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Review

A Comprehensive Review of the Properties, Performance, Combustion, and Emissions of the Diesel Engine Fueled with Different Generations of Biodiesel

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Abstract: Due to the increasing air pollution from diesel engines and the shortage of conventional fossil fuels, many experimental and numerical types of research have been carried out and published in the literature over the past few decades to find a new, sustainable, and alternative fuels. Biodiesel is an appropriate alternate solution for diesel engines because it is renewable, non-toxic, and eco-friendly. According to the European Academies Science Advisory Council, biodiesel evolution is broadly classified into four generations. This paper provides a comprehensive review of the production, properties, combustion, performance, and emission characteristics of diesel engines using different generations of biodiesel as an alternative fuel to replace fossil-based diesel and summarizes the primary feedstocks and properties of different generations of biodiesel compared with diesel. The general impression is that the use of different generations of biodiesel decreased 30% CO, 50% HC, and 70% smoke emissions compared with diesel. Engine performance is slightly decreased by an average of 3.13%, 89.56%, and 11.98% for higher density, viscosity, and cetane, respectively, while having a 7.96% lower heating value compared with diesel. A certain ratio of biodiesel as fuel instead of fossil diesel combined with advanced after-treatment technology is the main trend of future diesel engine development.

Keywords: diesel engine; combustion; performance; emission; biodiesel

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1. Introduction

Climate change and global warming caused by carbon emissions are both global crises. Approximately 200 countries attended the 21st United Nations Climate Change Conference and jointly signed the Paris Agreement to ensure the efficient and sustainable development of energy, economy, and society. Moreover, 184 countries, covering 97.9% of global carbon emissions, also submitted documents entitled "National Contribution Commitment" to fight against climate change [1]. According to the pollutant emission comparison by source sector shown in Figure 1, the rapid growth of the number of vehicle industries (see Figure 1a,b) in the world has increased the amount of exhaust emissions (see Figure 1b,c) in the environment [2].

Vehicular emissions such as particulate matter (PM), hydrocarbon (HC), carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen oxides (NO_x) are hugely responsible for air quality deterioration [3]. Two main internal combustion engine (ICE) types, namely, gasoline and diesel engines, contribute to degrading the air quality in the urban environment. Moreover, emissions from the ICEs were classified as a carcinogen by the International

Agency for Research on Cancer (IARC) in 2013, increasing the primary challenges that policymakers in several countries face [4].

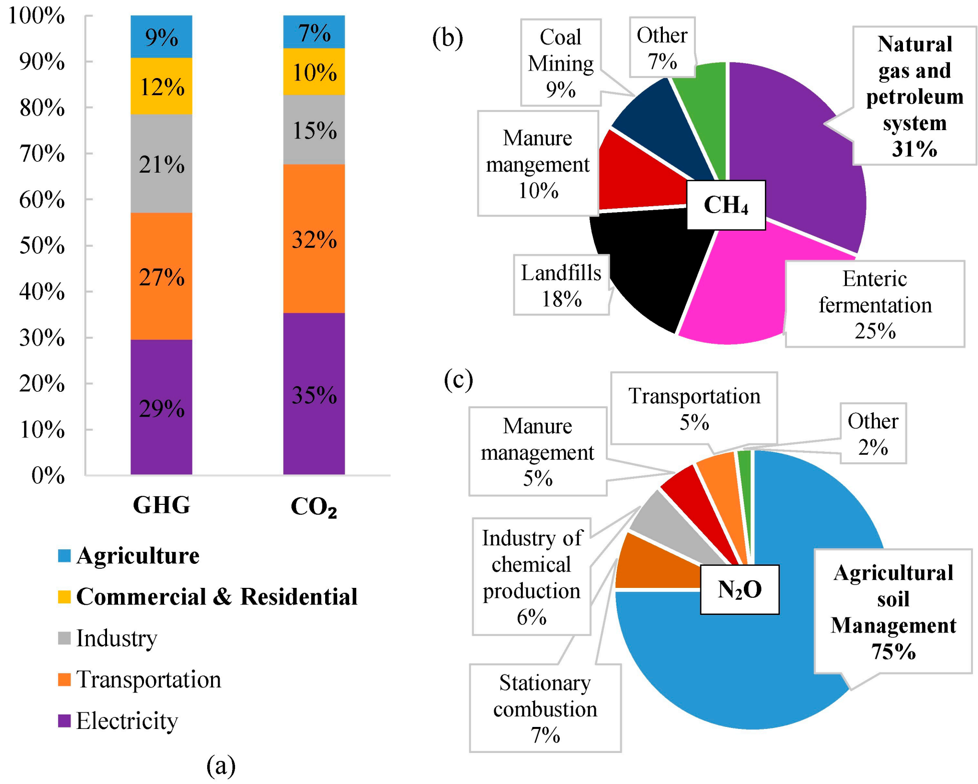

Figure 1. Percentage of pollutant emissions by industry [2]. (**a**) Total emission percentage, (**b**) CH_4 emission percentage; (**c**) N_2O emission percentage.

With the increasingly strict environmental regulations [3–5], the effective use of energy [6,7] and environmentally sustainable development [8] have become a focus of attention in various countries. Fossil fuels such as gasoline and diesel are dwindling [9]. According to the best guess scenario projections aggregated to the continent level shown in Figure 2, known reservoirs will sufficiently meet the worldwide demand for another 39 years for oil, 61 years for natural gas, and 216 years for coal [3,10]. The decrease in fossil fuel and the increasing demand for fuel pose a challenge to society and technology. To overcome this problem [11], many different technologies [12] such as exhaust gas recirculation (EGR) [13,14], emulsion technology (ET) [15,16], water injection (WI) [17,18], injection strategy modification [19,20], combustion chamber geometry modification [21,22], and low temperature combustion strategy [23,24] have been used to improve the combustion and emission characteristics of the diesel engine. However, compared with using new technologies to reduce various environmental pollution caused by fossil fuel combustion, using alternative renewable fuels to achieve high efficiency and clean combustion becomes more attractive. In this regard, sustainable and alternative fuels such as alcohols [25], natural gas [26], biodiesel [27], and dimethyl ether [28] are considered effective methods to reduce the NOx, greenhouse gas, and PM emissions from diesel engines [29–32].

Among these substitute fuels, biodiesel is considered the most promising and attractive alternative fuel because it is sulfur-free, non-toxic, biodegradable, eco-friendly, and more reliable [33]. Many researchers have shown that [34–37] the physical and chemical properties of biodiesel are very close to those of diesel fuel. Moreover, biodiesel can be applied to diesel engines without changing the engine systems because the combustion and emission characteristics of biodiesel are almost similar to conventional diesel [38]. In addition, compared to diesel, biodiesel has a higher cetane number [39], no aromatics, and 10–11% oxygen content [40,41]. These characteristics of biodiesel fuel can reduce CO, HC, and PM emissions in exhaust gases. However, there is no conclusive trend in oxygenated compounds such as aldehydes and ketones [42].

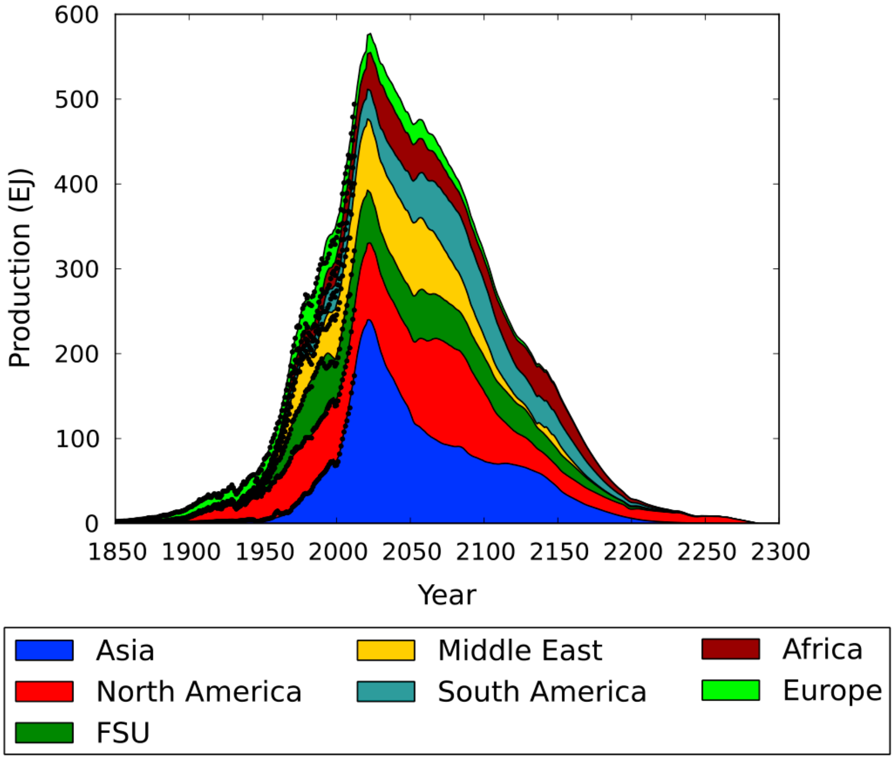

Figure 2. Fossil fuel use and projections (black dots represent actual production) [10].

On the other hand, certain disadvantages include poor storage stability, cold flow properties, inferior spray characteristics, and lower heat content. These shortcomings can be overcome by adequately choosing the raw material for biodiesel production through the transesterification process of different vegetable oils. As for the dynamic and economic characteristics of the diesel engine used biodiesel, many researchers generally believe that biodiesel could cause undesirable effects such as decreased engine torque, power reduction, increased brake specific fuel consumption, and decreased brake thermal efficiency [43,44]. The early research conclusions have been kept in many people's minds that biodiesel is more prone to oxidation, resulting in insoluble gums and sediments that can plug fuel filters, and thus it affects engine durability [45].

Although diesel engines fueled with biodiesel have been studied in many kinds of literature in the past few decades, the observation results are not always unidirectional and clear [46]. In addition, in recent years, in order to promote biodiesel, different researchers have adopted many advanced preparation technologies and potential raw materials to prepare biodiesel for the more efficient production of biodiesel [47,48]. The selection of feedstocks for biodiesel production mainly depends on the location and crop of the country. For example, in North and South America, such as the USA and Brazil, soybean oil was broadly used as a feedstock for biodiesel production [49], while in Europe, many countries such as the UK, Germany, and Italy usually used rapeseed oil as a raw material for biodiesel production [50,51]. Moreover, in Malaysia and Indonesia, people used palm oil and coconut oil to produce biodiesel [52,53]. In addition, in Southeast Asia and India, local jatropha oil and Mahua oil were commonly used to produce biodiesel [54,55]. Different feedstocks for biodiesel production may have different effects on the performance and emission characteristics of a diesel engine fueled with biodiesel [56]. Motivated by this, it is necessary to conduct a comprehensive review covering different aspects of biodiesel produced from different generations of oil feedstocks to help researchers analyze and compare different kinds of biodiesel.

The primary purpose of this paper is to provide a comprehensive review of the effects of biodiesel as an alternative fuel in diesel engines. Mainly includes the following aspects: First, the production technologies of different types of biodiesels are concluded, including the standards and requirements for preparing different types of biodiesels. Then, the classification according to the production of raw materials and the different properties of different generations of biodiesel compared with diesel. Furthermore, some interesting conclusions have been drawn regarding biodiesel as an alternative fuel for diesel engines on the combustion and emission characteristics of diesel engines. Finally, the improvement of performance and emission characteristics and the future development direction of biodiesel as an alternative fuel are summarized. The review structure employed in this study is shown in Figure 3.

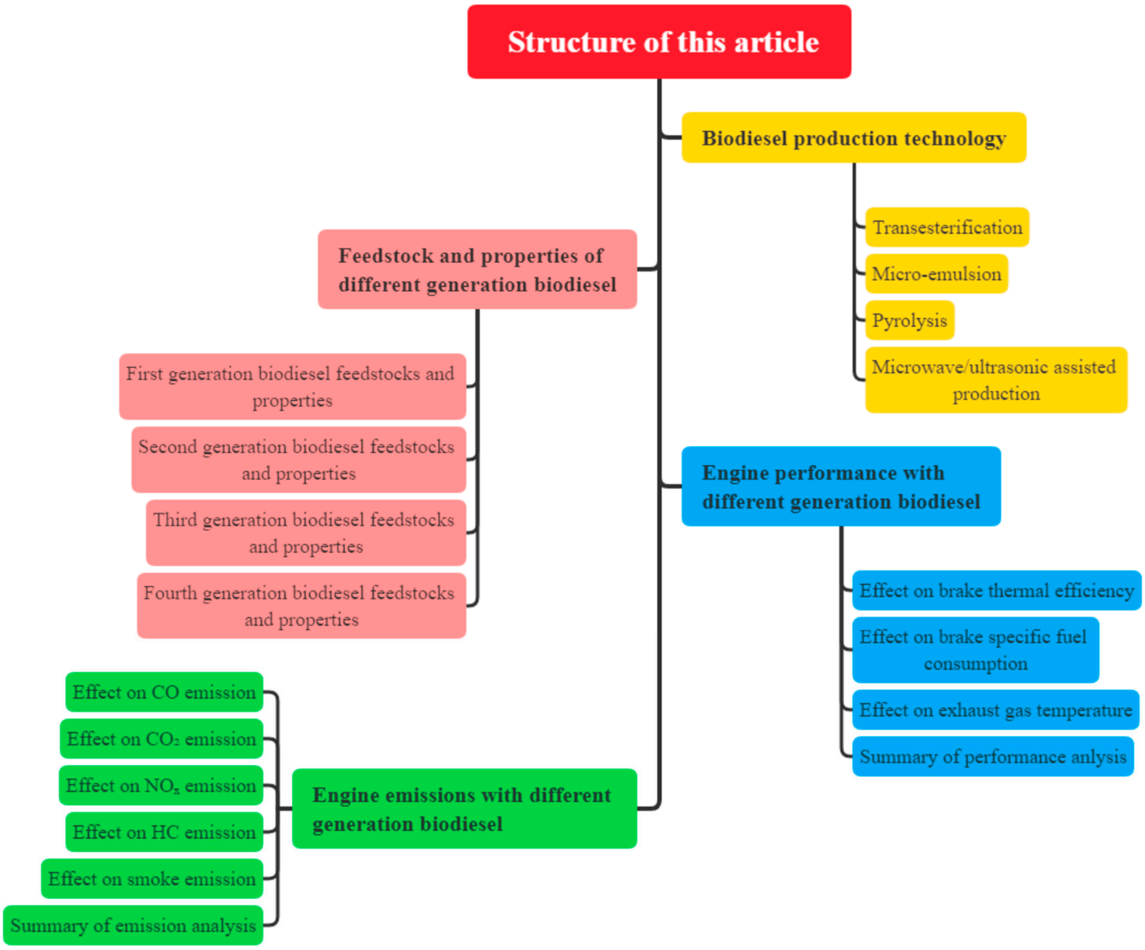

Figure 3. The structure of this article.

2. Biodiesel Production Technology

Biodiesel is the name of a clean-burning mono-alkyl ester-based oxygenated fuel made from natural, renewable sources such as new or used vegetable oils and animal fats. The resulting biodiesel is quite similar to conventional diesel in its main characteristics [57], and there are several generally accepted technologies for the production of biodiesel, such as transesterification [58], micro-emulsification [59], direct use, blending of oils, and pyrolysis [60]. Furthermore, some new technologies such as microwave-assisted reactions [61] and micro-algal biotechnology [62] were also used for biodiesel production. Therefore, this section mainly reviewed different biodiesel production technologies used for biodiesel production.

2.1. Transesterification

Transesterification is the most widely used method for biodiesel production, and it can significantly reduce the viscosity of animal fats and vegetable oils. Compared with other biodiesel production technologies, this method has superior advantages, namely, the reaction conditions are mild, the reaction process is environmentally friendly, and a wide variety of feedstock-based biodiesel can be processed through this technique [63].

Figure 4 shows the principle of the transesterification of triglycerides with alcohols to produce biodiesel. This reaction involves three consecutive reversible reactions. Moreover, the yield of biodiesel highly depends on the properties of reactants (purity, structure) and the catalysts used (see Figure 4a). Catalysts are often used to increase reaction rates and shorten reaction times(see Figure 4b). In addition to catalysts, mixing strength, reaction temperature, reaction time, reaction pressure, alcohol-to-oil ratio, and raw material species also affect the rate of transesterification.

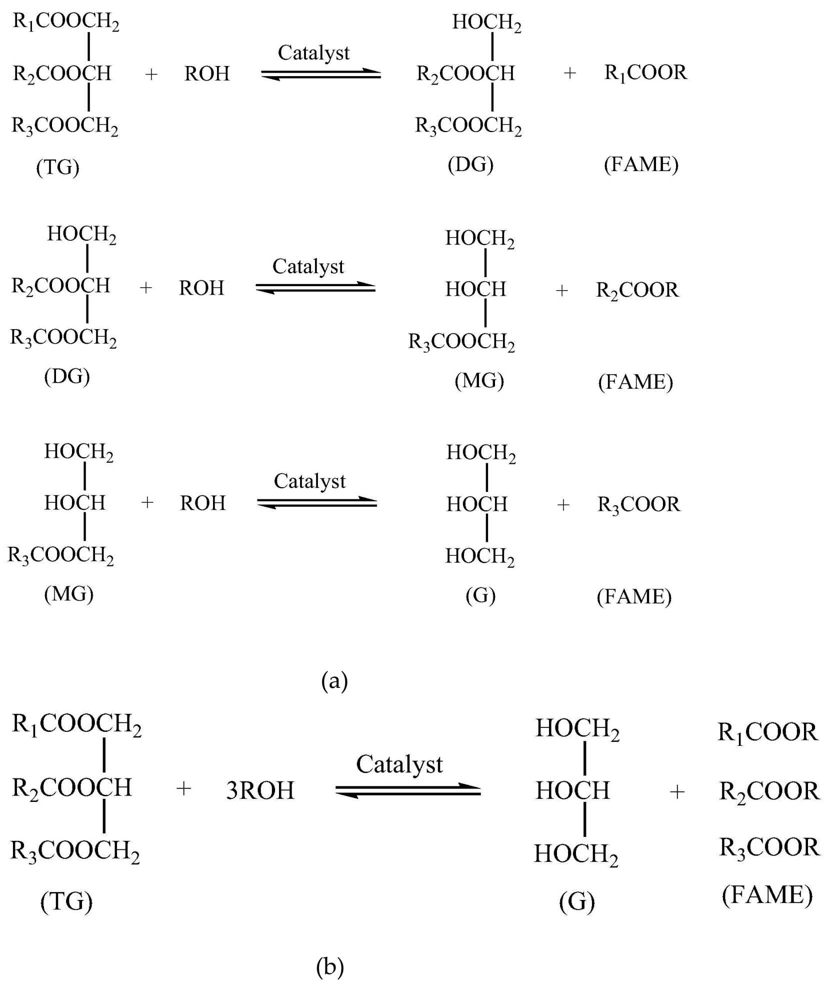

Figure 4. Transesterification reaction process [64]. (**a**) Transesterification of triglycerides; (**b**) Transesterification of triglycerides; (**b**) Fast transesterification.

2.2. Micro-Emulsification Technology

Schulman coined the term micro-emulsion for the optical isotropy of oil and water. Micro-emulsions are transparent and thermodynamically stable colloidal dispersions of polar and non-polar phases, stabilized by surfactants, with particle sizes smaller than a quarter of the wavelength of visible light [65].

Micro-emulsion technology has been developed as a potential method to improve the quality of fossil fuels by forming emulsified fuels, and it is also colloquially known as viscosity reduction technology [66]. It involves blending two immiscible liquids, a viscosity modifier (lower molecular weight alcohols), and a biodiesel blend, using a surfactant and co-surfactant to minimize the interfacial tension in-between these two liquid films and form a stable emulsion [67]. In brief, micro-emulsions are the anisotropic, transparent, and thermodynamically stable oil in water (O/W) or water in oil (W/O) mixtures. It can stabilize with the help of surface-active agents (surfactants/co-surfactants) [68].

Winsor had introduced four types of micro-emulsions, i.e., Type I; oil in water emulsion, Type II; water in oil emulsions (reverse micelle micro-emulsion), Type III; bi-continuous middle phase emulsion, and Type IV; single-phase isotropic emulsion. Figure 5 depicts the structural entity of a droplet of W/O type emulsions. In this, the polar head (hydrophilic) of the surfactant is directed towards the polar head of ethanol/water, and the non-polar tail (lipophilic) is slanted towards the non-polar bottom of the vegetable oil/-biodiesel, forming a Van Der Waals interactive bridge. When the fuel mixture sprays into the cylinder, it atomizes into fine droplets since the boiling point of water is lower than that of diesel. The water droplets reach the boiling point first once they absorb enough reaction heat. Water evaporation then causes the reservoir to disintegrate, resulting in smaller droplets [69].

