppm	Various reductions in CO, nitrogen, CO_2, HC, oxygen and flue gas opacity were found.	[95]
Waste cooking oil	20%	CeO_2-WCNT	90 ppm	BSFC decreased by 0.2501 (kg/ kW-h), NO_x was reduced by 18.90%, CO by 38.8% and HC by 71.40%.	[96]
Waste cooking oil	5–20%	Al_2O_3 and TiO_2	50–100 ppm	Performance parameters such as BTE and BFSC improved significantly, NO_x, UHC and CO emissions decreased, while CO_2 emissions increased.	[97]
Jatropha-n-Butanol (JME40B)	50%	GNP-Multi-walled carbon nanotubes (MWCNT)	50 ppm	NO_x, CO and UHC were reduced by 45%, 55% and 50% respectively	[98]
Jojoba (JB20D)	40%	Al_2O_3	50 ppm	12% reduction in BFSC, 4.5% increase in peak cylinder pressure, 4% increase in maximum pressure	[99]
waste frying oil	20%	Mn_2O_3 Co_3O_4	25–50 ppm	The engine consumes less fuel while producing the same power output. BTE has been improved. Both reduce emissions of NO_x and CO	[100]
10% astor oil +20%Ethanol	30%	cerium oxide	25 ppm	Increased BTE and IMEP, CO, reduced ignition delay, lower HC emissions, and lower smoke levels	[101]
Algae oil	20%	SiO_2 and TiO_2	50–100 ppm 50 nm	BSFC, BTH, CO, CH and CO_2 are well improved in performance characteristics and emission reduction.	[102]
water	10%	Al_2O_3, CuO, MgO, MnO and ZnO	100 ppm 34 nm	The BSFC reduction rate of Al_2O_3 is high. 17% reduction in CO emission when using ZnO	[103]
Lemon and orange peel oil	20%	CNT, CeO_2	50–100 ppm	Higher BTE and lower BSFCwith relatively low CO and HC emissions	[104]

5. Effect of Different Nano-Additives on Combustion and Emissions of Biodiesel-Diesel Engines

How to use nano-additives to improve the combustion and emission performance of engines is an important research topic [105]. Researchers have selected suitable nano-additives based on the fuel blends' viscosity, flash point, and solubility [106,107]. Moreover, the effects of using nano-additives and biodiesel-diesel blends on engine stability, combustion and emission characteristics were further investigated [108,109].

5.1. Effect of Nano-Additives in Diesel-Biodiesel on Engine Combustion

Many researchers have found that the addition of nano-additives can overcome the disadvantages of biodiesel, such as poor oxidative stability, high fuel consumption, excessive carbon deposition in engine combustion and so on. As shown in Table 3, the effect of adding nano-additives on performance parameters such as engine BTE, BSFC and power output was investigated.

Table 3. Effect of Nano-additives on engine performance.

Diesel Blended with	Nanoparticle	BTE	BFSC	Power	Refs.
Waste cooking oil	CNT and silver	–	−7.08%	+2%	[30]
Honge oil	Al_2O_3	+10.57%	−11.65%	–	[33]
cooking oil	CNTs	+8.12%	−7.12%	+3.67%	[34]
Soybean	ZnO	+23.2%	−26.66%	–	[65]
Dairy scum oil	graphene oxide	+11.56%	−8.34%	–	[94]
Cooking oil	MWCNT	–	−4.5%	+7.81%	[96]
Jatropha methyl ester	GNPs	+25%	−20%	–	[110]
Jatropha	Al_2O_3	+24.7%	Decrease	+3.85%	[111]
Ailanthus altissima	GO	–	−14.48%	+14.3%	[112]
Cooking oil	Fe_2O_3	+15.05%	−10.73%	–	[113]
Soybean	SiO_2	+6.39%	+9.88%	–	[114]
Neem	NiO	+2.9%	−1.8%	–	[115]
Algae oil	CeO_2	increase	decrease	–	[116]
Pungamia pinnata	coconut shell	increase	decrease	+0.65%	[117]
Waste Cooking Oil	Al_2O_3	increase	decrease	increase	[118]
Ricinus communis	Sr@ZnO	+20.83%	−20.07%	increase	[119]
Waste cooking oil	Al_2O_3	+5.80%	−14.66%	+5.36%	[120]
Pongamia	CuO	+4.01%	−1.0%	–	[121]
Lemongrass Oil	CeO_2	+3.55%	−5.87%	–	[122]
Jatropha Methyl Ester	GO	+17%	−20%	–	[123]

5.1.1. The Effect of Nano-Additives on Brake Thermal Efficiency

BTE represents the ratio between the energy produced by the engine and the heat provided by the fuel, which is an important performance parameter of the engine. Adding nanoparticles to diesel-biodiesel fuel blends can improve its radiation, heat and mass transfer performance, so as to obtain fuller combustion and higher thermal efficiency [124]. Ramarao et al. [125] investigated the incorporation of 30–50 nm CeO_2 nano-additives in different cottonseed oil methyl ester blends. It was found that the BTE of diesel-biodiesel fuel blends with CeO_2 addition increased with increasing loading. The BTE of fuel blended with 0.04 g of CeO_2 is approximately 2% higher than diesel at the whole load operation. Harish et al. [91] observed that the addition of different ratios of Al_2O_3 nanoparticles to ternary fuels (70% diesel, 20% jatropha biodiesel, and 10% ethanol) revealed that the addition of 20 ppm of Al_2O_3 nanoparticles improved the BTE by 7.8%. It could be due to the catalytic activity of the nanoparticles, which promotes micro-explosion of the droplets, thereby enhancing fuel vapour and air mixing and improving the possibility of complete combustion [126].

Raju et al. [127] studied alumina and MWNTs, which were added to tamarind methyl ester mixture with 30 ppm and 60 ppm, respectively. As shown in Figure 6, both nano-additives improve the BTE of the engine, and the BTE increases with the increase of nano particle content. It was due to the metal nanoparticles promoting better air-fuel mixing and larger specific surface area to volume ratio, which significantly improves the combustion efficiency. In addition, the incorporation of alumina nanoparticles had higher BTE than carbon nanotubes under the same conditions. Among the fuel blends with nano-additives, the addition of 60 ppm alumina nanoparticles had the highest BTE of 35.74%, which was 4.5% higher than the tamarind seed methyl ester blend at peak load conditions. It was due to alumina nanoparticles' relatively high oxygen content, which resulted in more oxygen atoms involved in the reaction during combustion, thus increasing the combustion efficiency. Syed et al. [128] observed that a similar increment in thermal efficiency was obtained for the higher concentrations of alumina oxide nanoparticles in biodiesel.