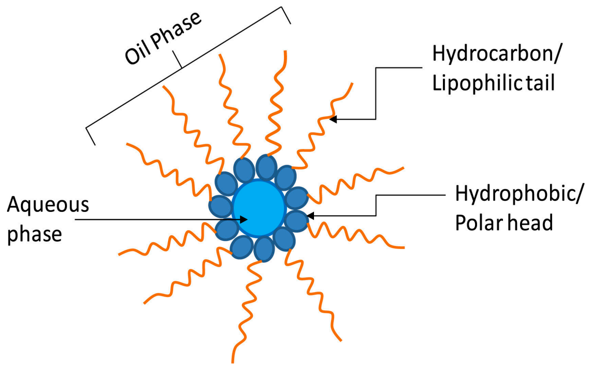

Figure 5. W/O type reverse micelle micro emulsion [59].

Figure 6 shows the schematic diagram of the effect of water addition on the combustion quality of water–diesel emulsion fuel. Due to micro-explosion, the surface area of droplets will increase. The atomization characteristic is improved since the droplets will be broken down into smaller sizes further in the micro-explosion process. Similarly, the micro-explosion increased the secondary atomization of fuel and the fuel-air mixing in the combustion chamber; thus, the poor air–fuel mixture zone can be improved. Compared with W/O type emulsions, O/W type emulsions due to a small quantity of oil dispersed in a large amount of water and stabilized by a surfactant leads to the formation of oil-in-water micro-emulsions. Therefore, this kind of micro-emulsion is widely used in the food industry for various purposes, such as glyceride production and forming coatings on citrus fruits, instead of being used as a fuel replacement [70].

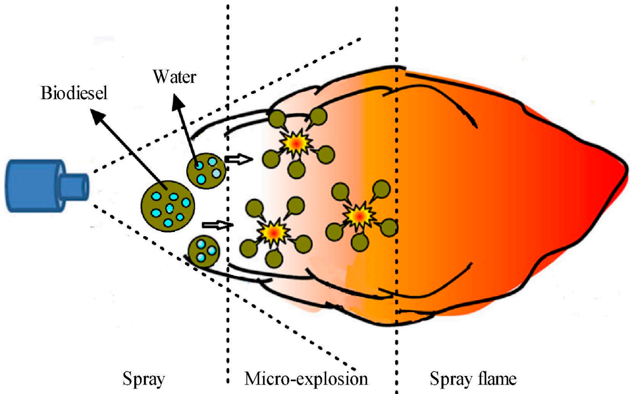

Figure 6. Micro-explosions in emulsion fuels [70].

2.3. Pyrolysis

Pyrolysis is based on the thermal decomposition of biomass by heat in the absence of oxygen, producing biochar (solid), bio-oil (liquid), and non-condensable gases [60]. Pyrolysis is a widely used technology to improve biodiesel quality [71]. Pyrolysis with catalytic reforming can effectively reduce the content of oxygen and increase the HC content in the bio-oil, respectively, and thus has great potential to be an alternative energy source [72]. According to the reaction temperature and time of pyrolysis, the pyrolysis process of biomass can be divided into three categories: (a) slow pyrolysis, (b) fast pyrolysis, and (c) flash pyrolysis. Generally speaking, fast pyrolysis and flash pyrolysis produce bio-oils in high yields, which makes them favorable for bio-oil production. Operating parameters for these processes are summarized in Table 1.

Compared with other biodiesel production technology, the pyrolysis process is simple, waste less pollution-free, and is effective compared to other cracking processes. The raw materials for pyrolysis can be extensive and include vegetable oils, animal fats, natural fatty acids, wood, bio-waste, methyl esters of fatty acids [73], and some biomass raw material in some ways [74]. In addition, the type and the concentration of catalysts will also affect the pyrolysis products. Many researchers have attempted in many research works to enable biodiesel combustion and emissions to work in diesel engines [75–78].

Table 1. Different kinds of pyrolysis processes and operating parameters [79].

Pyrolysis Process	Residence Time (s)	Heating Rate (K/s)	Particle Size (mm)	Temp (K)
Slow	450–550	0.1–1	5–50	550–950
Fast	0.5–10	10–200	<1	850–1250
Flash	<0.5	>1000	<0.2	1050–1300

2.4. Microwave/Ultrasonic-Assisted Production Technology

Microwave/ultrasonic-assisted technology is a green and efficient assisted production technology of biodiesel, whereby microwave irradiation directly delivers heat to the reactant, resulting in a rapid temperature increase, thus increasing the reaction rate [80]. Moreover, microwave irradiation also has better heat transfer than conventional heating and thus provides another potential energy source for process intensification. The main effect of ultrasonic on chemical reactions is the formation and collapse of micro-bubbles and the release of high energy locally in the shock waveform. Through increasing the local temperature and pressure in µs, molecules are induced to generate high reactive radical species for product formation [81].

Generally speaking, Microwave/ultrasonic-assisted production technology is widely used in transesterification as an assistive technology to improve the yield of biodiesel [82]. The ultrasound can reduce the droplet size in the transesterification and increase the contact surface between reagents, thus increasing the output. Ultrasonic irradiation is also applied in the transesterification process of various raw materials, such as soybean oil [83], animal fats, Jatropha oil, crude palm oil, and waste-cooked oil [84], with satisfactory efficiency. Most of the published papers investigating bulk transesterification processes have used ultrasonic baths. In addition, several studies report and propose a continuous method for biodiesel production for potential industrial scale-up [85].

In recent years, the application of microwaves in chemical reaction enhancement and energy efficiency has attracted significant attention to industrial and research institutions. Many researchers have attempted to improve the defect that microwaves penetrate less into reactive media [86] and make microwave-assisted technology usable in industrial production [87]. Ultrasonic cavitation has been shown to successfully facilitate the mixing of reactants with homogeneous or heterogeneous catalysts, resulting in a significant reduction in reaction time and reaction rate [88]. Most studies have focused on parameter and optimization studies, with some also investigating catalyst leaching, reusability, and biodiesel quality improvements. However, the current state of the art for ultrasound-assisted biodiesel production is still mainly at the laboratory scale, with some impressive pilot-scale demonstrations. Several areas worthy of future investigation include continuous ultrasonic reactor systems, primarily using heterogeneous catalysts, pilot-scale tests, and a few techno-economic feasibility studies.

3. Feedstocks and Properties of Different Generations of Biodiesel

The thermophysical properties of the fuel affect engine performance and emission characteristics. Specifically, these properties are viscosity, density, cetane number, calorific value, and flash point. In some literature, researchers have pointed out that biodiesel fatty acid content and chemical composition also significantly impact engine performance. In addition, the feedstocks will also affect the properties of biodiesel. According to the European Academies Science Advisory Council report 2012, biodiesel is usually classified as the first, second, third, and fourth generation of biodiesel that is primarily based on the feedstock of biodiesel [89]. Therefore, measuring the fuel properties of selected biodiesel is necessary before using different generations of biodiesels in diesel engines. Different standardization organizations specify different fuel standards for biodiesels, and Table 2 shows the main popular standards for biodiesel. The following section discusses the fuel properties of the different biodiesel based on the different generations [90].

Table 2. ASTM D6751 and EN 14214 standards for biodiesel fuel [91].

Property Specification	Units	Biodiesel Standard			
		ASTM D6751		EN 14214	
		Test-Method	Limits	Test-Method	Limits
Density at 15 °C	kg/m^3	ASTM D1298	880	EN-ISO 3675/12185	860–900
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	1.9–6.0	EN-ISO3104	3.5–5.0
Cetane number	-	ASTM D613	47 minimum	EN-ISO5165	51 minimum
Cloud point	°C	ASTMD2500	−3 to −12	-	-
Flash point	°C	ASTMD93	130 minimum	ENISO3679	101 minimum
Pour point	°C	ASTMD97	−15 to −16	-	

3.1. Feedstocks and Properties of First-Generation Biodiesel

First-generation biodiesel is produced from edible feedstocks. Examples of edible feedstocks are Rapeseed oil, Soybean oil, Coconut oil, Corn oil, Palm oil, Mustard oil, Olive oil, and Rice oil [92–95]. Table 3 and Figure 7a–e show various feedstocks for first-generation biodiesel production. Edible feedstocks for biodiesel production are very common when biodiesel has been widely used. The main benefits of first-generation feedstocks are crop availability and relatively simple conversion procedures.

Table 4 shows the main properties of the first-generation biodiesel compared to diesel fuel. It can be observed that the viscosity of the first-generation biodiesel is higher than that of diesel, and some of the first-generation biodiesel is even more than twice the limit of diesel. Mustard biodiesel had the highest viscosity at 5.53 mm^2/s, followed by sal-seed biodiesel. In addition, according to the viscosity standard of biodiesel, the first-generation biodiesels shown in Table 4, all meet the ASTM D6751 biodiesel standard and EN 14214 biodiesel viscosity standard, except for coconut mustard and sal-seed biodiesel. The higher viscosity of biodiesel than diesel may lead to poor atomization and vaporization; therefore, a larger droplet size in the cylinder chamber. Additionally, it increases oil dilution, narrows the injection angle, and improves the in-cylinder penetration of the fuel spray, resulting in incomplete combustion and higher emissions [96].

Density is one of the important properties, as some other key fuel properties such as cetane number and calorific value are related to it. Acaroglu et al. [97] reported that density is strongly affected by storage conditions, fatty acid composition, and water content. In addition, because the amount of fuel injected into the combustion chamber of a diesel engine is measured by volume, density changes directly affect engine output and fuel consumption. Additionally, density affects injection onset, injection pressure, and fuel spray characteristics, affecting combustion and emissions [98]. According to biodiesel standards, first-generation biodiesel is higher than diesel fossil fuels. Except for cottonseed, corn, peanut, hazelnut, olive pomace, poppy seed, rice bran, and soybean biodiesel, most biodiesels meet the ASTM D6751 density standards. Only groundnut biodiesel does not meet the EN 14214 biodiesel standard. Furthermore, most studies report that the increased density of biodiesel samples results from prolonged storage time. This increase has been reported to be more rapid in the later stages of oxidation due to the increased interaction between peroxide production and molecules that degrade biodiesel [99].

Another important parameter that affects combustion quality is the cetane number. The higher the cetane number, the shorter the ignition delays, ultimately increasing the combustion duration. Table 4 shows the cetane numbers of different generations of biodiesel. In general, biodiesel has a higher cetane number than petroleum diesel because of its longer fatty acid carbon chain. However, Table 4 shows that the cetane number range of soybean biodiesel and sunflower biodiesel is lower than diesel fuel. This can be explained by the growing area and ripening stage [100], with the content of oil, stearic acid, oleic acid, palmitoleic acid, and linoleic acid increasing as the fruit ripens. In contrast, palmitic, linoleic, and tocopherol isomers were decreased during fruit ripening [101]. These factors play a vital role in oil production. In short, the same oil can display different cetane numbers depending on its specific composition. It increases with fatty acid chain length and decreases with the number of double bonds [102,103].

Flash Point (FP) is an important parameter related to transportation, handling, and storage. It is the temperature at which it ignites when exposed to flame or spark at a standard pressure of 101.3 kPa. Sufficient vapor is generated to keep the concentration of flammable vapor above the lower flammability limit [104]. Therefore, the higher the vapor pressure, the lower the FP of the soft compound. The FP of first-generation biodiesel is higher than that of fossil diesel. All first-generation biodiesel shown in Table 3 meets the flash point standards of ASTM D6751 and EN 14214, except coconut biodiesel. In general, the FP of biodiesel is affected by various factors, such as the alcohol present in the biodiesel [105,106], the chemical composition of the biodiesel (such as the number of double bonds), the total number of carbon atoms [107], the experimental method [108], equipment, test pressure, and the temperature.

Cloud point (CP) is the lowest possible temperature at which the wax in the fuel first crystallizes and develops a cloudy appearance. CP is the most common criterion used to set the low-temperature fuel control [109]. Since different generations of biodiesel production use different feedstocks, different feedstocks have different fatty acid compositions; therefore, the CP of the produced biodiesel will vary with the feedstock [110]. It can be seen from Table 4 that the CP value of the first-generation biodiesel is the highest in both moringa and sal-seed biodiesel, at 18 °C. In contrast, the poppy seed biodiesel has the lowest value at −8 °C.

The pour point (PP) is the secondary temperature when a liquid fuel loses its flow characteristics. PP is an important characteristic of the cold flow process [111]. In other words, PP evaluates the gel point of biodiesel fuel. It is an important parameter for evaluating the flow behavior of biodiesel in pipeline distribution and storage [112]. ASTM standards can measure biodiesel PP, and Table 2 shows the ASTM D97 standard for biodiesel. According to Table 4, most first-generation biodiesels were above this range; Moringa biodiesel had the highest PP of 16.5 °C, while mustard and poppy seed biodiesel had the lowest PP.

Heating value is one of the most important properties of animal fats, vegetable oils, and biodiesels as fuels rather than petroleum [99]. The heating value measures the energy available per unit volume or mass of any fuel burned [113]. The higher the heating value, the less the fuel consumption for the same engine output [114]. Table 4 shows the heating value of first-generation biodiesel; it can be seen that the heating value of biodiesel is lower than that of diesel. Safflower biodiesel has the highest heating value at 42.2 MJ/kg. Many researchers have concluded that the heating value of biodiesel will increase with chain length, molecular weight, carbon/oxygen, and hydrogen/oxygen ratio, and decrease with increasing unsaturation and double bonds [115].

Table 3. Feedstocks for different generation of biodiesel production [89,116,117].

Edible Oil (1st Generation)	Non-Edible Oil (2nd Generation)	Waste Oils (3rd Generation)	Solar Biodiesel (4th Generation)
Almond	Babassu	Animal waste fat	Genetic algae
Canola	Carapa	Algae	Microorganisms
Cotton-seed	Castor	Chlorella	Solar fuels
Coconut	Camelina	Chicken waste fat	
Corn	Croton	Fish oil	
Groundnut	ETH-mustard	Grease-derived	
Hazelnut	Jatropha	Leather waste fat	
Moringa	Karanja	Lard	
Mustard	Linseed	Marginatum algae	
Olive-pomace	Mahua	Spirulina-platensis	
Palm	Meliaceae	Sheep fat raw oil	
Peanut	Merrill	Sheep skin oil	
Poppy-seed	Milkweed	Tallow oil	
Rapeseed	Nahar	Turkey render fat	
Rice-bran	Neem	Waste cooking oil	
Safflower	Papaya-seed	Waste fish oil	
Sal-seed	Polanga		
Sesame	Poon		
Soybean	Rubber		
Sunflower	Stone-fruit-kernel		
	Tobacco		
	Terminalia-catappa		
	Terminalia-belerica		

Figure 7. Edible feedstock for biodiesel production [118].

Table 4. Properties of first-generation biodiesel [12,118–121].

First Generation Biodiesel	Density (kg/m^3)	Kinematic Viscosity (mm^2/s)	Cetane Number	Cloud Point (°C)	Flash Point (°C)	Pour Point (°C)	Heating Value (MJ/kg)
Diesel	850	2.44–2.60	47–50	-	68–75	−20	42–44.3
Almond	881	4.90	59	-	145	-	41.761
Canola	878	4.42	54	−3.25	172.36	−8	38.75–40.748
Cotton-seed	887	4.19	48.1	1.7	210	−12.5	39.75
Coconut	867	3.20	64.65	−1.6	113.83	−8.3	35.2–38.2
Corn	883	4.19	55.4	−3	171	−2	39.9–43.1
Groundnut	920	4.40	59.85	8	132	3	39.8
Hazelnut	896	4.81	62.95	−7.65	172.7	−6	39.58
Moringa	873	4.92	64.57	18	173.3	16.5	40.89
Mustard	879	5.53	56	16	169.16	−18	40.4
Olive-pomace	894	4.26	56.3	2	138	6	39.96
Palm	870	4.53	60.21	14.25	176.7	14.33	34.4–40.13
Peanut	878.5	4.69	58.24	12.6	176	11.5	35.33
Poppy-seed	889	4.37	58	−8	175	−18	42.085
Rapeseed	879	4.40	48.25	−3.5	169.5	−11	35.8–41.1
Rice-bran	881	4.40	51.15	5	175	−11	40.87
Safflower	879	4.18	51.1	−4	174	−7	42.2
Sal-seed	879	5.44	52.5	18	143.5	12	39.96
Sesame	867	4.23	58.97	0.5	176.67	−4	40.25
Soybean	882	4.15	44.7	0	140.1	−3.2	35.74–39.84
Sunflower	869	4.26	45.7	1.33	180.33	−2	34.71–40.6

The risk of the limited food supply is the main disadvantage of using these ingredients, which increases the cost of food [121]. Adaptability to environmental conditions, high cost, and limited acreage are barriers to biodiesel production from edible feedstocks [122]. These shortcomings restrict users from turning to other alternative sources for biodiesel production.

3.2. Feedstocks and Properties of Second-Generation Biodiesel

Second-generation biodiesel is produced from non-edible raw materials such as neem oil, jatropha oil, Nagchampa oil, Karanja oil, Calophyllum inophyllum oil, rubber seed oil, Indian twist oil, etc. [123,124]. Table 3 and Figure 8 show some of the non-edible feedstocks used to produce biodiesel. The shortcomings of the first-generation feedstocks have attracted researchers to study non-edible feedstocks. The main advantages of non-edible oil production are environmental protection, low production costs, elimination of food inequality, and less demand for arable land. It has been observed that large amounts of non-edible plant oil are available in the future [116]. In addition, non-edible vegetable oils are promising crude oils for biodiesel production.

Many non-edible seeds can be used to produce non-edible oils. Rozina et al. [125] intended a comprehensive review of biodiesel synthesis from non-edible seed oils, mainly discussing the 35 species of renewable non-edible feedstocks for biodiesel production in Pakistan. Yang et al. [126] summarized 18 potential non-edible oil feedstocks for biodiesel production in Africa. Kumar et al. [127] have reported on more than 15 different non-edible oils for biodiesel production in India. Different countries use different types of non-edible oils to produce biodiesel; therefore, the properties of non-edible biodiesel from different regions may vary.

Table 5 shows the properties of non-edible biodiesel according to the ASTM D6751 Kinematic Viscosity Standard, the range of biodiesel fuel is 1.9 to 6 mm^2/s. As for the EN 14214 standard, it ranges from 3.5 to 5 mm^2/s. Among the non-edible biodiesel properties shown in Table 5, castor biodiesel had the highest kinematic viscosity at 17.14 mm^2/s, while papaya seed biodiesel had the lowest at 3.53 mm^2/s. The kinematic viscosity of castor biodiesel exceeds the range of ASTM D6751 and EN 14214. The higher viscosity of biodiesel results in uneven fuel injection, delayed injection start, and reduced injection quantity, thereby increasing in-cylinder combustion temperature and resulting in more

NO_x emissions. In addition, the temperature is also an important factor affecting fuel viscosity. During cold-start conditions and low ambient temperatures, higher viscosity may result in highly uneven fuel distribution within the injection assembly and difficulties with low-temperature cold starts [96].

Figure 8. Feedstocks of non-edible oil for biodiesel production [127].

Table 5. Properties of second-generation biodiesel [90,121,127–131].

Second Generation Biodiesel	Density (kg/m^3)	Kinematic Viscosity (mm^2/s)	Cetane Number	Cloud Point (°C)	Flash Point (°C)	Pour Point (°C)	Heating Value (MJ/kg)
Diesel	850	2.44–2.60	47–50	-	68–75	−20	42–44.3
Babassu	872.5	4.20	63.25	4	117	-	31.8
Carapa	871.4	4.75	42.6	−10	70	-	38.55
Castor	922	17.14	37.55	−11.16	178.56	−20	38.09
Camelina	885	4.11	48.91	2.5	150	−6.3	45.2
Croton	870	4.07	42.57	−4	164	−5	39.786
ETH-mustard	844.5	5.12	50.5	16	134.75	15	41.4
Jatropha	865	4.52	55.43	5.66	175.5	6	40.79
Karanja	889	4.79	56.55	13.3	157.4	6.4	36.56
Linseed	852	3.95	34.6	2.43	241	−9.6	37.45–41.8
Mahua	895	4.77	55	4.33	129.5	4.33	36.9–39.4
Meliaceae	893	4.72	44	8	188.5	8	39.96
Merrill	876	5.14	76.74	7.66	148.66	0.67	44.986
Milkweed	870	4.6	50	2.23	128	2.23	39.7
Nahar	893	5.67	54.6	6.1	131.5	−1.2	35
Neem	865	5.30	52	6.7	152	3.1	38.34
Papaya-seed	840	3.53	48.29	-	112	-	38.49
Polanga	878.6	4.75	56.8	11.73	151.66	8.43	39.39–41.3
Poon	876	5.82	54.83	1.6	153.75	−0.2	40.09
Rubber	875	5.60	53	3.1	173.4	−7	39.174
Stone-fruit-kernel	855	4.26	50.45	−4	105	−8	39.64
Tobacco	865	3.56	51.5	-	165	−12	42.22
Terminalia-catappa	876	4.3	57.1	-	90	6	37.73
Terminalia-belerica	883	4.98	53.2	5	126	3	39.22

Density is an important fuel property used to determine the approximate amount of fuel delivered by the injection system to obtain precise combustion energy [27]. Most second-generation biodiesels meet the 860 to 900 kg/m^3 limit according to the ASTM D6751 and EN 14214 standards, but castor biodiesel is above both. Ethiopian mustard, flaxseed, papaya seed, and stone nut biodiesel are substandard according to EN 14214. The density of biodiesel fuels limits its widespread use.

The cetane number (CN) value indicates the ability of a fuel to spontaneously ignite rapidly after delivery to the combustion chamber [132]. For biodiesel, CN increases with fatty acid saturation and chain length; a higher CN means it has more oxygen and better combustion efficiency. The minimum cetane number limits of ASTM D6751 and EN 14214 are 47 and 51, respectively. Most non-edible oil-based biodiesel meet the limits of ASTM D6751, except Carapa, Castor, Croton, Linseed, and Meliaceae biodiesel. However, EN 14214 recommends a CN threshold of 51. The higher CN standard of EN 14214 may limit the use of biodiesel.

The FP of the second-generation biodiesel is shown in Table 5. According to the biodiesel FP standard ASTM D93 and ENISO3679, most second-generation biodiesel falls within these two standards' scope. The highest FP was shown in linseed biodiesel, which is 241 °C, while the lowest was shown in carapa biodiesel, which is 70 °C. According to Bhuiya [42], the FP of non-edible biodiesel mainly depends on the number of major unsaturated acid chains of C18:1 and C18:2 in vegetable oil.

According to the CP and PP of the second-generation biodiesel shown in Table 5, papaya-seed, Tobacco, and Terminalia-catappa biodiesel have no CP. On the other hand, Babassu, Carapa, and Papaya-seed biodiesel have no PP. The highest CP and PP of the second-generation biodiesel is Ethiopian mustard biodiesel. In contrast, the lowest is castor biodiesel. The lower CP and PP temperatures suggest that biodiesel has better common temperature flow properties at low temperatures. Conversely, too high will cause problems such as clogging the cold filter, which will cause difficulty in cold start [133].

Most researchers have already investigated the heating value of biodiesel from different feedstocks [134,135]. According to Table 5, the non-edible oil-based biodiesel shows a lower heat value than diesel, except for the Camelina biodiesel and Merrill biodiesel. According to researchers [136], Camelina seeds have an oil content of (35–43% on a dry matter basis), containing about 90% unsaturated fatty acids, primarily linolenic acids, and linoleic acids. This may be why the Camelina biodiesel and Merrill biodiesel have a higher heating value than diesel.

The significant advantage of non-edible biodiesel is that there is no need to burden food crops compared to edible biodiesel. Additionally, second-generation feedstocks can be grown on non-farm or marginal land. This means that these feedstocks have better survival rates and higher crop economics. As a result, farmers may forcibly cultivate non-edible raw materials in their fields, affecting food production and socio-economics. To address the socio-economic issues of non-edible biodiesel, many researchers have focused on new feedstocks that are economically viable and readily available in production [27].

3.3. Feedstocks and Properties of Third-Generation Biodiesel

The third-generation biodiesel is mainly produced from animal fat, microalgae, and waste cooking oil [137]. Among the various available feedstocks, third-generation biodiesel is considered the most viable source of biodiesel because it is economical and reduces waste disposal problems [138]. Moreover, compared with first- and second-generation biodiesel, these feedstocks take up no land for cultivation. Therefore, the planting area of land is reasonably controlled, and at the same time, water resources for irrigation are saved to a certain extent. Currently, the primary source of third-generation biodiesel is waste cooking oil, which is produced after frying or cooking operations. Figure 9 shows the sources of waste cooking oil, mainly from households, restaurants, and the food processing industry.

Another important sustainable and high-quality feedstock for third-generation biodiesel production is microalgae. Figure 10 shows the primary production process of micro-algal biodiesel—species such as *Sp. Chlorella* can grow year-round, ensuring a constant supply of microalgae oil with minimal water requirements. Additionally, most micro-algal species are tolerant of high CO_2 levels and do not require herbicides or pesticides to grow. The lipid composition of micro-algal cells is more than 30% higher than other sources such as soybean and palm oil. In addition, industrial wastewater and sewage, coastal seawater, and brackish water are also suitable for the survival of microalgae [139].

Moreover, animal fat such as pork, beef, goat, and poultry is also a low-cost feedstock for third-generation biodiesel production [140,141]. The various raw materials of the third-generation biodiesel are shown in Table 3.

Table 6 shows the main properties of third-generation biodiesel compared to fossil-based diesel. The viscosity of microalgae oil-based biodiesel, animal fat-based biodiesel, and edible waste oil-based biodiesel is higher than diesel oil. Tallow biodiesel had the highest viscosity at 5.85 mm^2/s, while waste cooking oil-based biodiesel had the lowest viscosity at 3.658 mm^2/s. In addition, all the third-generation biodiesel shown in Table 6 meets the ASTM D6751 standard. According to EN 14214 biodiesel standards, the viscosity of algal biodiesel, spirulina biodiesel, and tallow-based biodiesel is out of range. Therefore, many researchers want to reduce the viscosity of biodiesel to increase the spray and combustion characteristics of biodiesel. According to researchers [142], at an electric field strength of 1667 V/mm, the viscosity of biodiesel is decreased by 25.5%; at the same time, the average droplet size is significantly decreased by 41%, and the combustion volume of the engine will increase by 20%.

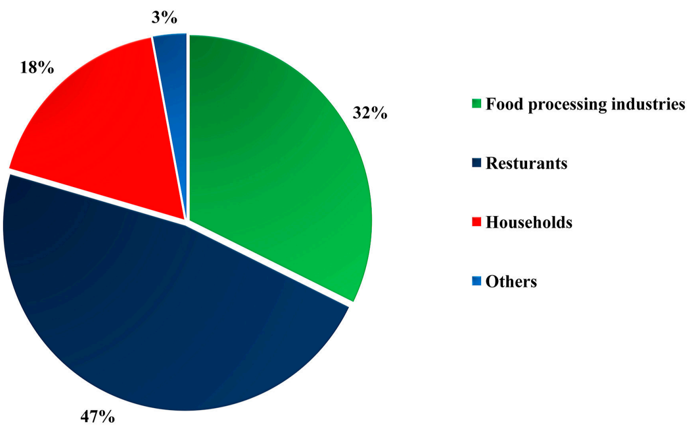

Figure 9. The Sources of waste cooked oil [138].

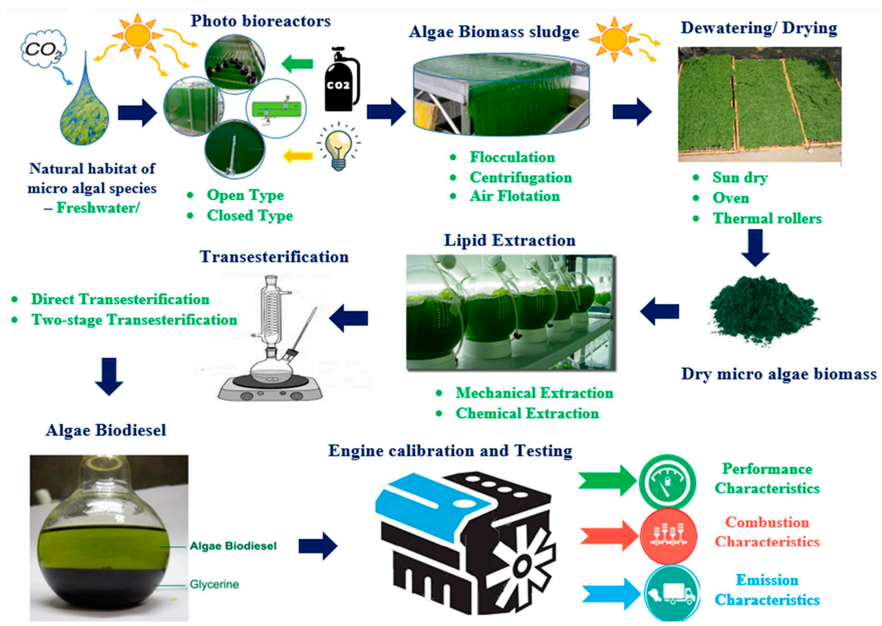

Figure 10. Micro-algal biodiesel production technique and components in processing [143].

Table 6. Properties of third-generation biodiesel [144–150].

Third Generation Biodiesel	Density (kg/m^3)	Kinematic Viscosity (mm^2/s)	Cetane Number	Cloud Point (°C)	Flash Point (°C)	Pour Point (°C)	Heating Value (MJ/kg)
Diesel	850	2.44–2.60	47–50	-	68–75	−20	42–44.3
Animal waste fat	882.04	4.92	58.7	11	170	-	37.327
Algae	880	5.58	-	6	46	3	30.881
Chlorella	900	4.22	52	-	124	-	40.04
Chicken waste fat	865	4.11	56	−5	170	-	40.2
Fish oil	866	4.4	56	-	142	-	37.58
Grease-derived	886	4.75	-	−5	140	−10	41.28
Leather waste fat	875.5	4.636	58.8	-	173.5	9	39.7
Lard	877	4.84	-	-	143.5	7	36.5
Marginatum algae	830	5.0	50	−4	181	−4	42.861
Spirulina-platensis	860	5.66	56.22	-	130	−18	41.36
Sheep fat raw oil	875	4.5	61	-	192	-	40.5
Sheep skin	875	3.73	-	15	178	11	35.769
Tallow	873.2	5.85	56	-	53	-	38.35
Turkey render fat	885.8	4.49	52.4	0	178.1	4	40.68
Waste cooking oil	876.08	3.658	50.54	-	160	-	39.767
Waste fish oil	875	4.14	41	-	169	-	51.5

Fuel density plays a vital role in injector design as it directly affects engine operation. Specifically, it can significantly affect fuel atomization, affecting engine brake thermal efficiency [151]. The density of the third-generation biodiesel is shown in Table 6; it can be found that the density of the third-generation biodiesel is higher than that of diesel. Except for Chlorella biodiesel, all densities of third-generation biodiesel meet ASTM D6751 viscosity standards from 860 to 900 kg/m^3. The highest density of the third-generation biodiesel is the chlorella biodiesel, 900 kg/m^3. The lowest density of the third-generation biodiesel is the marginatum algae biodiesel, 830 kg/m^3.

In general, biodiesel has a higher CN compared to that pure diesel. A higher CN generally indicates shorter ignition delay and earlier combustion, which helps the engine run smoothly. Conversely, a lower CN results in delayed ignition and increased HC and PM emissions [152]. According to the CN shown in Table 6, all third-generation biodiesel except waste fish oil-based biodiesel met the ASTM D6751 CN standard. The highest CN in Table 6 is suet feedstock oil-based biodiesel at 61. The lowest CN was for waste fish oil-based biodiesel at 41. In the case of waste fish oil-based biodiesel, polyunsaturated fatty acid methyl esters reduce CN and lead to poor ignition quality. Therefore, in order to improve the lower CN of biodiesel, many researchers have used different CN improvers to increase the CN of biodiesel for better engine performance and emissions [153,154].

Table 6 shows the FP of the third-generation biodiesel; it can be found that, except for algal biodiesel and tallow biodiesel, the FP of all third-generation biodiesel is higher than that of diesel. The highest FP was the sheep fat raw oil biodiesel at 181 °C, and the lowest was algae biodiesel at 46 °C. According to the ASTM D6751 and EN 14214 Biodiesel FP Standard, Algae, and tallow biodiesel are out of range. In addition, Chlorella biodiesel only meets EN 14214 biodiesel standards but is lower than the 130-standard specified by ASTM D6751.

Important parameters for cold-start and low-temperature flow characteristics are CP and PP. According to the CP and PP shown in Table 6, most third-generation biodiesels meet the ASTM D6751 standard, except for animal waste fat biodiesel, algae biodiesel, and Turkey-rendered fat-based sheep skin biodiesel. Sheep skin-based biodiesel had the highest CP and PP at 15 °C and 11 °C, respectively. In contrast, Grease-derived and chicken waste fat-based biodiesel had the lowest CP, while Spirulina-platensis-based biodiesel had the lowest PP. The results showed that animal fat-based biodiesel had worse cold-start characteristics than microalgae and waste-cooking oil-based biodiesel due to higher CP.

Heating value is an important property of fuels, especially biodiesel, related to brake thermal efficiency and brake specific fuel consumption. A higher heating value results in less fuel consumption and higher thermal efficiency. According to the heating value of the third-generation biodiesel shown in Table 6, there is no doubt that pure diesel has the highest heating value. The highest heating value of the listed biodiesels is shown in Marginatum algae-based biodiesel at 42.861 MJ/kg. In contrast, algal biodiesel had the lowest heating value of 30.881 MJ/kg. Interestingly, neither EN 14214 nor the US have specific standards for the heating value of biodiesel. Numerous researchers have predicted or estimated the heating value of biodiesel based on its fatty acid weight composition in other structures [155]. According to their study [156], the degree of unsaturation, O/H ratio, and bond energy strongly correlate with the heating value of biodiesel.

Overall, the main physicochemical properties of third-generation biodiesel are close to those of fossil diesel, according to EN and ASTM standards. The superior properties of third-generation biodiesel have led to the growth of the biodiesel industry; however, the main disadvantage of using third-generation biodiesel is the higher production cost due to the two-step transesterification reaction. Therefore, in order to increase the use of third-generation biodiesel, low-cost biodiesel production technology should be adopted for biodiesel production.

3.4. Research on the Fourth-Generation Biodiesel

Fourth-generation biodiesel uses photo bio-solar fuels and electric fuels as feedstock and utilizes advanced technologies to capture large amounts of CO_2, improving the productivity of biodiesel and the adaptability of microalgae in wastewater [157]. The potential of genetically modified biodiesel to increase biomass productivity while reducing cost and improving quality has attracted the interest of many researchers [158]. Different raw materials of solar energy-based biodiesel and genetically modified microalgae-based biodiesel are shown in Table 3. Compared with the previous three generations of biodiesel, the raw materials of the fourth-generation biodiesel mainly come from solar fuels, genetically modified microalgae, and microbial cell-based biofuels.

According to the research on solar fuel production, the production of fourth-generation biodiesel uses methanol, fresh oil, and sodium hydroxide as raw materials. It uses a chemical cogeneration process to produce biodiesel at 25 °C and 100 kPa [159]. The whole process is shown in Figure 11. It can be seen that the energy for biodiesel production comes from parabolic trough solar collectors, to which some specific nanoparticles and nanoparticle fluids have been added to enhance heat transfer in the solar field [160]. The efficiency of the proposed system is 94.42%, which can generate 991.42 kg biodiesel per hour and 1718 kW net power simultaneously.

Another important fourth-generation biodiesel feedstock is microorganisms, such as Clostridium, Pseudomonas putida, and Bacillus subtilis [161]. Figure 12 shows the fourth-generation biodiesel production process by microorganisms. According to the picture, the operation of the microorganisms can be divided into three steps: pretreatment, fermentation, and transesterification. Each step will affect the quality, yield, and properties of biodiesel. Wang et al. [162] recommended that an efficient pretreatment could enhance the utilization rate of raw materials and oil yield. Genetic engineering or screening models can strengthen the adaptation and utilization of oleaginous microorganisms to lignocellulosic biomass materials. Finally, a closed-loop green production system can be built. Immobilized lipase is an effective mechanism for biodiesel production because of its reusability and stability. At the same time, the byproduct glycerol can be used as raw material to produce biodiesel, and no waste is generated during the whole production process, forming a closed-loop green production system.

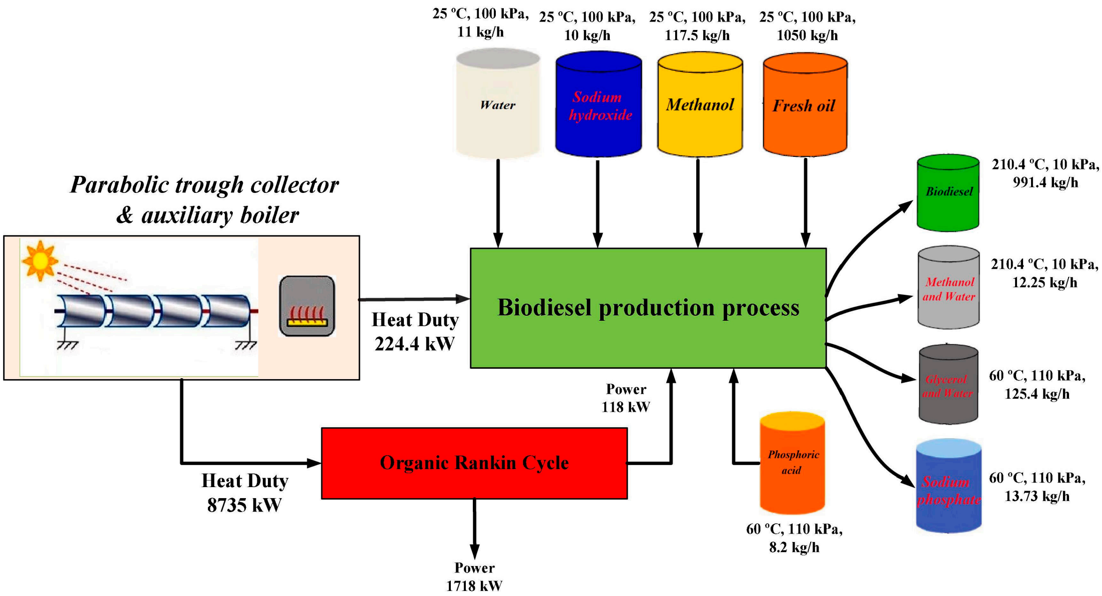

Figure 11. Biodiesel production using parabolic trough solar collectors [159].

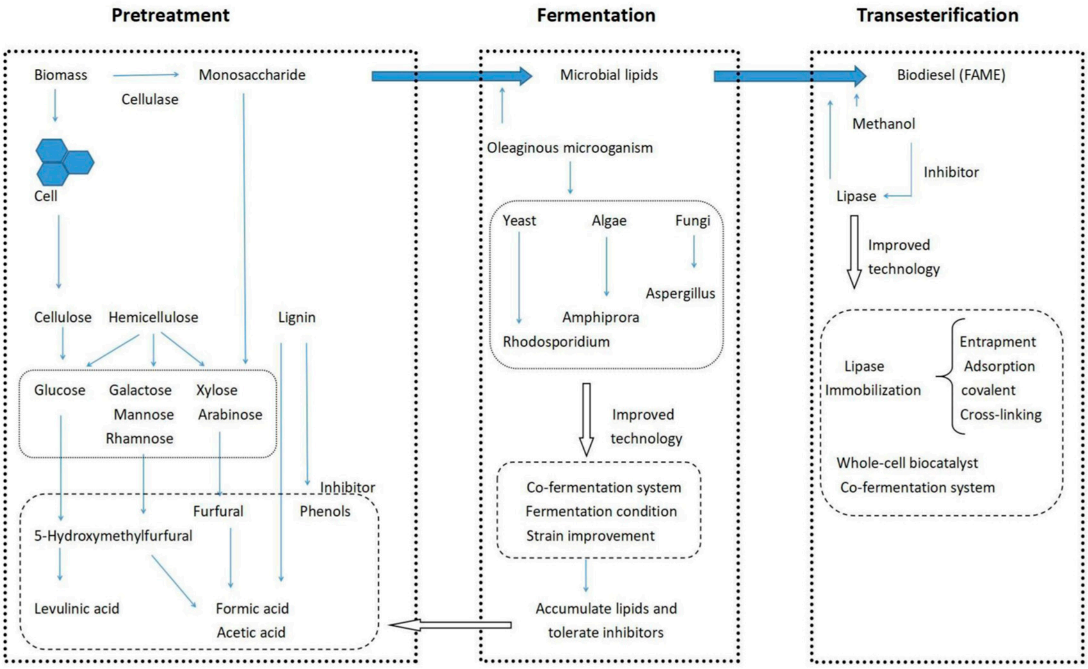

Figure 12. The Production process of using microorganisms to produce biodiesel [162].

For sustainable development, many researchers have been investigating different generations of biodiesel to enhance the properties of biodiesel, reduce the production cost of biodiesel, and enhance the use of biodiesel in different situations. Biodiesel is divided into four generations according to the feedstock of biodiesel. Table 7 summarizes the benefits and limitations of the fourth-generation biodiesel, which can provide a reference for more researchers to improve and enhance the use of biodiesel.

Table 7. Benefits and Limitations of different generations of biodiesel [163,164].

Generations	Benefits	Limitations
First generation	Accessible raw material for biodiesel production, easy availability of crops, and easy production processes.	Conflict with the food supply, lower crop yield, and less feedstock adaptability for the environment.
Second generation	No effect on food supply, fewer production costs, more getable feedstocks	Lower cost of conversion, and efficiency, lower crop yield for some feedstocks
Third generation	The feedstocks such as waste cooking oil can be produced from no land, have no effect on food supply, and have higher growth rates.	Higher costs for energy conversion and higher energy for algae culture, lower oil content in some feedstocks
Fourth generation	Higher energy conversion efficiency decreased the CO emissions, and carbon neutralization.	Higher cost in the production Infancy level in the research

4. Effects of Different Generations of Biodiesel on Engine Performance

Alternative or supplementary fuels used in diesel engines usually need to evaluate the engine performance in order to meet the limits and ensure that the alternative fuels will not lead to the knocking problem in diesel engines [165]. Generally speaking, brake thermal efficiency, brake specific fuel consumption, and exhaust gas temperature determine the working conditions of diesel engines. Therefore, this section discusses the use of different generations of biodiesel and blends in diesel engines and investigates engine performance compared to fossil diesel.