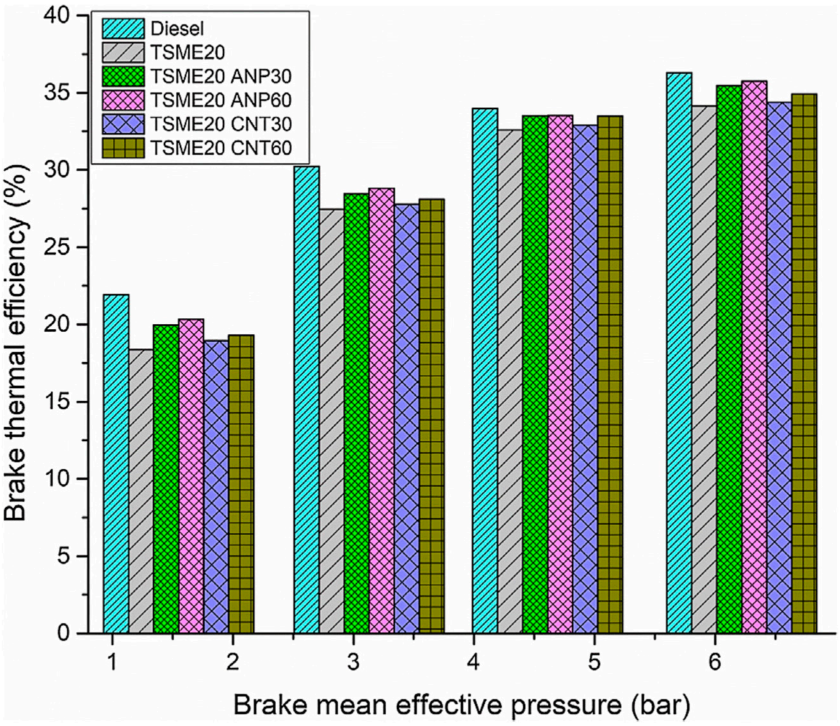

Figure 6. Brake thermal efficiency at various engine loads [127].

In addition, nano-additives can be used as catalysts. This is due to the ability of nanoa-dditives to improve surface area and reactive surfaces, which increases chemical reactivity [129]. As shown in Figure 7, Janakiraman et al. [61] found that the BTE of B20 + TiO 2 (25 ppm) blended fuel was close to that of diesel at high load, and it was 6.05% higher than that of B20 blend. This may be due to the nano-additives which helps in faster combustion and better atomization during the combustion process. GNPs can reduce the duration of late combustion in the exhaust stroke, thus reducing incomplete combustion of the fuel and increasing thermal efficiency [130,131].

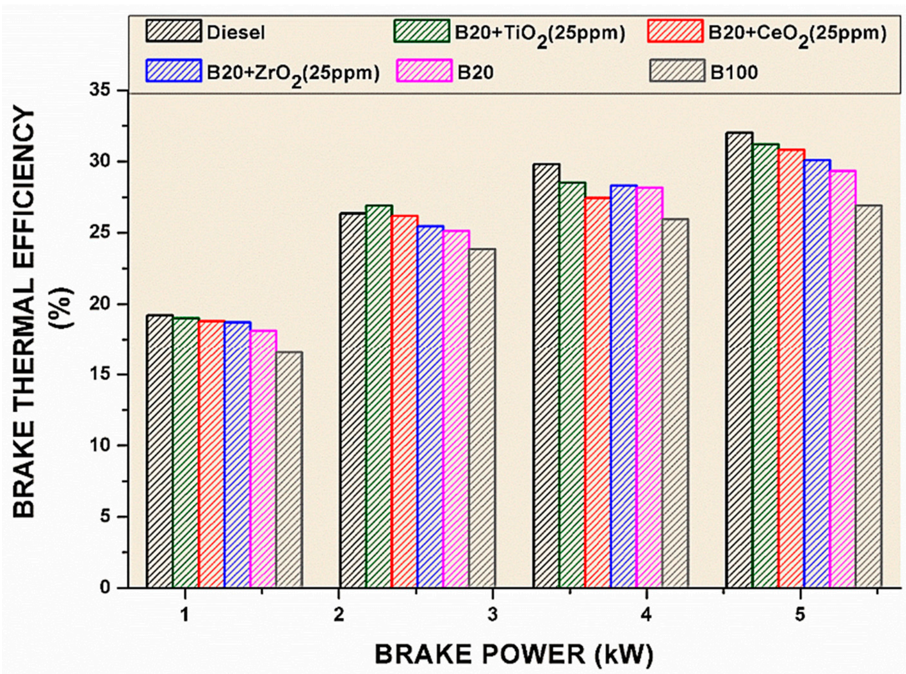

Figure 7. Variation of BTE with Brake power [61].

Dharmaprabhakaran et al. [93] CuO_2 nano-additives of 25 ppm, 50 ppm, 75 ppm and 100 ppm were added to the mixture of Staphylococcus brucei algal oil methyl ester. The experimental results show that BTE enhanced with increasing of load under various fuel blending. Diesel-biodiesel containing 100 ppm CuO_2 showed higher BTE in all cases compared with B20. It could be due to the high surface to volume ratio of CuO_2 nanoparticles, which produces good atomization and rapid evaporation of the fuel, improving the combustion efficiency (Figure 8).