4.1. Effect on Brake Thermal Efficiency

Brake thermal efficiency (BTE), defined as the ratio of the brake power produced by the engine to the energy released per unit of time when the fuel is completely burned, is an important indicator to measure the working capacity of the engine [166]. From an energy point of view, it is the most important parameter for evaluating engine performance. Due to the different properties of biodiesel, the following section reviews some studies on diesel BTE and attempts to find out the impact of biodiesel on diesel BTE.

Nidal et al. [167] observed a reduction in BTE in a single-cylinder diesel engine using almond biodiesel compared to the "baseline" diesel. The main reason for this result is the higher density and viscosity of the almond biodiesel, resulting in poor atomization. Furthermore, according to his research, as the ratio of almond biodiesel increased, the BTE decreased due to the high viscosity of the biodiesel blends. Thus, lower torque was observed. Öztürk et al. [168] observed a reduction in BTE in a four-stroke single-cylinder diesel engine using a rapeseed biodiesel blend due to lower heating value, viscosity, density, and higher surface tension of biodiesel. However, retardation of injection timing has no effect on BTE. How et al. [169] investigated the BTE of coconut biodiesel using a four-stroke four-cylinder high-pressure common-rail turbocharged diesel engine at a constant speed of 2000 rpm and five different engine loads. The results showed that BTE was lower at all loads due to the lower heating value of coconut biodiesel. Additionally, lower rail injection pressures were observed in coconut biodiesel.

Sathyamurthy et al. [43] used a four-stroke, single-cylinder, water-cooled diesel engine with corn oil methyl ester (corn biodiesel), which also observed lower BTE compared to diesel. The decreased BTE of the engine may also be due to the lower heating value and higher viscosity of biodiesel compared to diesel. Deiva Jothi et al. [170] used groundnut acid oil as an alternative fuel to investigate diesel engine combustion and emission characteristics. They found that diesel had a higher BTE of 31.21%, while the 20% groundnut acid oil and diesel blend had a lower BTE of 29.90%. The main reason for the reduction in BTE is that the heating value decreases with the addition of groundnut acid oil. Gumus [171] used hazelnut oil as an alternative fuel to investigate diesel engine combustion and emission characteristics. The results showed that diesel had the highest BTE at 27.82%. To improve the lower BTE due to the lower heating value of biodiesel, the author recommends advancing injection timing to improve the BTE of biodiesel. Teoh et al. [172] investigated the effect of Moringa oil biodiesel (MOB) and diesel blends (10, 20, 30, and 50% by volume) in a multi-cylinder high-pressure common rail diesel engine. The results shown in Figure 13 indicate that the BTE of MOB is generally close to that of standard diesel at 1500 rpm. The reason can be explained by the oxygen-enriched content and higher cetane number of MOB, which would make up for the lower heating value.

Furthermore, in a study by Satyanarayana et al. [173], they used mustard oil-based biodiesel and edible oil-based biodiesel in a Kirloskar AV-1 diesel engine to study the combustion and emission characteristics of biodiesel as an alternative fuel. The results shown in Figure 14 indicate that BTE was decreased with the addition of 10% and 20% mustard oil and used cooking oil biodiesel. This is because mustard oil methyl esters and used cooking oil methyl esters have a lower heating value; therefore, more fuel needs to be injected into the cylinder to obtain the same energy. In addition, the increased viscosity and density of these two biodiesels resulted in poor atomization and fuel vaporization. These inferior properties of the fuel result in more energy being consumed than converted into mechanical energy. Therefore, lower BTEs were observed in biodiesel fuels.

Rosha et al. [174] used a single-cylinder, direct-injection, variable compression ratio diesel engine to study the effect of different compression ratios on the performance and emissions of palm biodiesel. The results indicated that the BTE increased with the mean brake effective pressure, and the BTE of B20 fuel was lower than that of diesel. This reduction in BTE can be improved by a higher compression ratio (CR), which results in higher cylinder temperatures and pressures. Raman et al. [175] used 25%, 50%, 75%, and 100% rapeseed oil biodiesel in a four-stroke, single-cylinder, direct injection diesel engine to study the effect of different volumes of rapeseed biodiesel on engine BTE. The results showed that BTE decreased with increasing biodiesel ratio, mainly because the heating value of rapeseed oil biodiesel was lower than that of diesel. In addition, increasing the blend ratio of biodiesel also decreased the blending heating value, resulting in lower BTE. Asokan et al. [176] experimented with biodiesel produced from safflower oil in a constant speed (1500 rpm) single-cylinder four-stroke diesel engine. They found that B20, B30, B40, B100, and D100 had BTEs of 33.63%, 33.05%, 32.63%, 31.66%, and 34.63%, respectively, at maximum load. The results showed that the BTE of the B20 is very close to that of diesel, only 2.88% lower than that of diesel. In general, lower heating value and lower combustion output than diesel are the main reasons for the reduction. Pali et al. [177] investigated the combustion and emission characteristics of biodiesel fueled with Sal-seeded biodiesel and diesel blend on a single-cylinder, four-stroke, water-cooled diesel engine. They observed that the BTE of all tested fuels increased with load due to higher brake power reducing wall heat loss at higher engine loads. Furthermore, BTE decreased with increasing biodiesel volume fraction due to lower heating value, higher viscosity, and density of biodiesel. This resulted in poor atomization/vaporization and increased fuel consumption.

Dhar et al. [178] showed that almost the same BTE was observed when using the Karanja biodiesel blend compared to baseline mineral diesel. High viscosity, density, and evaporation energy result in larger droplets and insufficient mixing of air and fuel, resulting in lower BTE. On the other hand, however, the additional oxygen content of biodiesel increases combustion efficiency, resulting in a higher temperature and evaporation of the blend; therefore, a higher BTE. Gad and Shafay et al. [179] investigated changes in BTE using diesel and Jatropha seed biodiesel blends. They also observed that adding a percentage of biodiesel resulted in a reduction in BTE. Nguyen et al. [180] used fish oil biodiesel in diesel engines at maximum braking torque and engine speed of 1400 rpm; a lower BTE was also observed for biodiesel compared to diesel. Patel et al. [181] used three different biodiesels to study the BTE of biodiesel and its blends. The results showed that all blends had lower BTEs than the baseline mineral diesel due to the lower calorific value of biodiesel. Subramaniam et al. [182] used algae biodiesel to run in a diesel engine to investigate the combustion and emission characteristics of biodiesel. The results showed that the BTE of algae was slightly lower than that of diesel. The main reasons behind this situation are that biodiesel has a high viscosity, low volatility, and improper air–fuel mixing, which results in fuel combustion late in the expansion stroke.

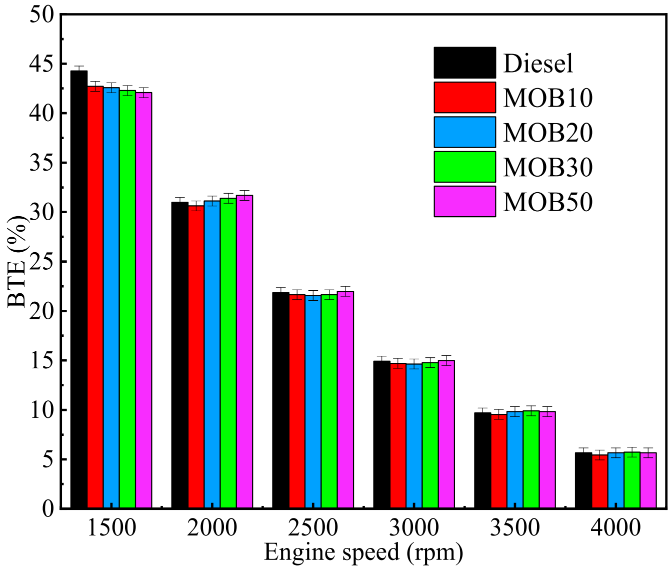

Figure 13. BTE of Moringa oil biodiesel blends at different engine speeds [172].

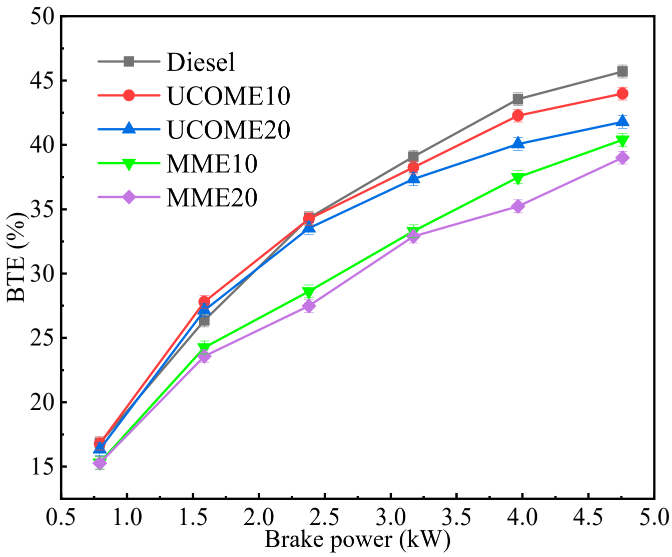

Figure 14. BTE comparison of mustard oil used cooking oil and diesel under different loads [173].

Dhamodaran et al. [183] used rice bran biodiesel (RBME), neem biodiesel (NME), and cottonseed oil biodiesel (CSME) with different unsaturations to study the engine performance of different biodiesel. The BTE differences in different biodiesel and diesel are shown in Figure 15. The results show that pure diesel (ND) has the highest BTE compared to biodiesel. This can be explained by the higher calorific value and lower viscosity of diesel compared to biodiesel. Although RBME has the highest viscosity compared to NME and CSME, it also has the highest BTE. This phenomenon can be explained by higher oxygen content in RBME leading to complete combustion. In addition, the higher CN of RBME leads to less ignition delay and longer combustion duration, which is another reason why the BTE of RBME is higher than others. Mathimani et al. [184] investigated biodiesel combustion and emission characteristics using chlorella biodiesel and diesel blend in a single-cylinder, water-cooled, four-stroke diesel engine. Biodiesel also has a lower BTE compared to diesel. Higher viscosity due to poor atomization and partial combustion of the fuel may account for the lower BTE observed. Furthermore, they unambiguously demonstrated that biodiesel with suitable unsaturation (69.03), methyl linolenic acid below 12%, and unsaturated esters (>4 double bonds) showed better BTE. Furthermore, Arunkumar et al. [185] used castor oil-based biodiesel in single-cylinder, four-stroke, and direct-injection diesel engines to investigate biodiesel combustion and emission characteristics. They also showed that BTE was decreased with an increasing ratio of biodiesel content. According to the authors, the reduction in BTE was due to the greater viscosity and poorer volatilization characteristics of biodiesel, the lower calorific value of CME, and the unsaturated fatty acid content of castor oil.

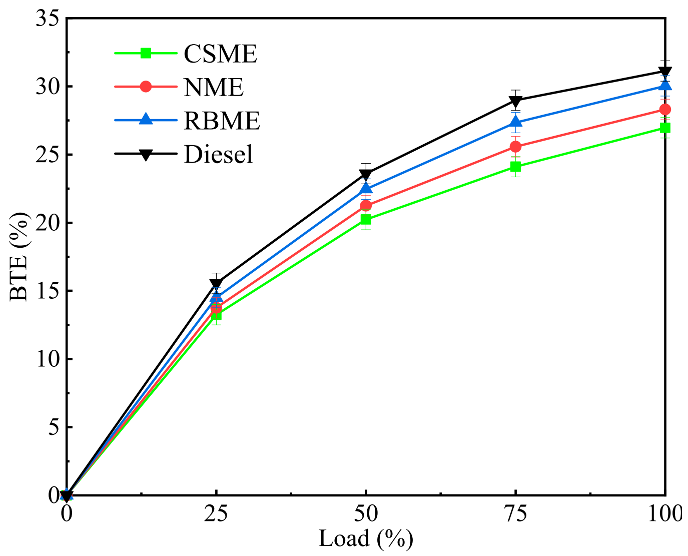

Figure 15. BTE comparison of three different biodiesel and diesel under different loads [183].

All studies in this section show that the BTE of different generations of biodiesel or biodiesel and biodiesel blends is similar or lower compared to fossil diesel or mineral diesel. The lower BTE of biodiesel and blends can be improved by changing the injection timing, compression ratio, or by adding additives. The main reasons for the lower BTE compared to diesel are concluded as follows: (1) The higher viscosity and density of biodiesel can lead to poor atomization during evaporation, which reduces fuel combustion and therefore a lower BTE. (2) Because the injected fuel is of the same quality, biodiesel has a lower calorific value than diesel, resulting in a low BTE. (3) Oxygen content and unsaturated ester content also affect the BTE of biodiesel; more oxygen content results in incomplete combustion that increases BTE, while unsaturated esters result in higher energy, disrupting the structure and lowering BTE.

4.2. Effect on Brake Specific Fuel Consumption

Brake-specific fuel consumption (BSFC) can be described as the amount of fuel consumed per unit of engine power produced. BSFC is an important indicator for the engine to convert the provided energy into useful work output. The smaller the value, the higher the efficiency of the engine's conversion to mechanical energy output [186]. In general, the lower calorific value of biodiesel means that more fuel needs to be injected into the cylinder to obtain the same amount of energy. Therefore, the BSFC of biodiesel will be higher than that of pure diesel. This section mainly summarizes and discusses the BSFCs of different biodiesel and biodiesel blends under different engine conditions and compared to pure diesel.

Özener et al. [187] observed that BSFC increased when soybean oil-biodiesel was added to fossil diesel, and BSFC increased with an increasing ratio of biodiesel addition. The same result was also observed by Asokan et al. [188]; the study used a four-stroke, single-cylinder diesel engine fueled with juliflora biodiesel and blends. They explained that BSFC is the actual mass of fuel consumed to produce "1 kW". Due to the lower calorific value and higher viscosity of biodiesel compared to diesel, more fuel is injected into the combustion chamber to achieve the same combustion heat release as diesel. Therefore, the BSFC of biodiesel is increased. How et al. [189] obtained the same result in BSFC when using Calophyllum Inophyllum biodiesel (CIB) blends. The detailed results of BSFC at different engine speeds are shown in Figure 16. The main reason for the decline is the combined effect of the lower heating value, higher density, and kinematic viscosity of the biodiesel blends.

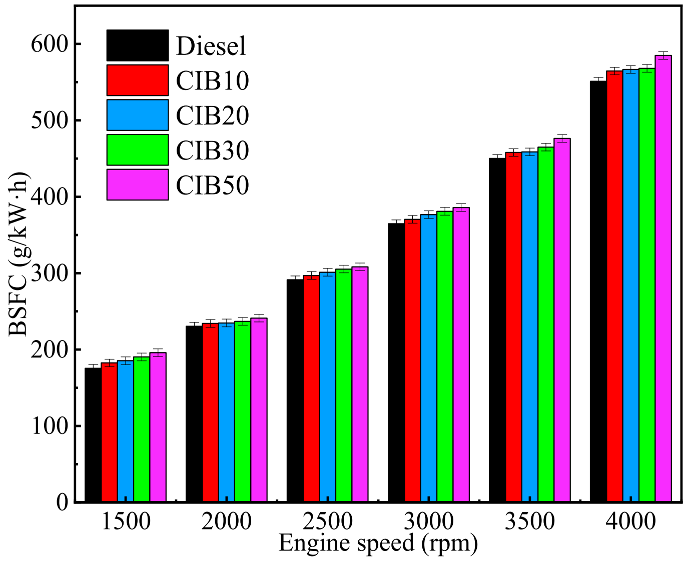

Figure 16. BSFC comparison of CIB biodiesel and diesel at different engine speeds [189].

Mubarak et al. [190] investigated the combustion and emission characteristics of Salvinia molesta oil biodiesel under different engine loads on a single-cylinder, four-stroke, air-cooled diesel engine. The results indicated that all the blends show higher BSFC compared to neat diesel. Furthermore, due to the higher viscosity and lower calorific value of biodiesel compared to diesel, the BSFC increases with the ratio of biodiesel. Shareef et al. [191] used a diesel engine with variable injection timing, fueled with scum biodiesel, and observed a higher BSFC than fossil diesel. Lower heating values, higher viscosity, and lower specific gravity are the main reasons for the results. Moreover, with the increase in injection timing, the BSFC will also increase. Sathiyamoorthi et al. [192] conducted an experimental study on a single-cylinder engine fueled with biodiesel derived from Cymbopogon Martini (PMO), which also showed an increase in the BSFC of biodiesel. Specifically, for diesel, PMO25, PMO50, and PMO100 fuel blends the BSFCs were 250 g/kW·h, 270 g/kW·h, 310 g/kW·h, and 340 g/kW·h, respectively. Zhang et al. [36] investigated four different types of biodiesel fuels in a four-stroke marine diesel engine. They found that the BSFC of the four biodiesels was 10% higher than that of pure biodiesel because the tested biodiesel had a lower calorific value and 5% higher density than diesel. Another experimental study by Ruhul et al. [193] using a single-cylinder diesel engine with variable load and speed conditions, fueled with Millettia pinnata (MP) biodiesel and Croton mega-locarpus (CM) biodiesel, also observed an increase in BSFC. The results of the two biodiesels at different speeds and loads are shown in Figure 17a,b, and the results show that the BSFC of the biodiesel blend is higher than that of diesel under the two different operating conditions. This may be attributed to biodiesel's higher density and viscosity than diesel. Perumal et al. [194] analyzed the combustion and emission characteristics of Pongamia methyl ester (PME) as a biodiesel with different addition ratios in diesel engines. Similarly, BSFC is higher than pure diesel due to the lower heating value of PME. Ogunkunle et al. [195] studied the effect of Parinari polyandra biodiesel on the performance, emissions, and combustion characteristics of a six-cylinder turbocharged four-stroke diesel engine. They also observed higher BSFC in biodiesel and diesel blends; this phenomenon is mainly influenced by diesel's higher calorific value, lower viscosity, and higher hydrogen efficiency index compared to biodiesel.

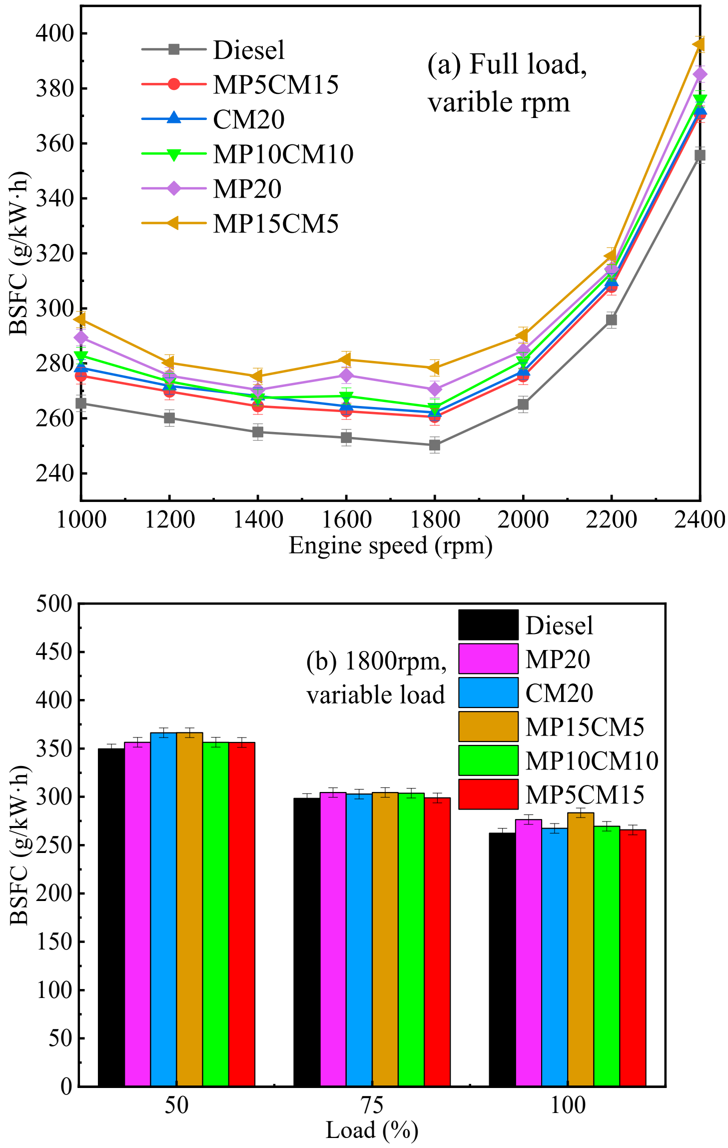

Figure 17. BSFC at different engine conditions. (**a**) Different speeds; (**b**) Different loads [193].