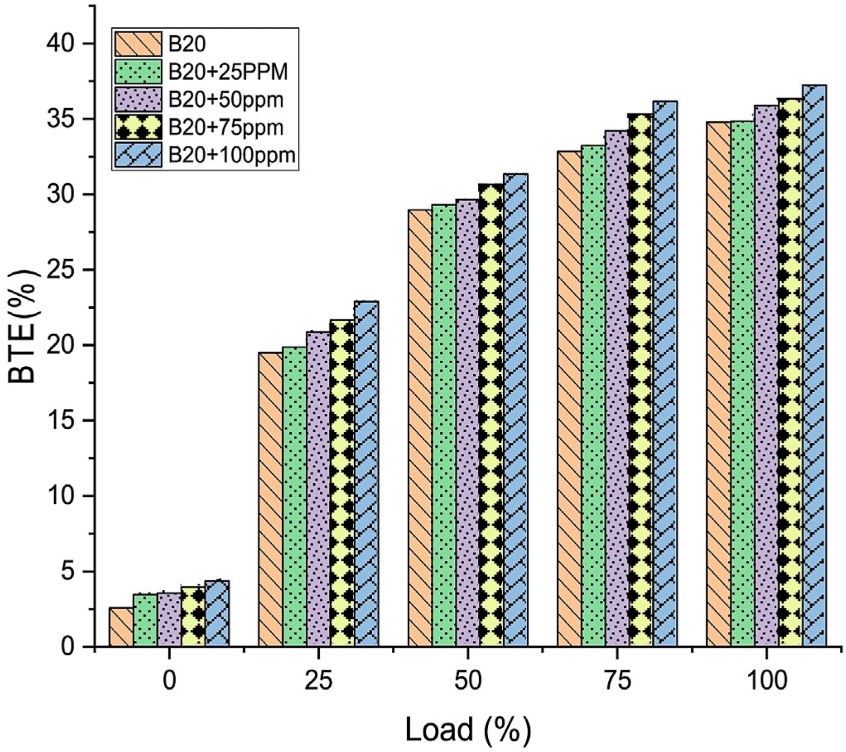

Figure 8. Variation of BTE with load [93].

5.1.2. The effect of Nano-Additives on Brake Specific Fuel Consumption

BSFC is the fuel consumption and utilization per unit of power and time. Generally, diesel-biodiesel has a higher BSFC than diesel, mainly because the calorific value of diesel-biodiesel fuel is lower than that of diesel when the engine output is constant, resulting in the need to consume more fuel to maintain the same power [132]. The researchers found that adding nanomaterials to the fuel to improve the engine's BSFC was a good method [133,134]. This section investigates the effect of adding various nano-additives to diesel-biodiesel on BSFC.

Fayaz et al. [135] prepared nano-fuel blends by dispersing three different nanoparticles (Al_2O_3, CNT and TiO_2) into diesel-biodiesel fuel blends. Figure 9 shows the variation of BSFC from 1050 rpm to 2300 rpm at full engine load. The results show that the BSFC decreases as the speed increases, and the BSFC of the fuel with nano-additives is significantly lower than that of diesel, especially additives containing Al_2O_3 will achieve superior results. The nanoparticles dispersed into the diesel-biodiesel were able to resolve blockage and atomization and improve the air-fuel mixture. In addition, these nanoparticles all increase the surface area to volume ratio, which leads to better combustion and lowers fuel consumption.

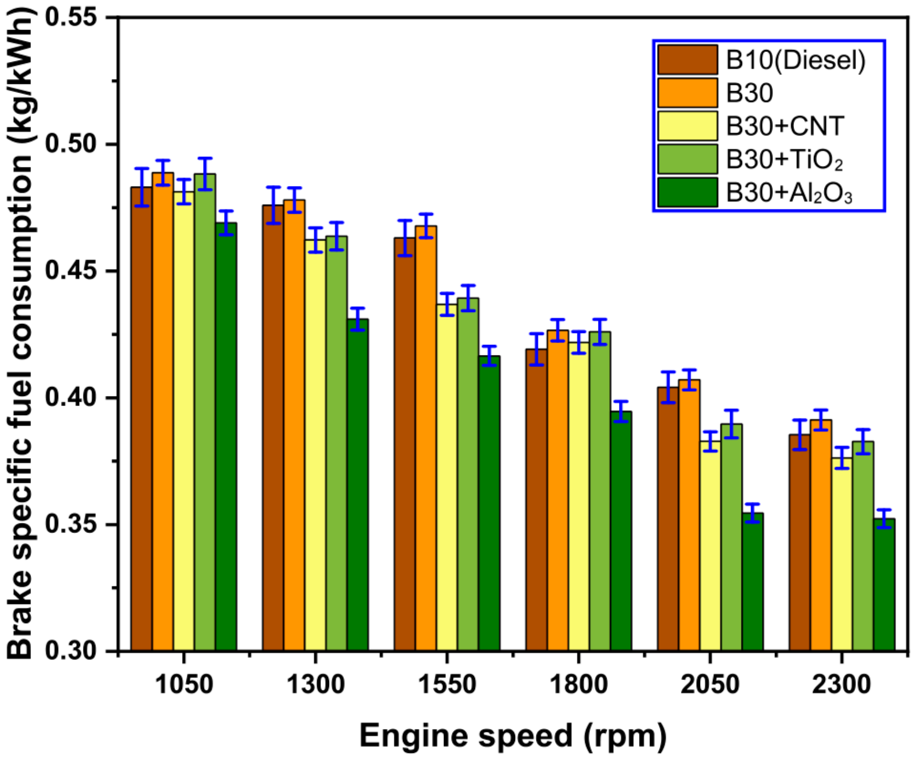

Figure 9. Variation of BSFC with Engine speed [135].

Hatami et al. [136] investigated the effect of adding Al_2O_3 and MWCNT to diesel-biodiesel on engine. As shown in Figure 10, the brake specific energy consumption at full load was reduced by 5.6%, 9.0%, 10.4% and 13.1% for 50 ppm of MWCNT, 100 ppm of MWCNT, 50 ppm of Al_2O_3, and 100 ppm of Al_2O_3, respectively, compared with diesel-Schleicher oleosa. It was due to the fact that the nanoparticles act as catalysts in the combustion reaction and increase the oxidation rate.