According to the report of the previous researchers, it can be concluded that the BSFC of biodiesel is generally higher than that of diesel due to the lower calorific value and higher viscosity of biodiesel. However, in a study by Viswanathan et al. [196] when Elaeocarpus Ganitrus (EG) was used as biodiesel in a diesel engine, higher BSFC in diesel fuel was observed. At full load, the BSFC in diesel is 307 g/kW·h, while the BSFC of the EG50 biodiesel blend is 233 g/kW·h; a 24.1% reduction in BSFC for EG 50 biodiesel due to the low kinematic viscosity and higher calorific value of the biodiesel blend. Arunkumar et al. [185] investigated biodiesel combustion and emission characteristics using different castor biodiesel (CME) ratios as fuel in a diesel engine. The result is shown in Figure 18 and notes that BSFCs have increasing brake power. This is due to the enhanced temperature of the cylinder under high load. It may be useful for reducing ignition delay, which assists engine combustion and lowers the load-rich fuel–air mixture supplied to the engine.

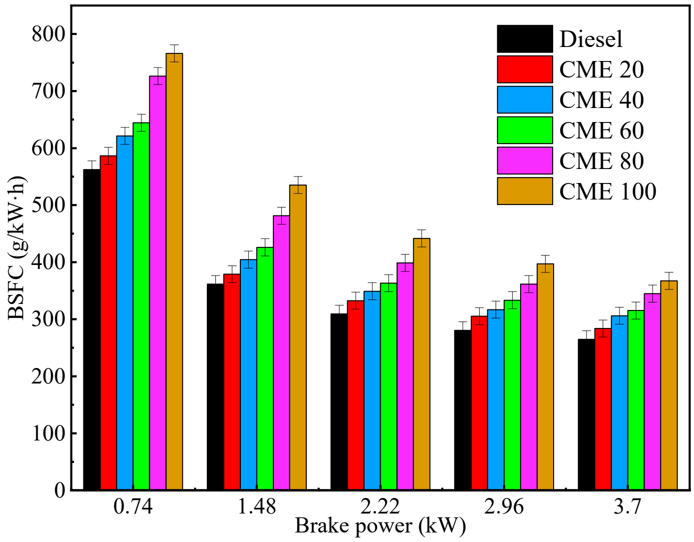

Figure 18. BSFC comparison of CME blends and diesel under different brake powers [185].

Tizvir et al. [197] investigated the performance and emission characteristics of biodiesel produced by Dunaliella tertiolecta microalgae in a single-cylinder, four-stroke, air-cooled diesel engine. The results showed higher BSFC in biodiesel blends compared to diesel. The author indicated that the lower calorific value of biodiesel (40.2 MJ kg^{-1}) relative to pure diesel (44.8 MJ kg^{-1}) is the main reason for the increase. Gowda et al. [198] used a multi-objective optimization of production metrics to produce biodiesel and investigated the performance and emission characteristics of diesel engines fueled with the produced biodiesel. Higher BSFC in the biodiesel blend was also observed. They explained it was because of the higher density, viscosity, and lower calorific value of biodiesel. Other research, by Parthiban et al. [199], used Annona squamosa seed oil biodiesel in a single-cylinder air-cooled four-stroke diesel engine to investigate the combustion and emission characteristics of biodiesel. They also observed higher BSFC compared to diesel. Furthermore, Azad et al. [200] used grape seed and waste cooking oil as biodiesel in a four-cylinder four-stroke diesel engine to investigate the combustion and emission characteristics of biodiesel. They observed that the BSFC of biodiesel was not significantly different at low and high rpm, but the BSFC of biodiesel was higher than that of diesel due to its higher calorific value, lower density, and viscosity compared to diesel.

Auti et al. [75] also found a similar trend with raw tire pyrolysis biodiesel and Karanja biodiesel in a single-cylinder four-stroke diesel engine. This may be due to the lower density and viscosity of diesel fuel. Furthermore, the higher CN of biodiesel blends compared to diesel may also be responsible for the increase in BSFC. Tayari et al. [201] compared the combustion and emission characteristics of engines fueled with three different generations of biodiesel and found that the different generations of biodiesel showed higher BSFC compared to diesel. Bharadwaj et al. [202] investigated the combustion and emission characteristics of biodiesel prepared from rubber seed oil in a single-cylinder four-stroke water-cooled diesel engine. The results showed that the BSFC of the biodiesel blend is higher than that of diesel due to the low calorific value and high density of biodiesel. Specifically, the BSFC (g/kW·h) of the B10, B20, and B30 were 389.5, 390, and 399.5, respectively, while the BSFC of the conventional diesel was 380. The author also recommended that B30 is the best blend for the diesel engine. Baweja et al. [203] investigated mustard oil as a feedstock for biodiesel production and investigated the performance and emissions characteristics fueled with mustard biodiesel. The result indicated that BSFC gradually drops with an increase in load because the rate of augmentation in the fuel flow rate is lower than the rate of augmentation in brake power with load. Moreover, the lower calorific value and higher density of biodiesel lead to the increase in BSFC. Less heat loss and more oxygen content are responsible for the lower BSFC of biodiesel at higher loads. Ellappan et al. [204] conducted a comprehensive review of the performance and emission characteristics fueled with eucalyptus biodiesel. They had been concluded various researchers' results of BSFC for eucalyptus biodiesel and diesel blends. The result indicated that higher BSFC was observed in biodiesel blends due to higher density and lower heating value of the biodiesel. Rai et al. [205] used robusta methyl ester biodiesel and diesel blends to investigate the effect of CR, engine load, and biodiesel blend ratio (10%, 20%, 30%, and 40% v/v) on diesel engine combustion and performance. The result indicated that at the CR of 17, higher BSFC was observed in the biodiesel blends, and the BSFC will increase with the increase in the biodiesel ratio. Furthermore, the fuel was found to have lower combustion efficiency and fuel energy rate at lower engine loads, resulting in lower BSFC.

At the end of this section, it can be concluded that almost all types of literature review the higher BSFC of biodiesel, except for a few researchers who observed a lower BSFC of biodiesel due to the higher calorific value and lower density of the fuel. The main reasons for this phenomenon are as follows: (1) The lower calorific value and higher density of biodiesel results in poor atomization and fuel evaporation; therefore, more fuel needs to be injected into the cylinder to obtain the same energy as diesel fuel. This increases the BSFC of biodiesel. (2) Important parameters such as engine speed, brake power, and load conditions also affect the BSFC of biodiesel. Specifically, BSFC will increase with engine load and brake power. Gradually increase after the speed reaches 1800 rpm. However, the CR of the diesel engine has little effect on BSFC. (3) For biodiesel and diesel blends, increasing the ratio of biodiesel will increase BSFC. The density and viscosity of the blends will be increased with the addition of biodiesel. (4) The higher oxygen content of biodiesel results in incomplete combustion, but higher density, viscosity, and CN are also major contributing factors to BSFC.

4.3. Effect on Exhaust Gas Temperature

The temperature of the gas mixture leaving the combustion chamber is an important parameter for optimizing performance and controlling the emissions of an internal combustion engine [206]. Exhaust gas temperature (EGT) also affects the performance of the after-treatment system. Furthermore, the temperature of the piston, cylinder head, and cylinder liner can be inferred by detecting the EGT, which is important for next-generation high-performance engines operating near the limits of engine materials [207]. Therefore, the EGT of diesel engines plays a vital role in performance; in this section, various pieces of literature reveal the EGT of biodiesel.

Generally, the EGT of biodiesel will be higher than that of diesel due to the higher BSFC and higher oxygen content of biodiesel. Rahman et al. [208] investigated the performance and emission characteristics of biodiesel produced from water hyacinth biomass using a Kirloskar TV1 single-cylinder four-stroke naturally aspirated engine. They observed that the EGT of all tested fuels increased with increasing engine load and showed higher EGT in the biodiesel blend. One possible reason is the lower CN of biodiesel. In their study, diesel fuel had a slightly higher CN than biodiesel, resulting in a shorter ignition delay and shorter premixed combustion period. As a result, the combustion process produces a higher maximum gas temperature, which results in a higher EGT for diesel. Similarly, the same trend was also observed by Arunkumar et al. [185] used castor biodiesel to study the engine combustion and emission characteristics of diesel engines. They found lower EGT in the biodiesel blend because of the lower calorific value and higher viscosity of the composite fuel. Rajak et al. [209] conducted an experimental study on a four-cylinder, four-stroke, water-cooled, multi-hole injection diesel engine using spirulina microalgae biodiesel. The experimental results showed that EGT can be decreased by increasing the ratio of biodiesel. They explained that the EGT of the experimental biodiesel is highly dependent on the amount of oxygen, and a higher percentage of oxygen in the biodiesel results in incomplete combustion, which reduces EGT. Balamurugan et al. [210] used corn oil biodiesel as an alternative fuel for diesel engines to evaluate performance, combustion, and emission characteristics. Figure 19 shows the EGT results of this research; it was observed that EGT increased with an increasing load, but it was lower compared to diesel. Furthermore, the increase in corn oil biodiesel concentration resulted in a decrease in EGT due to the high latent heat of vaporization and the quenching effect of biodiesel. Specifically, the high viscosity, low CN, and reduced volatility of the blended fuels led to poor mixture formation, and hence premixed combustion phase was less dominant. This may lead to lower EGT of biodiesel. Another study by Dhar et al. [211] using high-free fatty acid neem oil biodiesel found a similar trend. They explained that the lower EGT was due to the shorter combustion duration of the biodiesel blend.

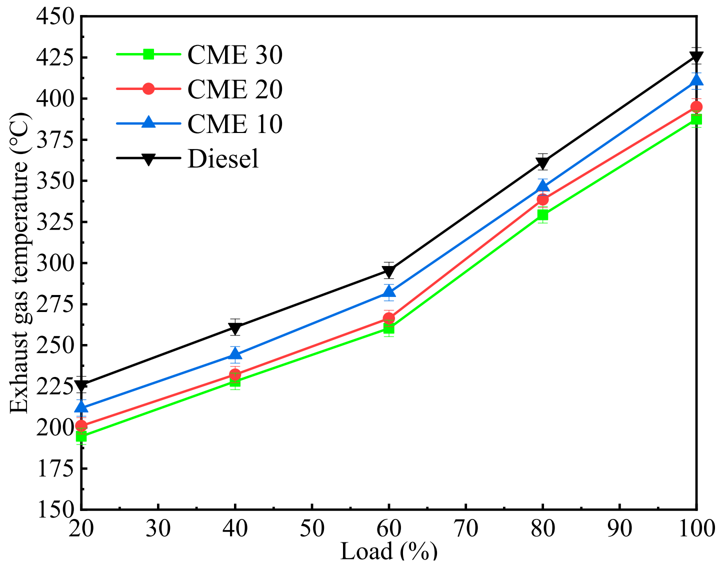

Figure 19. EGT comparison of CME biodiesel blends and diesel under different loads [210].

Chandra et al. [212] investigated the performance and emission characteristics of a diesel engine fueled with Pithecellobium dulce seed oil biodiesel (PDSOME). The biodiesel production process was optimized using the response surface methodology, and the results showed that EGT increased with increasing brake power. PDSOME blended fuel produced lower EGT values than diesel, and at full load, PDSOME with different blend ratios decreased by 8.25%, 10.1%, 11.5%, 12.5%, and 13.75%, respectively. Another experimental study by Tayari et al. [201] used three different generations of biodiesel to investigate the performance and emissions in an unmodified diesel engine with variable engine speed. The results indicated that the EGT increases with increasing engine speed. Moreover, the EGT is higher in diesel fuel. An experimental study by Asokan et al. [188] used juliflora biodiesel in a direct injection diesel engine to investigate the combustion and emission characteristics of biodiesel. The same trend was also observed in biodiesel and its blends: diesel had a higher EGT due to the shorter combustion duration and higher viscosity of biodiesel. Anawe et al. [213] used a single-cylinder, four-stroke, air-cooled, direct injection, and compression ignition engine to investigate the combustion and emission characteristics of biodiesel. Similar trends were also observed with Persea Americana Biodiesel and diesel blends. In addition, a comparative study on emissions and performance of two biodiesels with almond oil and palm oil as diesel fuels also found to have higher EGT in diesel [166]. One possible reason is the maximum gas temperature in the diesel fuel chamber, as diesel has a higher CN compared to biodiesel.

Raman et al. [175] investigated the performance and emission characteristics of biodiesel using biodiesel produced from rapeseed oil by transesterification in a single-cylinder, four-stroke, compression ignition, and direct injection diesel engine. EGT increased with increasing brake power, and higher concentrations of biodiesel increased EGT.

The main reason for this phenomenon is that the oxygen content in biodiesel enhances the combustion process, resulting in higher EGT. Baweja et al. [203] conducted experiments using a single-cylinder, four-stroke, water-cooled diesel engine to investigate performance and emission characteristics using mustard oil biodiesel. According to their research, the EGT of the blends mainly depends on the fuel and engine operating specifications. The B10 blend had the lowest EGT from 25% to 100% loading. This may be due to the oxygen content of biodiesel, which promotes complete combustion despite its lower calorific value. While under full load conditions, the mixtures B20, B30, and B40 showed higher EGT values. The higher injection volume of biodiesel, higher density, bulk modulus than diesel, and slow combustion of high-viscosity mixtures are the main reasons for the higher EGT.

Sinan et al. [214] investigated the performance and emission characteristics of diesel generators fueled with two different biodiesels and their blends. The results of the EGT diesel engine fueled with two different biodiesels are shown in Figure 20. As can be seen from the figure, the two different biodiesels showed different EGT compared to diesel; the EGT of animal fat biodiesel (AFB) was higher than that of diesel, while the EGT of vegetable oil biodiesel (VOB) was lower under all load conditions. The main difference is that the CN of the AFB is higher than that of the diesel, at 57, thus increasing the EGT.

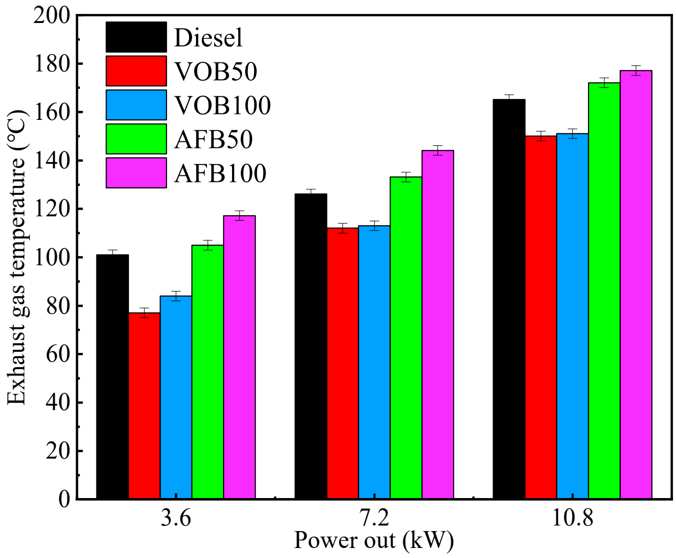

Figure 20. EGT comparison of AFB biodiesel and VOB biodiesel blends under different brake powers [214].

Sakthivel [215] also found the same trend of results by using fish oil biodiesel in a single-cylinder, four-stroke, water-cooled diesel engine. In their research, the authors investigated the effects of injection timing and biodiesel ratio on the performance and emission characteristics of a diesel engine. Higher EGT can be observed in biodiesel blends due to higher viscosity and poor volatility of biodiesel. In addition, the higher oxygen content in biodiesel improves combustion efficiency, which is another reason for the higher EGT of biodiesel. Moreover, the injection timing of the diesel engine also has a certain influence on the EGT. Specifically, advanced fuel injection leads to a better air–fuel mixture; thus, higher BTE and lower EGT were observed in the test biodiesel.

Another exciting report by Singh et al. [216] used argemone biodiesel and diesel blends in multi-cylinder diesel engines and observed that blending up to 20% biodiesel in diesel decreased EGT. They explained that with the addition of 20% biodiesel, the cylinder pressure peak and heat release rate peak were similar to diesel, thus leading to complete combustion and decreased EGT. However, with the addition of biodiesel, the shift in heat release rate peak away from the Top Death Center indicated late combustion and increased EGT. Sayyed et al. [217] evaluated the performance, combustion, and emission characteristics of diesel engines fueled with biodiesel or dual biodiesel blends. The study indicated that the Maximum (363.9 °C) and minimum (130.39 °C) EGT were observed for the blend at 3.3 kW and 0 kW engine loads. Due to the oxygen content in biodiesel, the EGT of the blend was slightly higher than that of diesel; the average increase in EGT compared to diesel was 9.94% for all blends. Yesilyurt [218] investigated the effects of the fuel injection pressure on the performance and emission characteristics of a diesel engine fueled with waste cooking oil biodiesel and diesel blends. Higher EGT was also observed with the increase in biodiesel ratio due to high oxygen content and improved combustion efficiency. Additionally, Dharmaraja et al. [219] used rice bran oil-derived biodiesel blends to study the performance and emission characteristics. Higher EGT was observed in biodiesel and diesel blends because biodiesel continued the combustion process during the primary combustion stage during the later combustion stage.

At the end of this section, two opposing results were obtained in the EGT of biodiesel. (1) The effect of engine load conditions can be summarized as follows: Higher EGT can be observed with increasing engine speed, load, and braking power. However, injection time and CR had little effect on EGT for biodiesel and biodiesel blends. (2) Due to the higher oxygen content of biodiesel, more complete combustion of the biodiesel and biodiesel mixture results in higher EGT; in addition, the higher CN and higher density of biodiesel results in more fuel being injected into the cylinder, increasing the EGT. (3) Conversely, some researchers study higher EGT in diesel fuel because the lower calorific value of biodiesel results in less heat release, which reduces EGT. In addition, the higher density and viscosity of biodiesel resulted in poorer evaporation and atomization of biodiesel; therefore, lower EGT was observed. (4) In summary, the EGT of biodiesel mainly depends on which factor dominates the combustion process; the high oxygen content of biodiesel leads to complete combustion, which reduces EGT, or the density and viscosity of biodiesel lead to poor evaporation and atomization of biodiesel, which increases EGT.

4.4. Summary of Performance Analysis

In this section, the performance of biodiesel and biodiesel blends running in diesel engines under normal operating conditions is derived from three important parameters: BTE, BSFC, and EGT. Different kinds of literature summarized the main changes in these three parameters.

As can be seen from all the summarized articles, the BTE was decreased for almost all biodiesel and biodiesel blends. Due to the lower calorific value and density and higher viscosity of biodiesel compared to diesel. Furthermore, for operating conditions, it can be seen that BTE increases with engine load and brake power but decreases with engine speed. In addition, the BTE of biodiesel and diesel blends will decrease with the increasing ratio of biodiesel.

For the BSFC of biodiesel and biodiesel blends in the current study, it was found that most biodiesel and biodiesel blends had higher BSFC compared to diesel. This is due to the lower calorific value and higher viscosity of biodiesel resulting in a poorer combustion process. For engine load conditions, higher load conditions and brake power will result in lower BSFC. This can be explained by higher cylinder temperature resulting in lower viscosity and density of biodiesel due to better atomization and evaporation with increasing engine load.

At the end of this section, it is concluded that due to the high viscosity and density of biodiesel, lower BTE and higher BSFC can be found in many studies. Some researchers have observed higher BTE and lower BSFC for biodiesel due to the lower density and viscosity and higher CN of specific biodiesel such as Elaeocarpus ganitrus biodiesel. In addition, higher oxygen content results in complete combustion efficiency, and lower ignition delay also results. As for the EGT of biodiesel and biodiesel blends compared to diesel, an interesting finding is that oxygen content, lower viscosity, density, and higher CN lead to better atomization and evaporation, resulting in lower EGT.

5. Effects of Different Generations of Biodiesel on Engine Emissions

Air pollution has negative effects on humans; according to the World Health Organization, approximately 4.2 million people die from air pollution each year [220]. In-home heating, industrial facilities, vehicle exhaust, and some energy production activities are the most important contributors to the PM increase in the environment [221]. In this regard, one of the major pollutants in vehicle exhaust is diesel engines and diesel fuels. Combustion of diesel fuel results in approximately 60% of greenhouse gas emissions (CO_2) along with other pollutants such as CO, NO_x, HC, and smoke. Therefore, many countries have established strict emission standards for pollution from internal combustion engines; strict emission standards may have an impact on the use of biodiesel. It is necessary to pay attention to the emissions of diesel engines fueled with biodiesel. In this section, emissions from diesel engines using different generations of biodiesel are critically reviewed and summarized based on the diverse research surveyed in the study.

5.1. Effects on CO Emissions

CO is a by-product of the incomplete combustion of fuel. Generally speaking, the carbon present in any fuel will be converted to CO_2, but due to the limitation of the oxygen content in the intake air, the carbon present in the fuel can cause incomplete combustion, resulting in the production of CO. Specifically, if CO_2 emissions increase, then CO emissions will naturally decrease. Since biodiesel has 11–13% oxygen content compared to diesel, CO emissions will decrease as the ratio of biodiesel increases, while CO_2 emissions will be reversed. This section summarizes and reviews CO emissions from some previous experimental and simulation studies of biodiesel-fueled diesel engines.