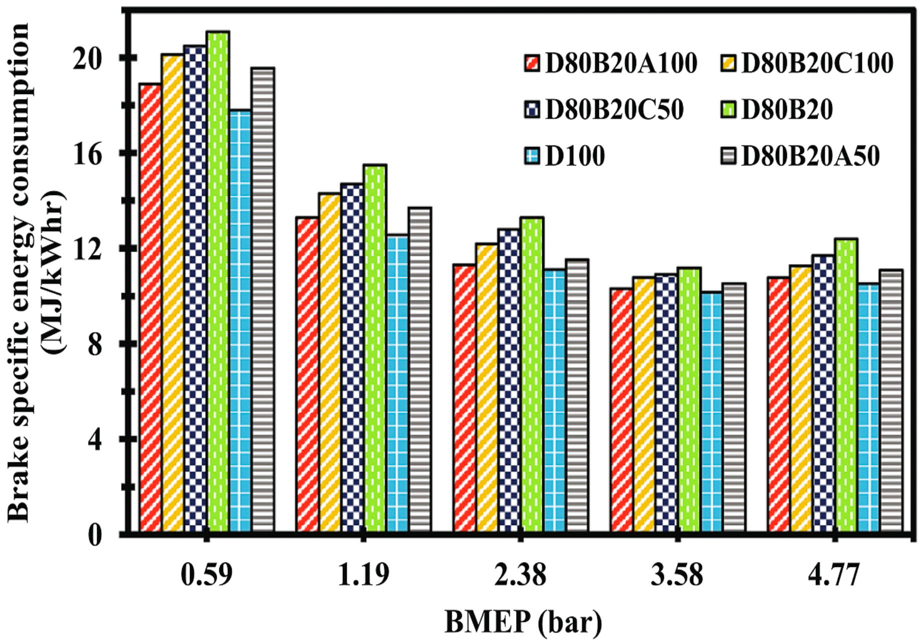

Figure 10. Variation of brake specific energy consumption [136].

Figure 11 shows the BSFC for different blends [137]. The results showed that the BSFC of the engine decreases significantly as the load increases. In addition, the BSFC was minimum when the concentration of nano-additive in the diesel-biodiesel was increased from 400 ppm. However, the BSFC increased when the concentration of nano-additives was increased from 400 to 600 ppm. This may be because further concentration increases may affect the fuel system components and thus the fuel spray characteristics.

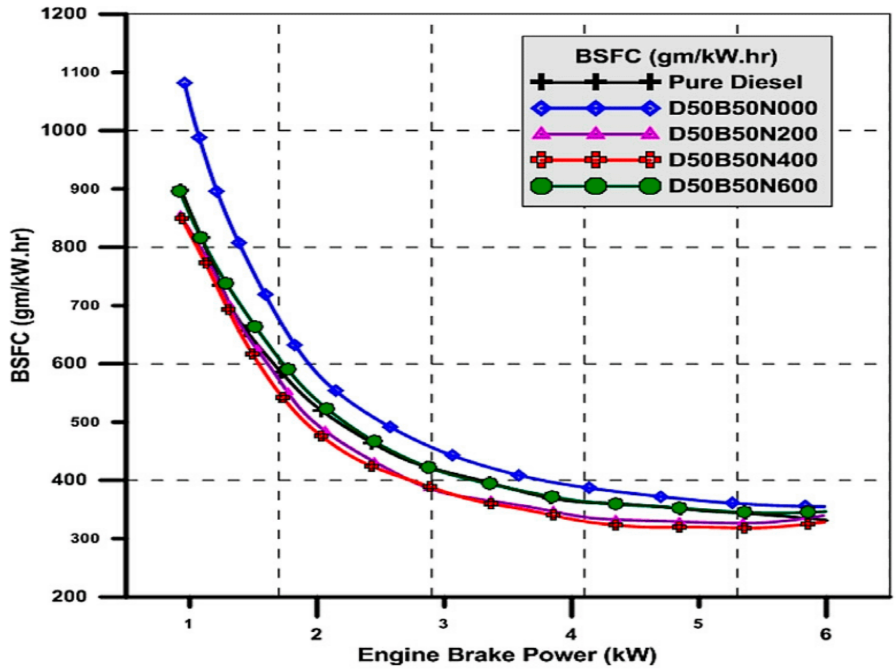

Figure 11. Variation of BSFC with Brake power [137].

In addition, nanoparticles affect engine power and exhaust gas temperature. Hoseini et al. [138] found that the addition of GO nanoparticles to diesel-biodiesel resulted in a significant increase in engine braking power. It was due to the increased surface-to-volume ratio of GO nanoparticles, which increases the heat transfer coefficient, resulting in higher peak cylinder pressures and faster heat release rates. Gad and Jayaraj [139] found that the addition of nanoparticles to jatropha biodiesel blends resulted in a reduction in exhaust gas temperature, with a maximum temperature reduction of 27%. This may be due to the improved fuel-air mixing and in-cylinder combustion characteristics of the nanoparticles, which improve engine efficiency.

5.2. Engine Emission Characteristics of Diesel-Biodiesel Fuel Blends with Nano-Additives

In the last few decades, scientists have reached a consensus and reported that nano-additives were causing a change in current energy sources. The addition of nanoparticles to diesel-biodiesel fuel blends has been widely used in diesel engines [19,126,139]. After identifying potential targets for expanding the application of nanoparticles, the researchers learned as much as possible about the effects of adding nano-additives on diesel engine emissions (Table 4).

Table 4. Effect of nano-additives on harmful gas emissions.

Diesel Blended with	Nanoparticle	NO_x	CO	HC	Refs.
Honge oil	HOME	+11.27%	−47.43%	−37.72%	[33]
Garcinia gummi-gutta	TiO_2	−22.57%	−35.89%	−6.39%	[61]
Oenothera lamarckiana	GO	+9%	−22%	−26%	[92]
Jatropha methyl	GNPs	−55%	−65%	−65%	[110]
Cooking oil	MWCNT	+8%	−20%	+28%	[114]
Pongamia	CuO	−9.8%	−29%	−7.9%	[121]
Jatropha	GO	−13%	−60%	−70%	[140]
Orange peel oil	TiO_2	−9.7%	−18.4%	−16.0%	[141]
Mahua	CuO	+3.2%	−33%	−5.33%	[142]
Pongamia	Fe_3O_4	−8%	decrease	+16.6%	[143]
Azadirachta indica	NiO	+6.1%	−25.4%	−10.8%	[144]
Flaxseed oil	Cr_2O_3	−6.66%	−14.05%	−12.93%	[145]
Waste Plastic Oil	rice husk	+14.1%	−7%	−15.3%	[146]
Palm oil	GNPs	+3.65%	−4.41%	−25%	[147]

5.2.1. The Effect of Nano-Additives on Nitrogen Oxide Emissions

NO_x is considered one of the leading pollutant gases emitted by CI engines. According to the thermal mechanism, the formation of NO_x is mainly the result of the interaction between oxygen and nitrogen at high temperatures in the cylinder. As can be seen from the Figure 12, the NO_x emissions of the blended fuel with CeO_2 nano-additive were higher than diesel -biodiesel fuel blends. This may be caused by the higher oxygen content in the fuel mixture and the higher temperature in the cylinder [148]. The nanoparticles would improve the oxidation process during combustion, leading to increased NO_x emissions.