Jamshaid et al. [222] used different cottonseed and palm oil biodiesel blend ratios in a single-cylinder, four-stroke, and naturally aspirated diesel engine to investigate the combustion and emission characteristics of biodiesel. The results shown in Figure 21 indicate that CO emissions decreased with increasing engine speed, with the lowest CO emissions at 2400 rpm for a 20% cottonseed biodiesel and diesel blend. Poor atomization and higher fuel viscosity can lead to local enrichment of the fuel mixture, resulting in incomplete combustion. Therefore, more CO is produced during the combustion process. As engine speed increases, more air enters the cylinder resulting in increased oxygen content and complete combustion, leading to the observed decrease in CO as the speed increases.

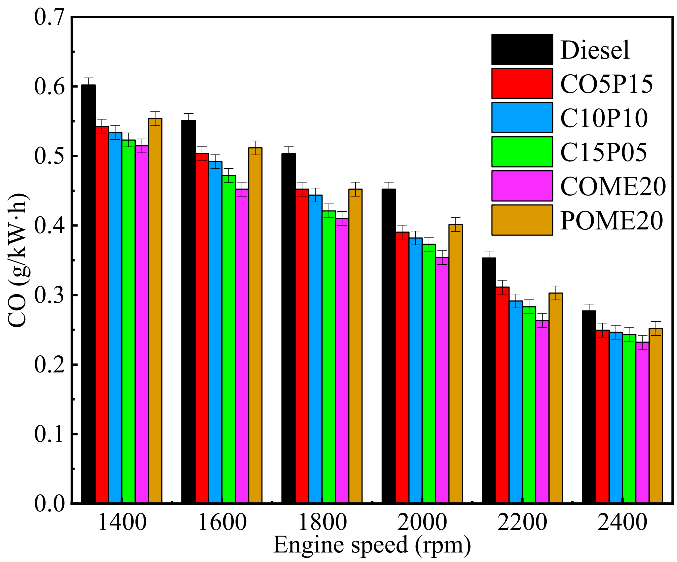

Figure 21. CO emission comparison of COME and POME biodiesel blends at different engine speeds [222].

Sathyamurthy et al. [43] used corn oil methyl ester as an alternative fuel to investigate the effect on diesel engine performance and emissions. The same tendency was also observed at different engine loads due to the decreased availability of oxygen content in diesel fuel during in-cylinder combustion. Compared to fossil fuels at full load, the CO_2 emission reductions by using different ratios (10%, 20%, and 30%) of corn oil methyl ester were 28.33%, 30%, and 33.33%, respectively. Excess oxygen content leads to better complete combustion mainly pays for this phenomenon. Another work by Mubarak et al. [190] used Salvinia molesta oil biodiesel and diesel blends to study the effect of Salvinia molesta oil biodiesel on engine performance and emissions of a water-cooled single-cylinder diesel engine. Lower CO emissions were also observed in the biodiesel due to the presence of oxygen in the biodiesel, which enhanced complete combustion. Moreover, all the tested fuel emissions increased with the increase in brake power and load conditions due to the formation of a rich zone at higher loads, resulting in localized hypoxia. Baweja et al. [203] investigated the effect of mustard oil as an alternative fuel for diesel engines on the combustion and emission characteristics of diesel engines under different engine loads. The results indicated that CO emissions were higher at no-load conditions, and they decreased to 60% load for diesel, 60% load for B10 blend, 67.5% load for B20 blend, and 62.5% load for B30 and B40 blends. This trend in CO emissions is due to more CO being oxidized and converted to CO_2 at higher in-cylinder temperatures. Of all the blends, the B20 blend had the largest reduction in CO_2 emission compared to diesel, at nearly 87.5%.

Ellappan et al. [204] conducted a comparative review of the performance and emission characteristics of diesel engines using eucalyptus-biodiesel blends. The results indicated that biodiesel has decreased CO emissions compared to diesel at all load conditions. This can be explained by an excess of O_2 in biodiesel leading to oxidation of CO to CO_2 and better combustion. Uyumaz et al. [223] conducted experimental studies on the combustion, engine performance, and exhaust emission characteristics of poppy oil biodiesel and diesel blends in diesel engines. The results indicated that CO increased with the engine load at an engine speed of 2200 rpm. The oxygen concentration in the cylinder decreased; therefore, the fuel molecules cannot be oxidized is the main reason. On the other hand, it was determined that CO decreased when the biodiesel fraction in the fuel mixture for each engine load increased. They explained that because biodiesel has more oxygen in its chemical structure than diesel, it improves combustion. Sun et al. [224] carried out an experimental study to investigate the effect of EGR and Dimethyl ether on biodiesel engine performance and emission characteristics. The results showed that the CO emissions of B5, B10, and B15 increased by 19.2%, 16.0%, 15.5%, and 17.1%, respectively, with the increase in the EGR rates when the engine speed was 1262 r/min, and the BMEP was 0.4 MPa. The authors also noted that an increase in the EGR rates resulted in incomplete combustion products due to a decrease in combustion temperature and O_2 concentration. Alagu et al. [225] used novel water hyacinth biodiesel (WHB) as a potential alternative fuel for existing unmodified diesel engines. Similar trends were also observed in engine performance, combustion, and emission characteristics. They explained that biodiesel alters the O_2 content, oxidation rate, fuel spray characteristics, in-cylinder temperature, and ignition center, which play an important role in the formation of CO. In their study, due to O_2 deficiency in diesel fuel, WHB, and diesel blends that have in-built fuel O_2, lower CO formation than diesel fuel (0.144%) was observed in blends. Additionally, increasing engine load results in increased CO emissions as more fuel is burned and more fuel-rich and oxygen-deficient regions are formed. At full load, the CO emissions of the B100 are 3.7%, 6.9%, and 8.2% lower than those of the B20, B30, and B40, respectively.

Sayyed et al. [217] used four different types of biodiesels (Jatropha, Karanja, Mahua, and Neem) and a dual biodiesel and diesel blend to investigate and evaluate the performance and emission characteristics of diesel engines. The results shown in Figure 22 indicate that the CO emissions of the dual biodiesel blend are lower than that of diesel. Since the composition of fossil fuels does not contain oxygen molecules, the average CO emissions of the blended fuels are decreased by 31.11%, 11.38%, 23.96%, 36.78%, and 46.91%, respectively, compared to diesel fuels. How et al. [189] studied the engine performance and emission characteristics of Calophyllum Inophyllum biodiesel as an alternative fuel in a multi-cylinder diesel engine. The results indicated that lower CO emissions were also observed in the blends. This improvement may be related to the enrichment of oxygen in the biodiesel fuel, thus enabling a cleaner burn during the combustion process. Additionally, a comparative study by Dhamodaran et al. [183] investigated the combustion and emission characteristics of biodiesel using three different degrees of unsaturation in a single-cylinder diesel engine. They also found that biodiesel emitted lower CO concentrations than fossil diesel, with the lowest CO emissions of the three biodiesels being the rice bran-based biodiesel. The main reason for the lowest CO emissions from rice bran-based biodiesel is that it has the highest oxygen content in the tested biodiesel blends. On the contrary, cottonseed oil biodiesel has the highest CO emissions in the test biodiesels, possibly because it has less oxygen than the other biodiesel blends. Conversely, cottonseed oil biodiesel had the highest CO_2 emissions of the tested biodiesel; one possible reason for this is that it has lower oxygen levels than other biodiesel blends.

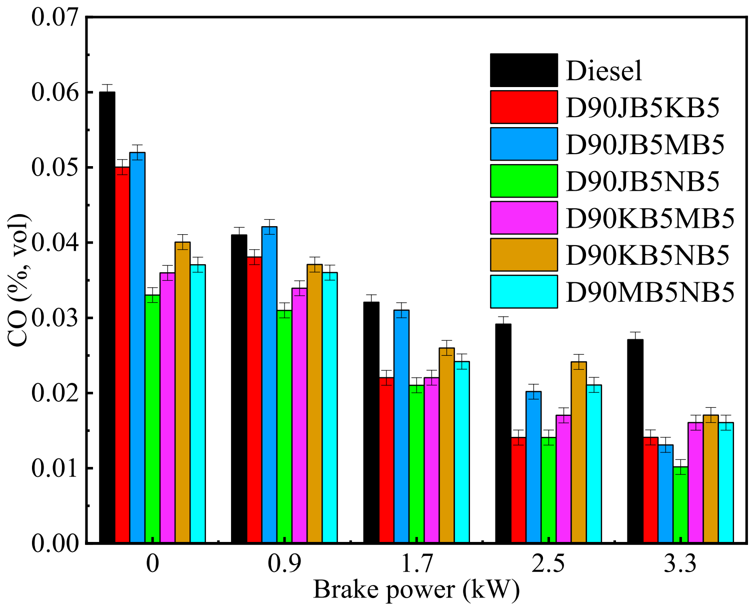

Figure 22. CO emission comparison of two biodiesel blends and diesel under different brake powers [217].

Gharehghani and Mirsalim [226] used a single-cylinder diesel engine fueled with different waste fish oil biodiesel and diesel blends ratios to investigate the diesel engine performance and emission characteristics. Figure 23 shows the CO emission results fueled with different biodiesel blends. When using B25, B50, B75, and B100, the CO emissions of biodiesel and its blends were decreased by an average of 5.2%, 11.2%, 22.5%, and 27%, respectively, compared to pure diesel. The oxygen content in biodiesel leads to increased combustion efficiency, which is the main reason for this phenomenon. Compared to diesel, the oxygen availability in biodiesel results in lean burn in the cylinder, and as the mixing ratio increases, more carbon molecules will be oxidized compared to diesel. Similar results were also found by Kodate et al. [227] who studied biodiesel engine performance and emission characteristics using preheated Dhupa seed oil biodiesel as an alternative fuel in a four-stroke single-cylinder TV-1 Kirloskar diesel engine. They also explained that the presence of oxygen molecules in the biodiesel promotes the oxidation of CO to CO_2 during combustion; thus, lower CO shows in biodiesel.

Moreover, Omidvarborna et al. [228] investigated the effects of unsaturated bonds and chain lengths of biodiesel feedstocks on CO, CO_2, and methane emissions for biodiesel fuels. The higher oxygen content can explain the decreased CO emissions for the test biodiesel in the short fatty acid molecules of C16:0, leading to complete combustion. In addition, longer chain length and unsaturated structure have higher boiling and melting points than shorter chains, thus less likely to be completely vaporized and combustion, thereby increasing CO emissions. In addition, the comparative experimental study by Tayari et al. [201] used three different generations of biodiesel to study the engine performance and emission characteristics of a single-cylinder four-stroke direct-injection diesel engine. The result showed that the test biodiesel significantly decreased CO emissions compared to diesel. Specifically, the lowest CO emissions of all fuels tested were the microalgae Chlorella biodiesel blend, which was 47.4% lower on average compared to diesel, due to the higher oxygen content of biodiesel due to complete combustion.

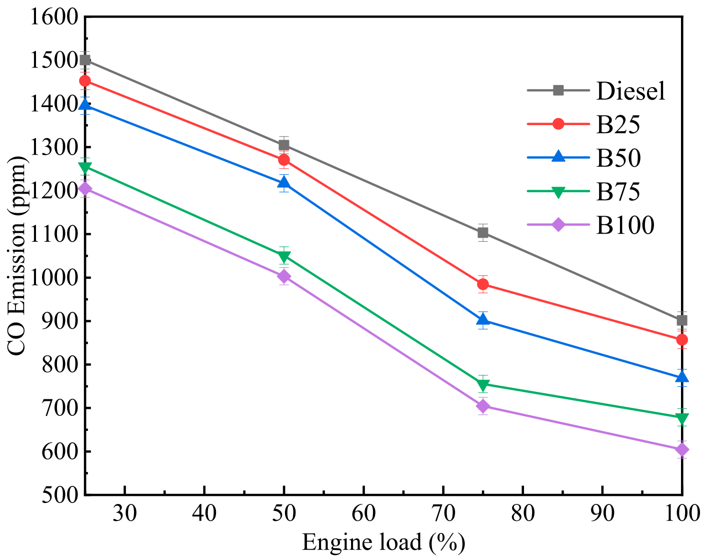

Figure 23. CO emission comparison of biodiesel blends and diesel under different engine loads [226].

In the conclusions of this section, it is observed that the CO emissions of biodiesel-fueled diesel engines are decreased by nearly 25–30% compared to diesel. The reasons why biodiesel CO emissions are lower than diesel can be concluded as follows: (1) The 11–13% oxygen content in the biodiesel structure of biodiesel causes more fuel to be oxidized and completely combusted, thus converting CO into the complete combustion product CO_2. (2) As for the effect of engine operating conditions on CO emissions, it can be summarized that with the increase in engine speed, braking power, and load conditions, lower CO emissions can be observed due to increased intake of air. The additional oxygen content of biodiesel improves and reduces rich areas, thereby reducing CO emissions.

5.2. Effect on CO_2 Emissions

CO_2 is a well-known complete combustion product of the combustion chamber and is named a greenhouse gas. Therefore, the CO_2 emissions in the diesel engine fueled with biodiesel need to be strictly controlled. Most researchers try to find out the relationship between CO and CO_2 emissions from diesel engines. In most literature, different operating conditions and the generation of biodiesel also affect CO_2 production.

To improve the diesel engine performance and emission characteristics of diesel engines fueled with biodiesel, Mourad et al. [229] used different EGR rates (0%, 5%, 15%, and 25%) and different preheated sunflower oil temperatures (30 °C, 40 °C, 50 °C, 60 °C, and 70 °C) in a single-cylinder, air-cooled, diesel engine. The results indicated that with the increase in EGR rates, the CO_2 emissions increased. The increase in CO_2 emissions was due to the amount of exhaust entering the cylinder combustion chamber with the suction air, which decreased the volumetric efficiency and thus decreased the engine power and more BSFC; therefore, more CO_2 emissions were observed. In addition, the preheating of biodiesel decreased the CO_2 emissions because preheating provides more combustion energy. Shrivastava et al. [230] investigated different injection pressures on diesel engine performance and emissions fueled with roselle biodiesel. They also observed that with the increase in injection pressure and biodiesel ratio, the CO_2 emissions increased. Due to the Roselle biodiesel's higher molecular weight and carbon content, the maximum increase was shown in full load at 260 bar, about 10.27%.

Rajak and Nashine et al. [231] investigated the effects of different spirulina microalgae biodiesel (SMB) ratios with diesel fuel on engine performance and emissions in a four-cylinder, four-stroke, water-cooled diesel engine. The CO_2 emissions with different engine loads are shown in Figure 24. It can be found from the picture that with the increase in biodiesel blends and engine loads, CO_2 emissions increased by about 3.4% with a 20% replacement of biodiesel. Anwar et al. [232] studied the emission characteristics of four different types of non-edible biodiesel from a naturally aspirated four-stroke multi-cylinder diesel engine under different load conditions and observed similar trends. They explained that when oxygen is plentiful, CO is converted to CO_2, and oxygen content in the fuel facilitates the reaction. In addition, the higher CN and higher oxygen content of biodiesel are also responsible for the increased CO_2 emissions.

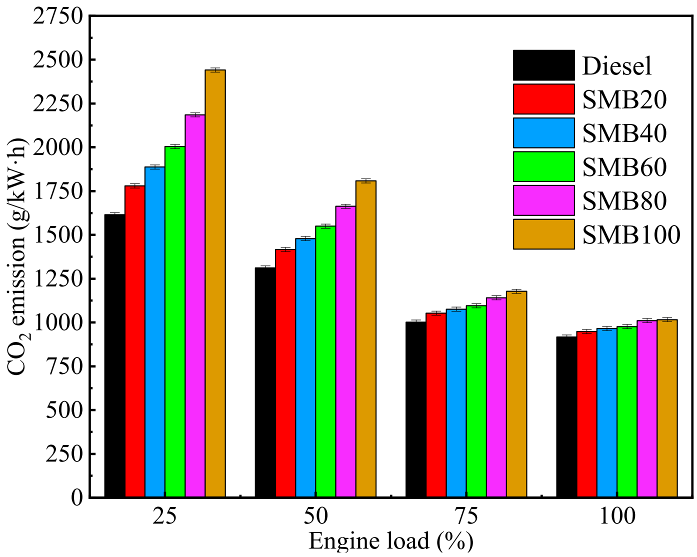

Figure 24. CO_2 emission comparison of SME biodiesel and diesel under different loads [231].

Moreover, Suleyman Simsek [233] investigated biodiesel produced from canola, safflower oils, and waste oils on the engine performance and emission characteristics of a four-stroke, single-cylinder air-cooled, direct injection diesel engine. They observed that with the increase in engine load, the CO_2 emissions of B10, B20, B30, B50, B75, and B100 fuel blends increased by an average of 4.83%, 26.92%, 30.85%, 35.42%, 38.04%, and 42.62%, respectively, compared to diesel. The emissions of CO_2 increased with the increase in biodiesel ratios due to the oxygen-fuel reaction being improved by the oxygen content abundant in biodiesel. On the other hand, Viswanathan et al. [196] analyzed Elaeocarpus ganitrus biodiesel used in diesel engines. The results indicated that at full load, diesel CO_2 emissions are decreased by 5.9%. Mehmet [234] used alcohol-based fuels and biodiesel in a four-cylinder, four-stroke, water-cooled diesel engine. The CO_2 reduction in alcohol-based fuels and biodiesel is due to the excess oxygen content in the alcohol, while the low carbon in the biodiesel chemical chain results in incomplete combustion. On the contrary, Oni et al. [136] carried out an experimental study in a 1.9 multi-jet diesel engine fueled with neem seed and camelina biodiesel and also observed lower CO_2 emissions.

Furthermore, Tizvir et al. [197] used biodiesel produced from Dunaliella tertiolecta microalgae by a transesterification process to investigate the diesel engine performance and emission characteristics fueled with biodiesel. The CO_2 emissions for pure diesel, B10, and B20 fuels at different loads and speeds are illustrated in Figure 25a–c. The figure establishes that at 600 rpm, 1.47% and 5.44% increases in CO_2, mean emissions exist for B10 and B20 compared to pure diesel, respectively. These two mean values are 1.63% and 7.11% at 900 rpm and 0.82% and 3.73% at 1200 rpm, respectively. These increases are due to the oxygen content of biodiesel fuel and, consequently, the complete combustion process of fuels comprising biodiesel compared to pure diesel fuel. Moreover, the authors indicate that microalgae could be used as a source of biodiesel production to stabilize the CO_2 in the environment; they explained that absorbed CO_2 consumption during microalgae growth balances the CO_2 production from the engine.

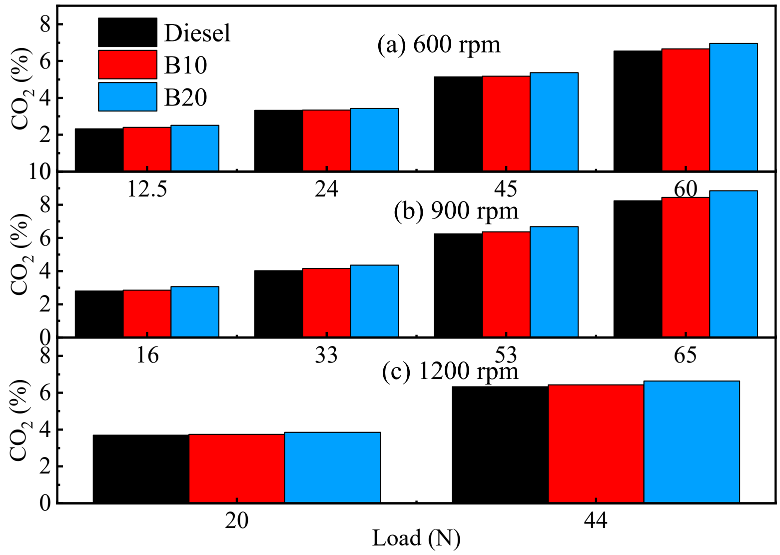

Figure 25. CO_2 emission comparison of biodiesel blends and diesel under different loads [197].

In addition, Valente et al. [235] studied the effect of waste-cooked oil-based biodiesel emissions from a diesel power generator and indicated that CO_2 concentration is decreased with increasing load power. Conversely, the CO_2 emissions increase with biodiesel ratios due to oxygen content in the biodiesel molecular chain, thus leading to more CO oxidized to CO_2. Krishania et al. [236] investigated the effects of microalgae, tire pyrolysis oil, and jatropha biodiesel on engine performance and emissions in a single-cylinder, four-stroke naturally aspirated engine. They observed that the CO_2 emissions of three different biodiesel were 8.06%, 6.21%, and 0.266% higher than diesel due to the oxygen content in biodiesel leading to a better combustion process, thus increased CO_2 emissions.

On the contrary, Ogunkunle et al. [195] analyzed a new type of biodiesel produced from Parinari polyandra in a marine diesel engine. The results of CO_2 emissions indicated that with the addition of biodiesel, the blend showed lower CO_2. This indicated that higher biodiesel blends at higher torques tend to initiate higher heat release to complete fuel combustion. With the addition of biodiesel, the CO_2 emissions were more than CO due to the excess oxygen in biodiesel, making carbon and oxygen react to form CO_2. Another experimental study, by Hoang [237], used preheated straight coconut biodiesel and diesel blends and observed higher CO_2 emissions in blends. They explained that oxygenated fuel or added oxygen in the combustion process provides the combustion with more oxygen aiming to oxidize and convert CO into CO_2. Rajak et al. [231] investigated a renewable and sustainable microalgae biodiesel (MAB) in a single-cylinder, compression ignition engine with different engine loads and compression ratios. The CO_2 emissions with different engine loads and compression ratios are shown in Figure 26a–d. It was observed that CO_2 emissions increased with the compression ratios and decreased with engine loads. The CO_2 emissions are similar to diesel at all loads and compression ratios with the addition of 20%, 40%, and 100% biodiesel and increased with the increased engine loads due to better combustion efficiency. Furthermore, the highest CO_2 emissions for diesel show in a low engine load with a compression ratio of 17.5. For 80% MAB and 20% methanol, the CO_2 emissions increased significantly. This is because MAB and methanol contain an amount of oxygen, resulting in CO being oxidized to CO_2.

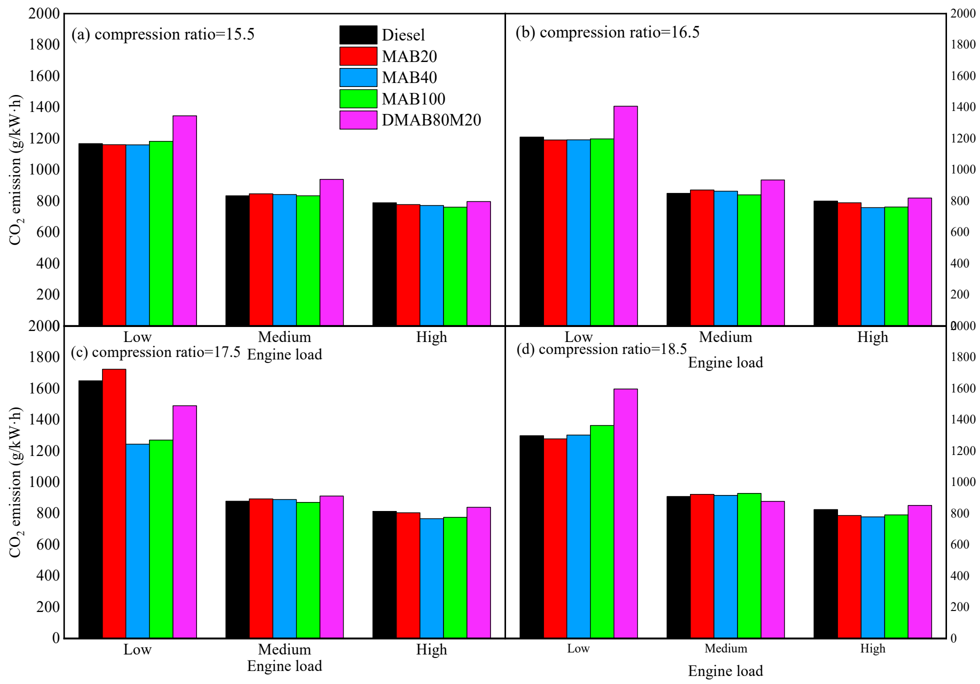

Figure 26. CO_2 emission comparison of biodiesel and diesel under different engine loads [231].

In this section, different studies showed two different trends in CO_2 emissions. Theoretical investigation indicates that CO_2 emissions from diesel engines should increase with the addition of diesel because of improved combustion due to the presence of oxygen in the molecular structure of biodiesel. However, due to the low carbon to hydrogen ratio in some biodiesel, CO emissions are decreased in these biodiesels. The final CO_2 emissions of a CI engine fueled with biodiesel will depend on the relative impact of these two factors, and this can only be studied experimentally.

5.3. Effect on NO_x Emissions

NO_x, consisting of NO and NO_2, as well as PM, CO, and SO_2, are the main harmful constituents in exhaust gases [238]. According to the most reported literature, biodiesel has higher NO_x emissions than fossil diesel. The formation mechanism of NO_x is complex and is affected by several different features such as operating points, combustion chamber design, fuel system design, combustion temperature, oxygen concentration, residence time, and combustion temperature in a diesel engine fueled with biodiesel [239]. Therefore, in this section, the NO_x emissions from different researchers using different types and generations of biodiesel are summarized, and some recommendations for decreasing NO_x emissions from biodiesel are summarized.

Sayyed et al. [217] reviewed four different types of biodiesel NO_x emissions. They concluded that the blend produced 16.56% more NO_x than pure diesel due to the higher oxygen content of biodiesel. Rajendran [240] used three different types of antioxidant additives to reduce NO_x emissions of Annona biodiesel. The increase in biodiesel NO_x emissions is due to the 12–13% excess oxygen content in biodiesel, which provides high in-cylinder temperature for premixed and diffusion combustion conditions compared to diesel. Additionally, the addition of 250 mg concentration of p-phenylenediamine additive to a 20% Annona biodiesel blend resulted in a 25.4% reduction in NO_x emissions compared to diesel. Mourad and Mahmoud et al. [229] indicated that NO_x emissions decreased with increasing EGR rates when sunflower biodiesel was used. High EGR rates reduce the coefficient of excess air and oxygen concentration in the cylinder, thereby reducing the oxygen required to generate NO_x. Biodiesel preheating leads to increased NO_x emissions, as preheating the fuel causes more energy to enter the cylinder, which increases the cylinder temperature and, thus, increases the chance of NO_x emissions.

Baweja et al. [203] used mustard oil biodiesel. The result showed that NO_x emissions increased with load for all blends. With increasing load, fuel accumulation and fuel–air mixture increase near stoichiometric ratio, resulting in increased in-cylinder temperature and, therefore, increased NOx emissions. Sathiyamoorthi et al. [192] observed an increase in NO_x emissions of 3.27%, 10.75%, and 15.21% for B20, B50, and B100, respectively, compared to diesel. The higher NO_x emissions from palmarosa oil biodiesel may be attributed to the higher oxygen content of biodiesel, which leads to complete combustion and higher combustion temperatures, resulting in increased NO_x emissions. How et al. [169] also observed that when coconut biodiesel was used in a high-pressure common rail diesel engine, the NO_x emissions of biodiesel increased at a medium load setting of 0.52 MPa compared to diesel. The results may be related to the inherent oxygen content in biodiesel, as oxygen is required for NO_x formation. Furthermore, the reduction in radiative heat dissipation could also explain the increase in NO_x emissions. Prasada Rao et al. [241] investigated the effect of compression ratio and EGR on various characteristics of diesel engines operating under different load conditions using a 20% palm oil methyl ester blend. NO_x emissions under different engine loads are shown in Figure 27. The results indicate that with the addition of EGR, NO_x emissions are decreased due to dilution of the fuel/air mixture, resulting in incomplete combustion and lower cylinder temperatures. However, at higher compression ratios, this results in emissions such as NO and NO_x due to higher cylinder temperatures and oxygen inherent in Palmyra biodiesel.

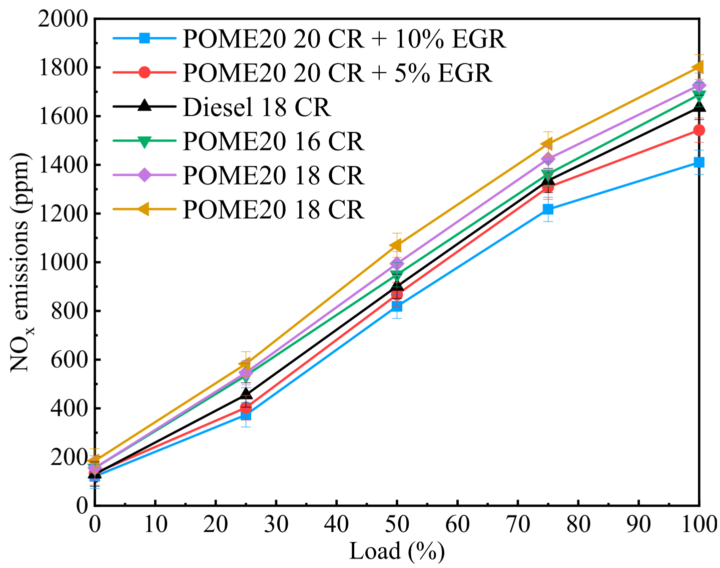

Figure 27. NO_x emissions comparison of POME biodiesel blends and diesel under different loads [241].

Conversely, in an experimental study by Hoang [237], coconut-preheated biodiesel and diesel fuels found that NO_x emissions were decreased. This result indicated that NO_x emissions decreased with the addition of biodiesel. Their study explained that the water content of biodiesel is 432 ppm compared to 200 ppm for diesel. The vaporization and sensible water heat are considered possible reasons resulting in the reduction in local temperature for adiabatic flame and NO_x formation. A similar trend was also observed by Krishania et al. [242] used 20% spirulina, waste cooking, and animal fats blended with biodiesel fuel in an auto-ignition diesel engine with different compression ratios. The results shown in Table 8 indicate that the biodiesel blend reduces NO_x emissions compared to diesel due to lower combustion temperature.

Moreover, Tizvir et al. [197] carried out an experimental study that used Dunaliella tertiolecta microalgae biodiesel in a diesel engine to investigate biodiesel engine performance and emission characteristics. A reduction in NO_x emissions was also observed. They explained that NO_x production is related to combustion interval; the shorter the combustion interval, the less NO_x produced. Higher CN of the test biodiesel leads to a shorter combustion interval; thus, less NO_x is produced. Mubarak et al. [190] investigated biodiesel produced from Salvinia molesta oil and observed the same trend. They explained this phenomenon due to the presence of more saturated fatty acids in biodiesel, and the lower heating value of biodiesel causes lower peak temperatures, thus decreasing NO_x emissions.

Table 8. Comparison of NO_x emissions at full load and different CRs [242].

CR	Diesel (ppm)	Generation	Biodiesel (ppm)	% (Lower)
16.5	2998.2	First	2553.8 for soybean	14.82
		Second	2974.8 for Jatropha	0.78
		Third	2663 for spirulina	11.18
17.5	3148.8	First	2668.7 for soybean	15.24
		Second	1900.8 for Jatropha	39.63
		Third	2668.5 for spirulina	15.25
18.5	3388.8	First	2770.3 for soybean	18.25
		Second	1941.6 for Jatropha	42.7
		Third	2770.4 for spirulina	18.24

However, Teoh et al. [172] observed increased NO_x emissions in a common-rail diesel engine fueled with Moringa oleifera biodiesel (MOB) and diesel blends. Figure 28 shows the results of NO_x emissions at different engine speeds and different ratios of biodiesel. The highest increase in NO_x emissions of all MOB blends compared to the baseline diesel was observed at 2000 rpm, with an increase of 19.55%. This is due to the 10.8% oxygen content present in biodiesel. Moreover, an experimental study by Can et al. [243] also observed higher NO_x emissions in soybean biodiesel and diesel blends due to the oxygen content of biodiesel that accelerates the oxidation reaction during the mixed-controlled diffusion combustion stage. Additionally, delayed fuel injection timing can significantly decrease NO_x emissions compared to lower EGR rates and ethanol additions.

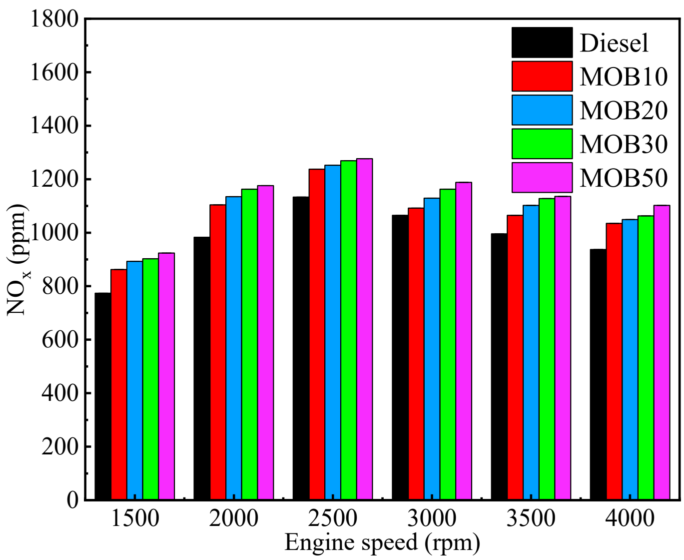

Figure 28. NO_x emissions comparison of MOB biodiesel blends and diesel at different engine speeds [172].

Furthermore, an experimental study by Metin et al. [244] used biodiesel produced from waste chicken fat oil. They also observed a 5% increase in NO_x emissions from B10 and introduced higher NO_x emissions despite having a higher CN than diesel. Additionally, oxygenated fuels improve fuel oxidation during combustion, resulting in localized temperature increases. Therefore, NO_x emissions increased due to thermal formation mechanisms.

Zhang et al. [70] used rapeseed biodiesel in a marine diesel engine. They also observed higher NO_x emissions from biodiesel and tried adding 2%, 4%, and 6% water to biodiesel to decrease the NO_x emissions. The result indicated that with the addition of water, the cylinder temperature of biodiesel decreased due to the evaporation of water; thus, lower NO_x emissions were observed in the blends. Badawy et al. [245] investigated the engine performance and emissions of a diesel engine fueled with Jatropha biodiesel and also observed that NO_x emissions increased compared to diesel. They explained that the oxygen content of biodiesel increased the cylinder temperature and, thus, increased the NO_x formation. In order to decrease the higher NO_x emissions of biodiesel, the authors mixed in carbon nanoparticles to decrease the NO_x emissions due to the carbon nanotubes' improved convective heat transfer, which reduced the in-cylinder temperature. Uyumaz [246] observed that with the addition of 30% biodiesel, the NO_x emissions increased by about 22.1% compared to diesel due to higher density, viscosity, and O_2 content in biodiesel structure. The same results were also found by Sathiyamoorthi et al. [192] whereby higher oxygen content of biodiesel leads to higher combustion temperature, thus increasing the NO_x emissions.

This section summarizes the different studies and reasons for the increase or decrease in NO_x emissions fueled with biodiesel and biodiesel blends. In most cases, biodiesel increases NO_x emissions for the following reasons: (1) Higher oxygen content in biodiesel leads to increased cylinder temperature, which increases combustion efficiency and leads to thermal mechanism formation of NO_x. (2) The higher viscosity of biodiesel results in poorer fuel evaporation and atomization; therefore, more oil-rich regions in the cylinder increase the cylinder temperature, resulting in higher NO_x formation.

Conversely, some researchers have also observed a reduction in NO_x emissions due to the addition of biodiesel. According to different studies, the reason for this phenomenon can be explained by the lower cylinder temperature of biodiesel fuel due to the lower calorific value of biodiesel, thereby reducing NO_x emissions. In conclusion, the increase or decrease in NO_x emissions fueled with biodiesel mainly depends on the following factors: the structure of the test biodiesel, the working conditions of biodiesel, and the air–fuel blend rates in the cylinder.

5.4. Effect on HC Emissions

Engine unburned hydrocarbon (UHC) emissions depend on fuel combustion efficiency and combustion process [247,248]. According to a report, there are six mechanisms identified as the main cause of HC emissions from diesel engines [237]: (1) crevices, (2) oil layers, (3) deposits (fuel trapped or retained in the injector hole at the end of the injection process), (4) fuel and mixture (fuel–air mixture so rich or so lean that it cannot be ignited), (5) cylinder wall flame quenching, and (6) leakage of the exhaust valve. In addition, the chemical structure and structural energy of biodiesel, as well as incomplete combustion, are believed to be responsible for UHC emissions. Some of the important studies reported in the literature have been described here by different researchers on a diesel engine fueled with biodiesel.

Simsek [233] observed the HC emissions of B10, B20, B30, B50, B75, and B100 fuel blends decreased by an average 1.29%, 4.43%, 8.23%, 11%, 14.42%, and 17.49%, respectively, compared to diesel. Due to biodiesel oxygen content, increased EGT led to the UHC in the chamber oxidizing towards the exhaust outlet, thus reducing the HC emissions. Ogunkunle et al. [195] used biodiesel produced from Parinari polyandra in a marine diesel engine and observed the HC decreased by 7.8%, 11.0%, and 13.8% while using B10, B20, and B30, respectively. They explained that HC emissions are a function of oxygen and the temperature of the combustion environment. Higher oxygen and temperature ensure complete combustion of the fuel constituents, thus reducing HC emissions. Nguyen et al. [180] conducted experimental studies on engine performance and emissions using a common rail diesel engine fueled with fish oil biodiesel and diesel blends. The results of HC emissions with the addition of different biodiesel are shown in Figure 29a,b. The results indicate that the blends containing a higher ratio of biodiesel will have lower HC emissions than diesel. The presence of oxygen content in biodiesel and lower viscosity leads to a more complete and cleaner combustion, thus causing lower HC emissions.

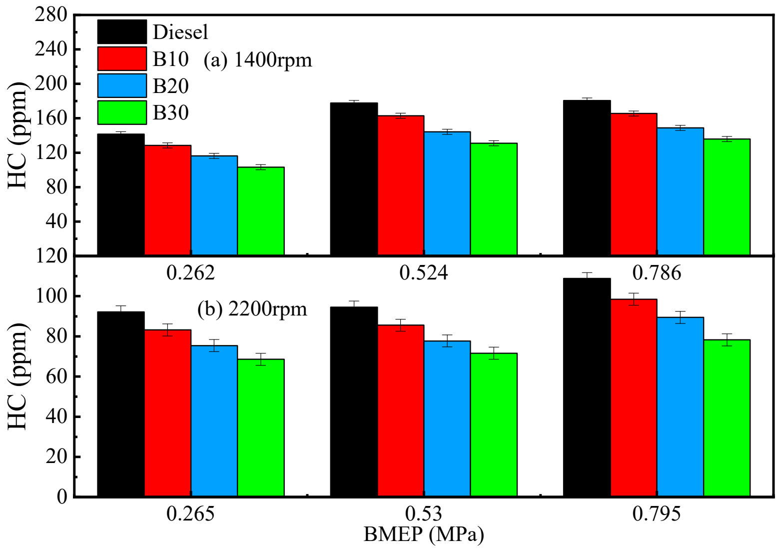

Figure 29. HC emission comparison of biodiesel blends and diesel under different BEMPs [180]. (**a**) 1400 rpm; (**b**) 2200 rpm.

Gharehghani et al. [226] indicated that with the addition of biodiesel ratios, the HC emissions of the blends were decreased by about 11.6%, 39.8%, 61.5%, and 70% on average than diesel throughout the engine loads. The 9.3% oxygen and higher CN result in incomplete combustion, and higher CN leads to shorter ignition delay, decreasing the fuel-rich regions through the combustion process, and thus decreasing HC emissions. Kanimozhi et al. [249] investigated the effects of biodiesel and oxyhydrogen addition to biodiesel on HC and other emissions. They observed that HC emissions decrease with the addition of oxyhydrogen and biodiesel. They explained that high HOO content in the fuel increased the oxidation process and lowered ignition energy, thus reducing HC emissions. In a comparative review of performance and emission characteristics of diesel engines using the eucalyptus-biodiesel blend by Ellappan et al. [204], biodiesel significantly lowered HC emissions as with diesel in the engine. The reduction may be due to the excess O_2 available in the biodiesel, which improved the evaporation rate and allowed better mixing, enhancing the combustion, and decreasing the HC emissions.

In addition, Shareef et al. [191] conducted an experimental study on the engine performance emission characteristics of dairy scum biodiesel in diesel engines with variable injection timing. The emissions of HC shown in Figure 30 indicate that with the addition of biodiesel, the HC emissions decreased due to higher oxygen content in diary scum, and high CN improved combustion and led to complete combustion. Rajesh et al. [250] observed that the HC emissions of biodiesel blends B20, B40, B60, and B100 showed a significant reduction of 11.2%, 16.9%, 25.4%, and 36.6%, respectively, compared to diesel. The higher HC emissions for diesel fuel can be explained by the rich carbon nature of fuel leading to limited time for combustion. Reduction in HC intensity of biodiesel due to oxygen content of biodiesel, higher CN presence of short-chain saturated fatty acids, advanced fuel injection, and combustion timing are the factors contributing to lower HC emissions.

In addition, Arunkumar et al. [185] observed an 8.9% reduction in HC emissions from the B20 blend. They explained that eminent CN leads to better combustion due to its oxygenated nature, thus reducing HC emissions. Chandra Sekhar et al. [212] used biodiesel produced from Pithecellobium dulce methyl esters (PDSOME) and studied the engine performance and emissions of biodiesel blends. The percentage of reduction in the HC emissions was observed to be 17.64%, 23.52%, 26.47%, 29.41%, and 33.82%, respectively, for PDSOME20, PDSOME40, PDSOME60, PDSOME80, and neat PDSOME compared to diesel fuel at full load. They explained that 9.41% oxygen substance in PDSOME leads to greater flame speed and post-flame oxidation throughout the air–fuel interaction process. Viswanathan et al. [196] pointed out that the HC emissions of diesel at full load were 118 ppm, while 60 ppm was with the 50% ratio of biodiesel. Lower HC emissions due to high in-cylinder temperature lead to more HC oxidization. Ge et al. [149] observed that the HC emissions of B100, B10, B30, and B50 were 402 ppm, 470 ppm, 466 ppm, and 450 ppm, respectively, at 1800 rpm. The reduction in HC emissions with the increase in biodiesel ratio due to oxygen present in biodiesel promotes more combustion in the blends.