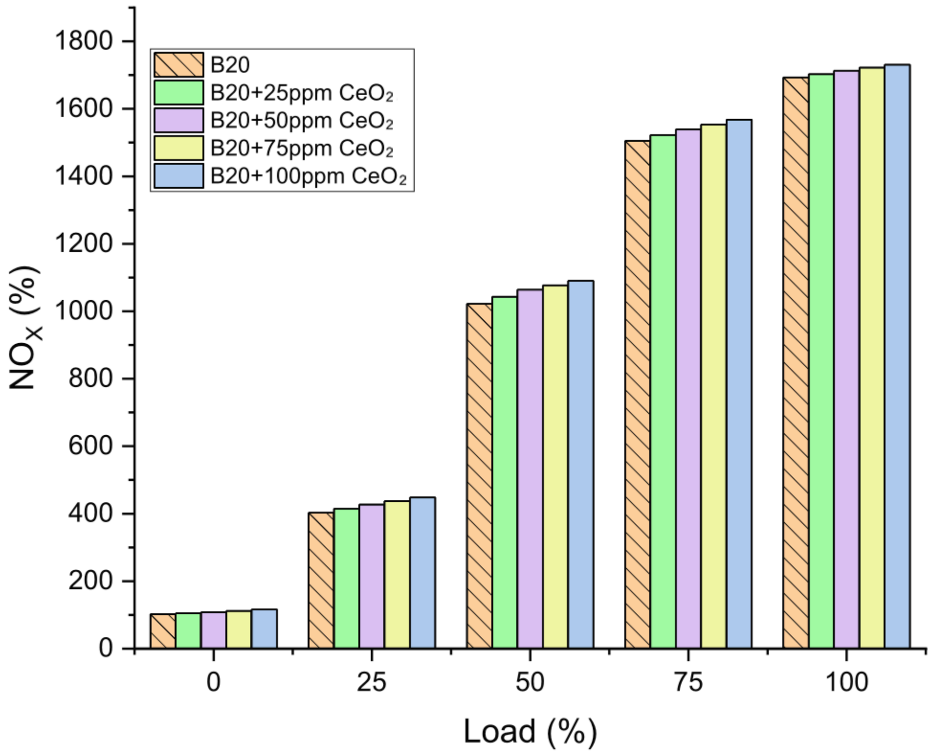

Figure 12. Variation of NO_x with Load [148].

Vellaiyan [149] studied the addition of nanoparticles to a modified fuel blend (diesel-soy biodiesel) and compared the emission characteristics with those of diesel. The results showed that the emission levels of CO and UHC emissions were significantly reduced, although NO_x emissions increased slightly at full load. This is because alumina nanoparticles can better use the oxygen inherent in soybean biodiesel.

In addition, some researchers found that nano-additives could reduce NO_x emissions.As shown in Figure 13, Perumal et al. [121] CuO nanoparticles of 50 ppm and 100 ppm sizes were mixed into malachite biodiesel as fuel for CI engine. The experimental results showed that after adding CuO nanoparticles, the NO_x, CO and HC emissions of the fuel were significantly reduced, and the NO_x emissions are reduced by about 9.8%. It could be due to the catalytic reaction of CuO nanoparticles improving the heat transfer in the combustion chamber. In addition, the addition of copper nanoparticles can improve the oxidation stability of Soya bean biodiesel and prevent its oxidation, thus reducing the NO_x emissions to a greater extent [150].

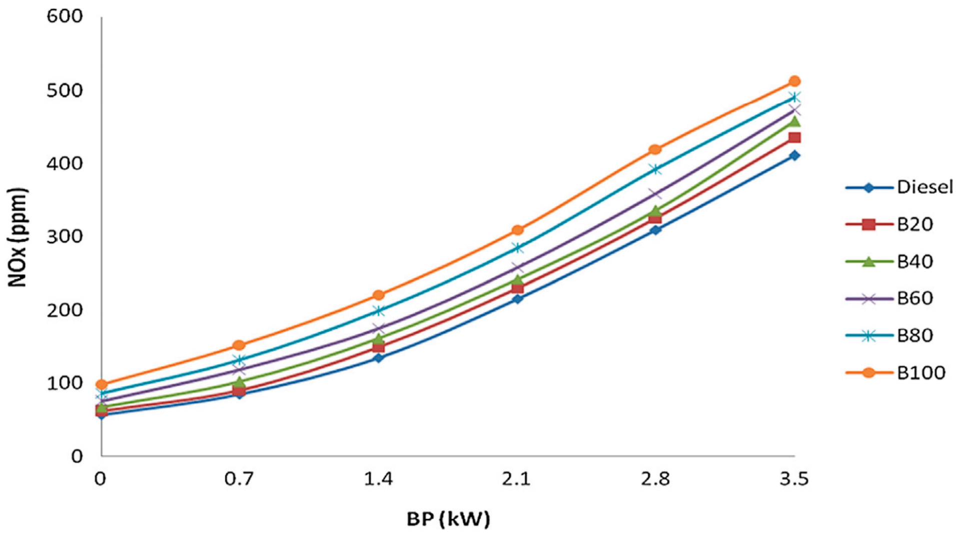

Figure 13. Variation of NO_x with Brake power for different blends of PME with CuO additive [121].

5.2.2. The Effect of Nano-Additives on HC Emission

Unexploded HC are mainly pollutants produced by the incomplete combustion of fuels. Many researchers have found that when engines run on biodiesel-diesel, the high amount of oxygen in the biodiesel's structure leads to complete combustion, resulting in lower HC emissions [151–154]. In addition, the addition of nanoparticles can further reduce HC emissions.

As shown in Figure 14, Dhinesh et al. [155] investigated the effect of adding 20 ppm cerium oxide nano-additive to Cymbopogon flexuosus biofuel with cerium oxide on the engine. The results show that compared with diesel-biodiesel without nanoparticles, HC emission is reduced by 3.63% due to the oxygen vacancy capacity of ceria nanoparticles.

Kataria et al. [156] investigated the effect of WCO and 5 wt% of zinc-doped calcium oxide nano-additives on diesel engine performance in a four-stroke, water-cooled, single-cylinder, variable compression ratio direct injection diesel engine. The results showed that the combustion of different percentages of biodiesel and blends with nanoparticles reduced HC emission compared to diesel fuel. The nanoparticles could reduce further HC emission, which indicated cleaner and more complete fuel combustion. In addition, as shown in Figure 15, carbon nanotube particles have an additional carbon structure that leads to increased HC emission compared with diesel fuel. At the same time, oxygenated additives promote complete combustion and silver nanoparticles can reduce HC emission [30]. EL-Seesy et al. [123] selected graphene oxide as a nanomaterial to prepare Jatropha curcas biodiesel nano fuel at different concentrations (25, 50, 75 and 100 mg/L). The results showed a 50% reduction in UHC emission of JME-GO blends compared with pure JME fuels. A comprehensive comparison revealed that graphene oxide at a concentration of 50 mg/L had the best effect on engine performance and emissions. In addition, the incorporation of nanoparticles (TiO_2, CeO/CeO_2, Al_2O_3, and GO/GNP) commonly used in nano fuel into diesel-biodiesel can all reduce HC emission to varying degrees [157–163].

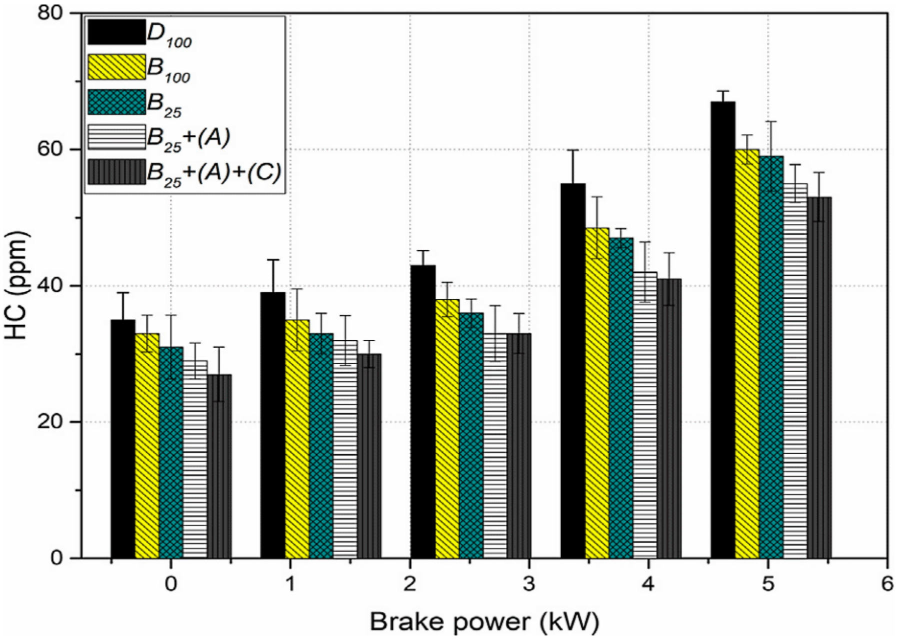

Figure 14. Variation of HC emission for the test samples [155].

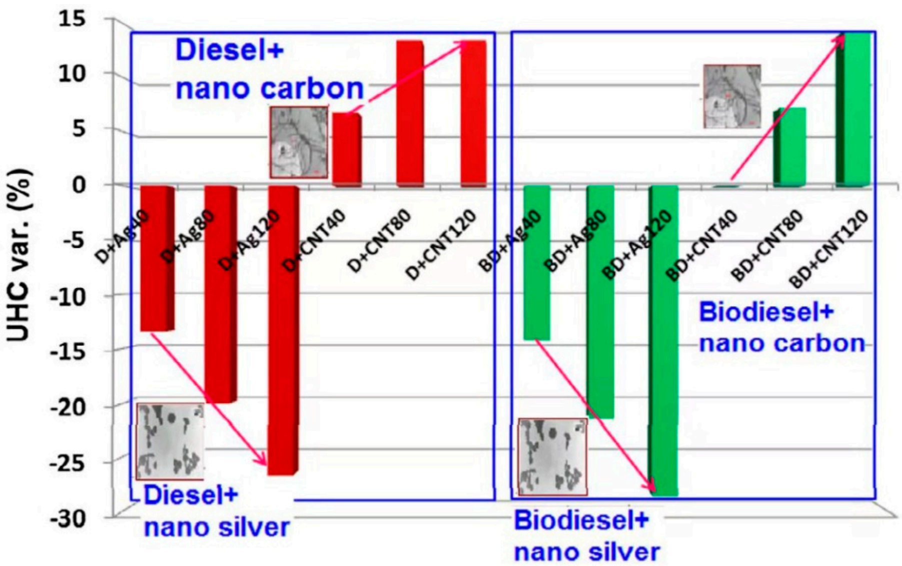

Figure 15. Variation of UHC with nano–diesel–biodiesel fuel blends [30].

5.2.3. The Effect of Nano-Additives on CO Emission

The main causes of CO production are insufficient oxygen, long oxidation residence time, and high in-cylinder temperature, which leads to incomplete fuel combustion [164,165]. It is well known that biodiesel to diesel fuel can significantly reduce CO emission. In addition, researchers have delved deeper and found that the addition of nano additives to diesel-biodiesel can significantly reduce CO emission [114,166,167]. This section explains the effect of nanoparticle addition to diesel-biodiesel fuel blends on CO emission.

As shown in Figure 16, Prabu [168] investigated the combustion and emission characteristics of nano Al_2O_3 and CeO_2 as additives to Jatropha curcas biodiesel in a single cylinder four-stroke direct injection diesel engine. The results showed a 60% reduction in

CO emission from the nanoparticle blend compared with diesel. The reduction of CO emission is mainly due to the catalytic nature and redox ability of Al_2O_3 and CeO_2 nanoparticles, which can further oxidize CO to CO_2 [169]. Shaaf and Velraj [170] investigated the effect of adding alumina as a nano additive to modified fuels on the combustion and emissions of single cylinder direct injection engines. As shown in Figure 17, the CO emission of the fuel with nanoparticles added at a 0–75% load were higher than that of diesel fuel because the presence of alumina nanoparticles hindered the fuel mixing process at low loads. However, the CO emission of the fuel with nanoparticles at full load are significantly lower than that of diesel because the nanoparticles increase the atomization rate and redox characteristics of the fuel at full load, which leads to complete combustion.