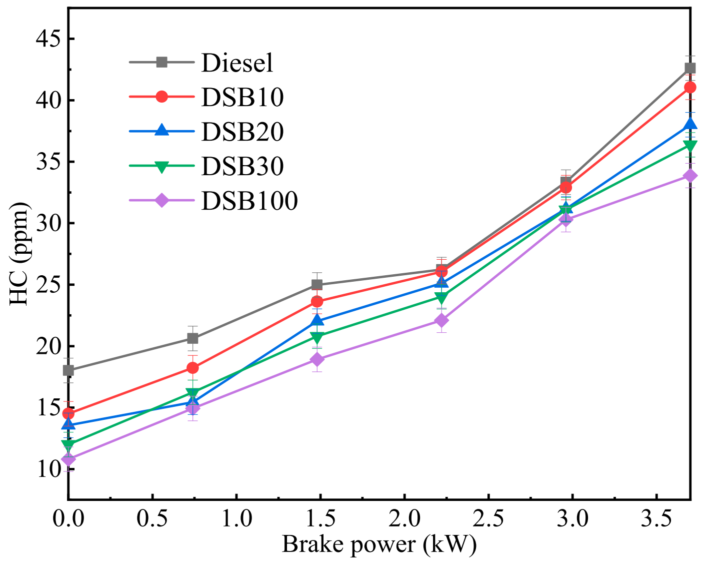

Figure 30. HC emission comparison of biodiesel blends and diesel under different brake powers [191].

On the other hand, a study by Prasada Rao et al. [241] investigated the combined effects of CRs and EGR rates in diesel engines fueled with palm biodiesel blend (POME). The results shown in Figure 31 indicate that with the increase in EGR rates, the increase in HC emissions is mainly due to the decrease in combustion efficiency in the combustion chamber after applying EGR. In addition, higher HC emissions for higher CRs due to better fuel combustion will occur because of enhanced swirl motion in the engine chamber.

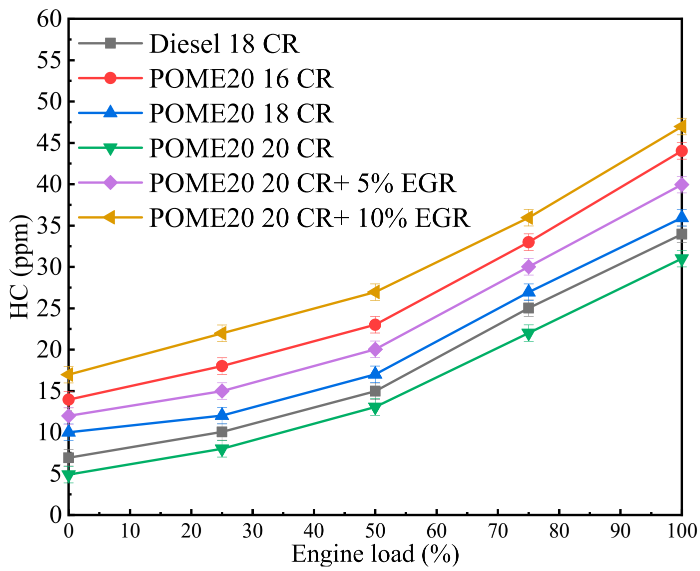

Figure 31. HC emission comparison of POME biodiesel and diesel under different loads [241].

Moreover, Baweja et al. [203] used biodiesel produced from mustard oil methyl esters and also observed higher HC emissions than diesel. They indicated that more fuel injected into the cylinder leads to a poor fuel mixture, thus increasing HC emissions. Ramesh et al. [251] used biodiesel produced from Karanja and observed higher HC emissions with biodiesel blends than with diesel. They explained that poor atomization and vaporization of Karanja biodiesel led to incomplete combustion and incomplete oxidation; thus, HC emissions increased. Wei et al. [252] used n-pentanol addition on biodiesel and observed higher HC emissions compared to diesel. They explained that the smaller CN of n-pentanol results in a longer ignition delay; thus, more time for vaporization leads to a broader lean outer flame zone, which results in higher HC emissions with the addition of n-pentanol.

In a summary of HC emissions fueled with different biodiesel and diesel blends, most researchers have observed an average of 33.89% HC reduction with different types of biodiesels. This reduction can be explained due to 11–13% average oxygen content and higher CN of biodiesel, which leads to shorter ignition delay and higher combustion temperature. The oxygen content of biodiesel leads to more HC oxidization, thus reducing HC emissions. On the other hand, in some literature, biodiesel has poor atomization and evaporation due to its higher density, viscosity, and lower calorific value, and these factors increased the HC emissions of biodiesel.

5.5. Effect on Smoke Emissions

Smoke is an incomplete product of fuel during combustion. Many previous studies have shown that smoke may form due to fuel-rich areas and oxygen levels in the fuel and intake air [253,254]. In this section, the smoke emissions from the use of diesel engine alternative fuel biodiesel are summarized.

Hazar et al. [255] observed fewer smoke emissions in diesel engines for biodiesel produced from safflower methyl esters. They explained that the oxygen content in biodiesel increased the end of combustion temperature, resulting in better combustion and decreased smoke formation under all load conditions. Similar trends were also observed by Uyumaz [256] using mustard methyl esters. According to their research, at full load, the smoke emissions of diesel, B10, B20, and B30 were determined to be 3.99 m^{-1}, 2.67 m^{-1}, 1.95 m^{-1}, and 1.57 m^{-1}, respectively. The main reason is that the oxidation is more complete due to the higher oxygen content of biodiesel. Shrivastava et al. [230] investigated the effect of fuel injection pressure on the performance and emission characteristics of a diesel engine fueled with biodiesel produced from Roselle oil. Among all tested fuels, diesel fuel has higher smoke emissions than the other tested fuels because biodiesel has higher oxygen content than diesel, reflecting complete combustion of biodiesel in the richer regions of the cylinder, reducing smoke formation. Baweja et al. [203] used mustard oil methyl esters (MOME) to study diesel engine performance and emission characteristics. As the oxygen in biodiesel improves the combustion process, smoke opacity decreases as the ratio of MOME in diesel increases.

Can et al. [243] investigated EGR rates, injection delay, and ethanol addition for combustion, performance, and emissions of a diesel engine fueled with canola biodiesel and diesel blends. Compared to diesel, the B10 biodiesel blend produces lower smoke emissions due to the inherent oxygen and low aromatic and sulfur content of biodiesel. Another study by Dhamodaran et al. [183] used rice bran, neem, and cottonseed oil biodiesel to investigate the engine performance and emission characteristics of a diesel engine fueled with biodiesel. They also observed higher smoke opacity for diesel compared to biodiesel at all loads due to reduced local oxygen levels resulting in the poor fuel–air mixture and, thus increasing smoke emissions. In addition, an experimental study by How et al. [169] used coconut biodiesel in a common-rail diesel engine. The smoke emissions at different brake power shown in Figure 32 indicate that smoke opacity is decreased with the addition of biodiesel. Specifically, the smoke opacity decreased by 5.4%, 15.1%, 20%, and 52.4% for B10, B20, B30, and B50, respectively, compared to diesel fuel at full load. The reduction in smoke opacity is mainly due to high fuel-borne oxygen and lower carbon content in biodiesel, which results in complete combustion and restricts the formation of smoke. Keskin et al. [148] observed a similar trend by using biodiesel produced from turkey-rendered fat biodiesel. They explained that the higher oxygen content and lower C/H ratio of biodiesel led to the reduction. In addition, with increasing engine load, the smoke opacity of biodiesel was significantly decreased due to high load, and higher cylinder temperature reduces the density and viscosity of biodiesel. Thus, better atomization and evaporation lead to more smoke being oxidized.

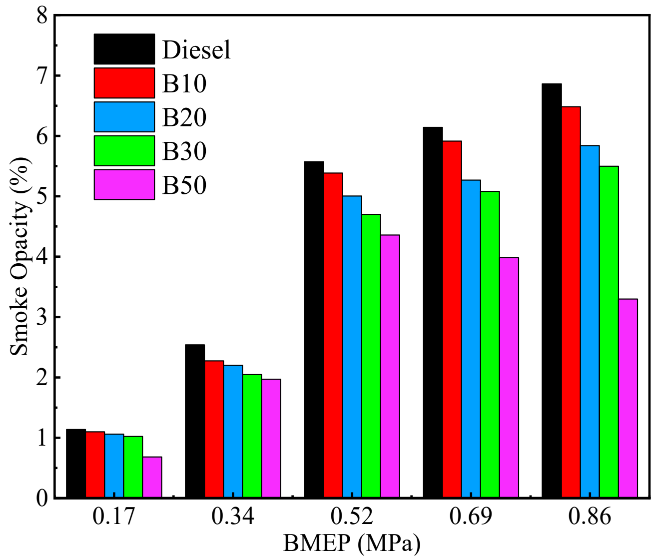

Figure 32. Smoke emission comparison of biodiesel blends and diesel under different BMEPs [169].

Elumalai et al. [257] investigated the effects of injection timing and N-butanol antioxidants on smoke emissions. Figure 33a–c indicates the smoke emissions of pure Mahua biodiesel and the biodiesel added N-butanol antioxidant. The smoke opacity with 20% biodiesel was 2.5% lower than diesel at 21° BTDC. Furthermore, with the increase in injection timing and N-butanol antioxidant, the smoke opacity decreased significantly due to the increased injection timing leading to a better air–fuel mixture, thus decreasing smoke emissions. In addition, Ellappan et al. [204] reviewed the combustion and emission characteristics of diesel engines fueled with eucalyptus-biodiesel. They also observed that smoke emissions decreased with the addition of biodiesel. They indicated that the nearly 13% oxygen content in biodiesel structure results in better combustion in the cylinder; thus, smoke emissions were decreased by about 35.7% compared to diesel.

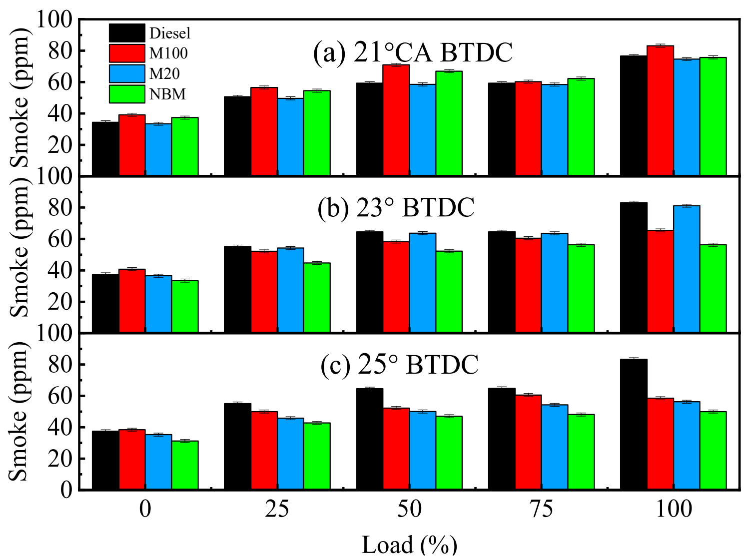

Figure 33. Smoke emission of NBM biodiesel blends and diesel under different loads [257].

Rajak et al. [231] investigated the effects of different CRs and loads on the engine performance and emission characteristics of a single-cylinder diesel engine. The smoke emission results for different engine loads and different CRs showed that the smoke emissions increased at low loads due to the poor atomization caused by the higher viscosity of biodiesel, thus increasing smoke emissions. Prasada Rao et al. [241] also observed similar results using palmyra biodiesel blends. The decreased smoke opacity is the higher combustion chamber temperature; therefore, the improved combustion process results in more smoke being oxidized. Teoh et al. [258] used pyrolysis oil-based biodiesel in a common-rail direct injection diesel engine to investigate two different blends on engine performance and emission characteristics. Figure 34 shows interesting findings on smoke emissions from these two different fuels. The results indicate that the smoke emissions of the biodiesel blend are significantly higher than that of diesel at 1000 rpm engine speed. The incomplete combustion caused by the higher fuel–air equivalence ratio and lower calorific value of biodiesel is the main reason for the higher smoke emissions of biodiesel. With increasing engine speed, smoke opacity is significantly decreased due to better combustion and higher oxygen content of biodiesel.

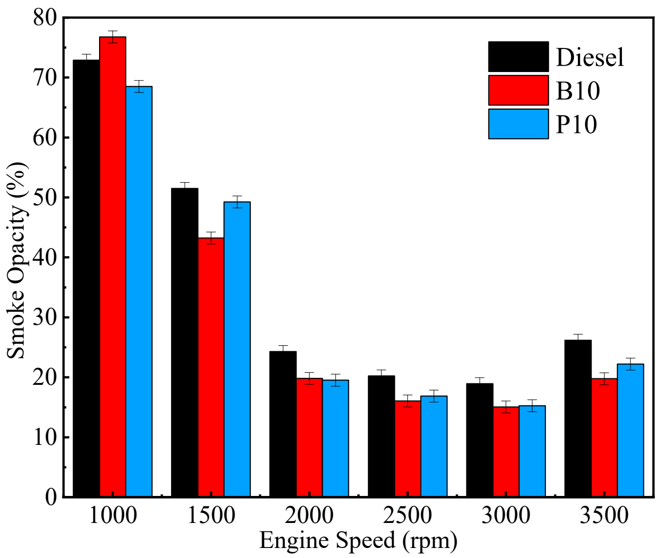

Figure 34. Smoke emission comparison of biodiesel blends and diesel at different engine speeds [258].

On the contrary, Arunkumar et al. [185] used castor biodiesel to investigate diesel engine performance and emission characteristics. The smoke emissions for different castor biodiesel addition ratios in Figure 35 indicate lower smoke generation for B20 at loading conditions due to better fuel–air mixing. However, as the ratio of biodiesel increases, due to the higher viscosity of castor oil, a localized poor fuel–air forms in the cylinder, producing more smoke emissions than diesel. A similar trend was also observed by Banapurmath et al. [259] using Honge, Jatropha, and sesame oil methyl esters. They indicated that the heavier biodiesel molecular structure and higher viscosity, poor atomization, and the evaporation of biodiesel lead to higher smoke emissions.

In a summary of different biodiesel smoke emissions from diesel engines, the researchers observed two opposite trends. The main reasons for reducing biodiesel smoke emissions are: (1) Since biodiesel has 11–13% oxygen content, higher temperatures result in complete combustion and more fuel being oxidized; therefore, less fuel-rich areas reduce smoke formation. (2) Due to the lower heating value and higher CN of biodiesel, the biodiesel combustion process is shorter than diesel, resulting in decreased smoke emissions.

On the other hand, some researchers observed nearly 26% of smoke emissions increased when using specific biodiesel fuels. The main reasons for this phenomenon are the higher viscosity and heavier molecular structure of biodiesel, which results in poorer combustion and leads to excess smoke formation.

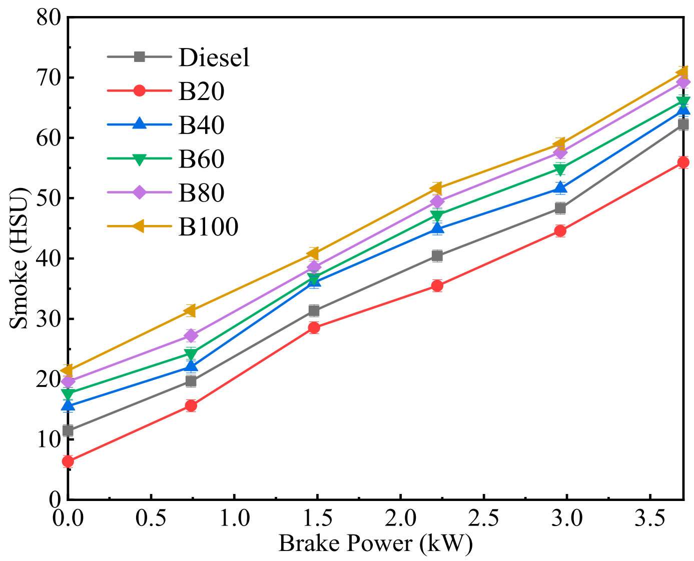

Figure 35. Smoke emission comparison of castor biodiesel blends and diesel under different brake powers [185].

5.6. Summary of Emission Analysis

At the end of this section, it can be found that the structure molecules in biodiesel play a crucial role in the emissions of biodiesel in diesel engines. Specifically, the formation of different pollutants mainly depends on the oxygen content, viscosity, and density of biodiesel. When using biodiesel and biodiesel blend, biodiesel's average 10% oxygen content enhances the combustion process compared to diesel. As a result, most studies observed a decreased average of 30% CO, 50% HC, and 70% smoke emissions. However, biodiesel has an average of 13% and 26% higher NO_x and CO_2 emissions, respectively, than diesel due to its higher combustion temperature and 11–13% additional oxygen content.

As for the effect of engine operating conditions on biodiesel and diesel blends emissions, the results showed that as the engine load and brake power increased, the CO, HC, and smoke emissions of incomplete products and by-products from biodiesel will be decreased. However, due to the higher cylinder temperature of biodiesel, more NO_x was observed for each operating condition. Some researchers have indicated that suitable EGR rates, preheating technologies, and suitable additives can improve NO_x emissions from biodiesel.

6. Conclusions

Due to the increasing energy demand in the world and the shortage of resources, many countries struggle to find renewable and green energy [260–270]. Biodiesel, as an alternative fuel due to its combined advantages, such as renewability, biodegradability, non-toxic properties, reduced cost of imported oil, and overall being less pollutant, has attracted the interest of many researchers. According to the feedstocks of different biodiesels, it was divided into four generations. Many researchers reported that biodiesel has a higher density, viscosity, and cetane number, while having a lower heating value compared with diesel. This may influence the engine performance and emissions of different generations of biodiesel. Therefore, this paper looked at the engine performance and emission characteristics of different generations of biodiesel and diesel blend in diesel engines. The main conclusions are as follows:

(1) The feedstocks and production technologies of different generations of biodiesel can affect the properties of different biodiesels. Specifically, according to different researchers, different biodiesel production technologies mainly affect the density, viscosity, and cetane number of the same biodiesel. Therefore, in the production process of biodiesel, the selection of appropriate production technology is of great significance to improve the properties of biodiesel and the use of biodiesel in diesel engines.

(2) The 11–13% oxygen content in the biodiesel structure plays an important role in engine performance and emissions. Specifically, due to the additional oxygen content and higher cetane number, biodiesel has a better BTE compared with diesel, theoretically. However, due to the average 3.13% and 89.56% respective higher viscosity and density, while having a 7.96% lower heating value compared with biodiesel, the BTE of biodiesel was lower than 2–5% on average in most literature reported by different researchers. This decrease in BTE can be significantly improved by using Metal-based and oxygenated additives such as cerium dioxide and n-butanol.

(3) Because of the lower calorific value, higher density, and viscosity of biodiesel compared with diesel, which results in poor atomization and evaporation of the fuel in the cylinder, the BSFC of biodiesel is approximately 13% higher than that of diesel. Additionally, a nearly 10% higher average EGT was observed in biodiesel due to higher BSFC resulting in more fuel energy in the combustion chamber. Moreover, with the increase in engine load, due to the larger mass quantity of biodiesel injected into the cylinder, the BSFC and EGT difference decreased compared with diesel. Therefore, preheated biodiesel is recommended to decrease BSFC at low load conditions.

(4) The 11–13% oxygen content in the biodiesel structure plays an important role in emission characteristics. Specifically, due to the higher oxygen content in biodiesel than in diesel and more fuel injection in the cylinder, the oxygen in the biodiesel structure reduces nearly 30% CO emissions, 50% HC emissions, and 70% smoke emissions. On the other hand, higher cylinder temperature and EGT were observed because the higher oxygen content of biodiesel improved combustion efficiency, and the NO_x emissions of biodiesel were 12–14% higher than that of diesel. Since the CO in biodiesel is oxidized to CO_2 by the additional oxygen content, the CO emissions of biodiesel are also 11–13% higher than that of diesel.

In general, biodiesel–diesel blended fuels can significantly reduce the emissions of harmful pollutants other than NO_x and CO_2, with only minor effects on engine performance. Many researchers suggest adding after-treatment technologies, such as exhaust gas recirculation, to reduce the harmful exhaust gas from biodiesel, or adding some oxygenated fuels, such as methanol and ethanol to reduce harmful emissions from biodiesel. With the increasingly serious energy crisis and environmental deterioration, a certain ratio of biodiesel as fuel, instead of fossil diesel, combined with advanced after-treatment technology is the main trend of future diesel engine development.

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