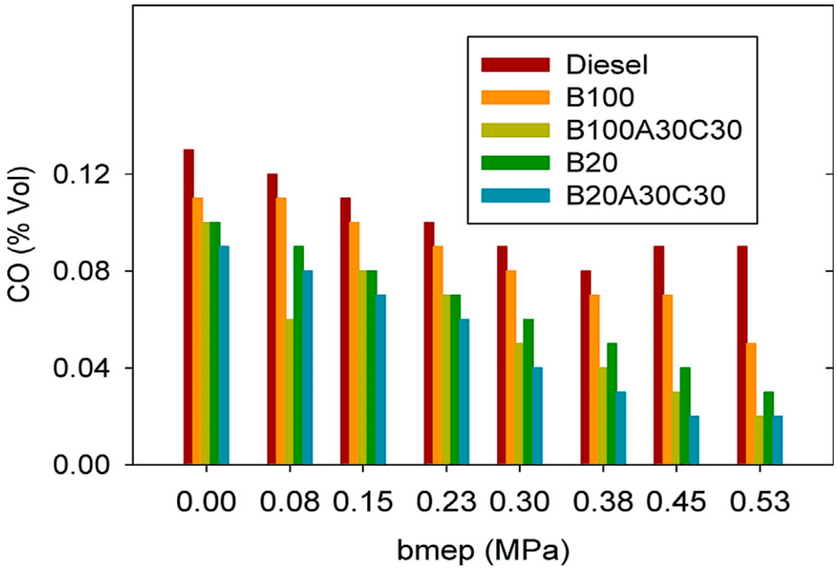

Figure 16. Variations of CO under BMEP [168].

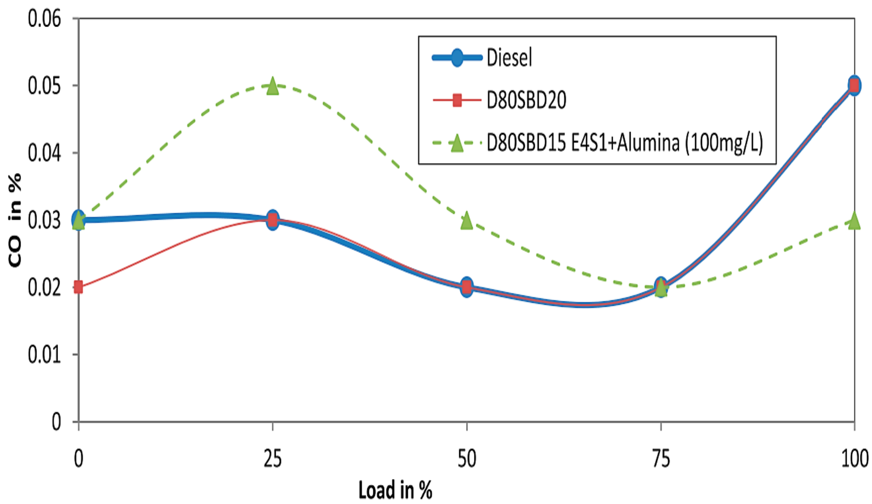

Figure 17. Variation of CO emission at different loads [170].

6. Limitations of Nano Additive in Engine Applications

In the past few decades, researchers have discovered many excellent properties of nano-additives (as shown in Figure 18), which have been widely used in engine applications. However, their development in the engine field is hampered by several factors, such as preparation costs, damage to engine components, and the effects of toxicity to plants, animals, and humans when released into the atmosphere. Pantzali et al. [171] identified the need for advanced and sophisticated equipment to prepare nanofluids, which could lead to high prices and was a significant factor preventing their mass application. Qibai et al. [172] found that the use of carbon-coated aluminum may lead to higher ash accumulation in the diesel particulate filter, hindering the performance of the after-treatment system and the engine itself. Deqing et al. [173] found that fuel blends containing highly doped CeO_2 nanoparticles could lead to premature engine ignition, and the nanoparticles left at the end of the engine combustion process could be released into the atmosphere through smoke, causing severe air pollution. Gantt et al. [174] analyzed CeO_2 nanoparticles in exhaust gases using electron microscopy. They found that about 40% of the cerium particles were attached to micron-sized volcanic ash particles, and the rest were released into the air as separate particles. The researchers also found some released cerium nanoparticles in water and soil [175,176]. In addition, researchers found that carbon nanotubes, CeO_2, TiO_2, and other particulate matter were released into the environment, and these nanoparticles, which were about 10 nm in size, rapidly combined and fused into clusters of 100 nm or larger, entering the air through the respiratory process, causing damage to the lungs, brain, eyes, and liver, and possibly transferred to the fetus of a pregnant woman [177,178]. Exposure of carbon nanotube nanoparticles in humans causes skin-related problems, ocular allergic effects, and cardiovascular-related problems [179]. Gatti [180] evaluated 18 colon tissue samples affected by cancer and Crohn's disease and found nanoparticles in all cases.

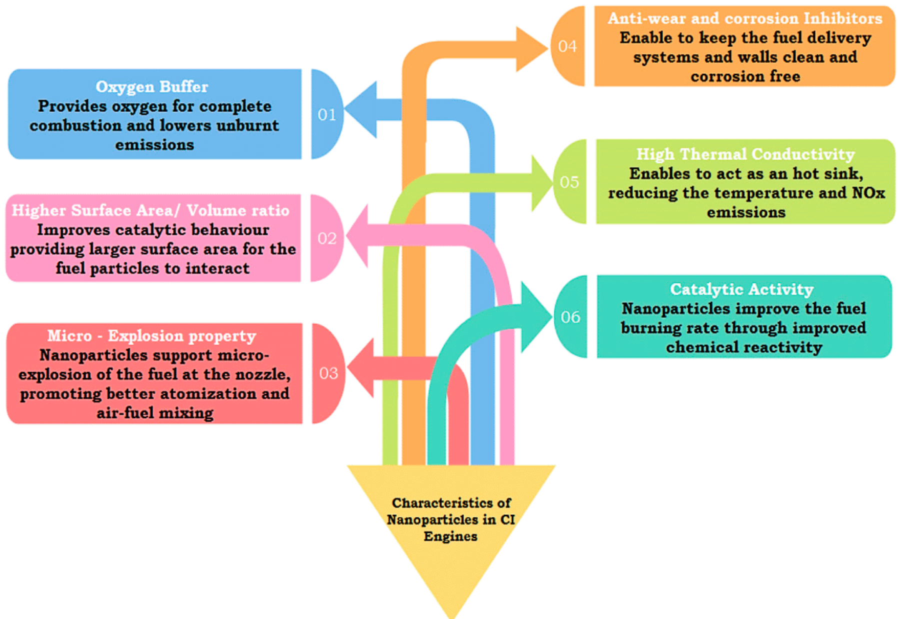

Figure 18. Characterization of nanoparticles in CI engines [159].

7. Comprehensive Evaluation of Nanoparticle-Doped Diesel-Biodiesel Using Life Cycle Assessment

The addition of nano-additives is often considered a more environmentally friendly fuel compared with diesel-biodiesel. However, this subjective decision may change when considering the environmental burden of exhaust emissions during the production phase and late combustion of the fuel. Therefore, there is a need to introduce new concepts and methods to comprehensively assess the benefits and harms of biofuels for human health and the environment [181]. Life cycle assessment (LCA) is an integrated environmental analysis method that can be used to assess the environmental impact of different fuel blends [182,183]. More precisely, the conventional combustion characteristics of diesel-biodiesel engines with nano-additives are translated into several combined outputs (human health, ecosystem quality, climate change, and resource damage categories) to derive the most environmentally friendly blends. Mukhopadhyay et al. [184] conducted a comprehensive analysis of nano-additives added to diesel-biodiesel using a LCA system, and the most environmentally friendly diesel engine hybrid fuel was obtained. This approach maximizes engine performance while minimizing environmental and human hazards. As shown in Figure 19, Hosseinzadeh-Bandbafha et al. [185] conducted a comprehensive study on the emission index of carbon nanoparticles-doped diesel-biodiesel emulsion engines using LCA. It was found that carbon nanoparticles blended fuel with 38 μM addition was the most preferred as well as the most environmentally friendly. Overall, LCA can be used as a "cradle-to-grave" analytical tool to evaluate the beneficial and/or adverse engine and environmental impacts of various nano-additives added to diesel-biodiesel at various stages of its life cycle.

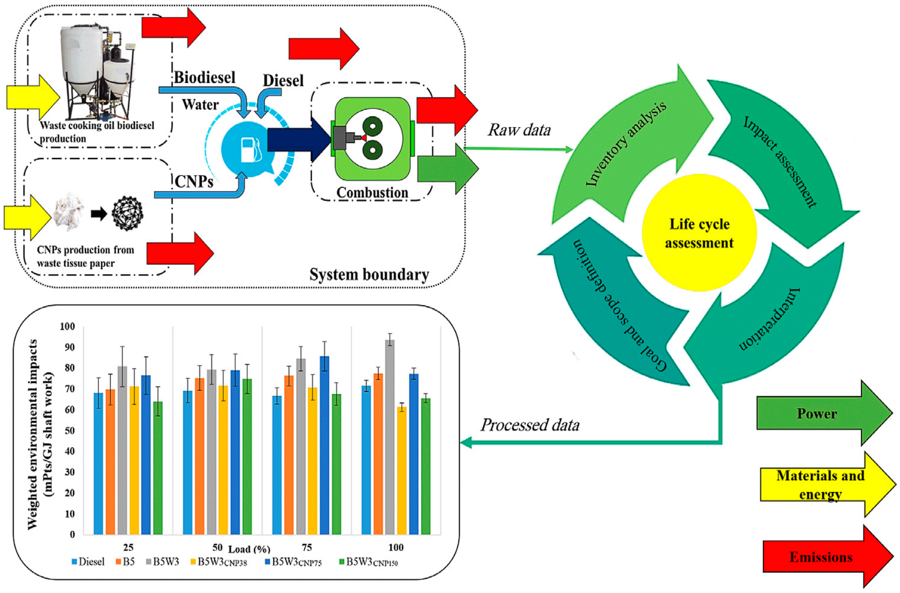

Figure 19. Flow chart using the life cycle approach [185].

8. Conclusions

From this study, the selection of suitable nano-additives according to the physical and chemical properties of biodiesel is important to improve engine performance and reduce harmful emissions. This paper reviews the application of nano-additives in the field of diesel-biodiesel fuel blends. The following conclusions can be drawn:

(1) Nano-additives have many excellent properties, such as large contact surface area, good stability, good catalytic performance, fast oxidation rate, high heat of combustion, etc. These advantages can be applied in the fuel field to improve the combustion of internal combustion engines and reduce harmful gas emissions.

(2) The stable presence of nanoparticles in solution is significant, and among the two-step methods, sol-gel and mechanical grinding are relatively simple and less costly methods for making nanofluids.

(3) In general, researchers have usually studied with CuO, Al_2O_3, MWCNT, CeO_2, GO, CNT, and TiO_2, which are nano-additives added to diesel-biodiesel fuel blends and have achieved remarkable results. In terms of engine performance, CeO_2 was the most effective in reducing BFSC by as low as 30%, and MWCNT was the best in improving BTE by up to 36.81%. In terms of emission, TiO_2 has the best effect in reducing NO_x, with a minimum reduction of 22.57%, GNPs has the best effect in reducing CO, with a minimum reduction of 65%, GO has the best impact in reducing HC, with a minimum decrease of 70%.

(4) Nano-additives in the field of internal combustion engines should be concerned about their harmful effects when they achieve significant results. After the engine combustion process, the nano-particles left behind that are not involved in combustion are released into the atmosphere; atmospheric pollution and human toxicity are severe. Moreover, the introduction of LCA to fully evaluate the benefits and hazards of biofuels to human health and the environment is described in detail.

Therefore, nano-additives have a bright future in diesel-biodiesel engines. It should be emphasized that the addition of nano-additives to diesel-biodiesel fuel blends is seen as an important way to protect human health and improve the environment.

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