Review

A Comprehensive Review of the Application Characteristics of Biodiesel Blends in Diesel Engines

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Abstract: Since the advent of biodiesel as a renewable alternative fuel, it has attracted wide attention from researchers. The raw materials of biodiesel generally produced by transesterification of animal fats, plants, algae or even waste cooking oil, which makes full use of natural resources and alleviates increasingly problematic oil shortages and environmental pollution. Biodiesel can be directly applied to vehicle engines without any modification and will both improve the combustion quality of the engine and reduce the harmful emissions from the engine. This study mainly summarizes the influence of biodiesel applications on diesel engines, including the impact on engine performance, combustion characteristics, emission characteristics, vibration, noise characteristics, and compatibility. In particular, unregulated emissions such as volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs), which are rarely mentioned in other review articles, are also discussed in this study.

Keywords: biodiesel; diesel engine; engine performance; combustion characteristics; emission characteristics; noise and vibration; compatibility

1. Introduction

As the limits of oil reserves are becoming more obvious and the peak of global oil production will soon pass, more and more people believe that petroleum resources can be exhausted [1]. As early as 2010, half of global oil production was used in the transportation sector. CO₂ released by the transportation sector accounts for more than 20% of the global emissions, of which the emissions from road vehicles unexpectedly contribute more than 70% [2]. These are important factors that have led to tight oil reserves and the growing greenhouse effect. Biodiesel has gradually played a role as a powerful substitute for petroleum fuel, resulting in increased attention and related research. Biodiesel is usually used in vehicle engines in neat form or in a blended form without any modification to the engine [3,4]. Unlike conventional fossil diesel, the feedstocks of biodiesel are not unique. Under current conditions, raw vegetable oil (palm oil, corn oil, etc.), animal fat (tallow, lard, etc.), non-edible oil (algae oil, jatropha oil, etc.) and waste vegetable oil can all be used as raw materials for biodiesel [5]. Biodiesel crude oil with fatty acid glycerides as the main components needs to undergo transesterification reactions with alcohols using acidic or alkaline catalysts to generate monoalkyl esters, which are the main ingredients of biodiesel [6]. The viscosity of the biodiesel after transesterification will be greatly reduced, which facilitates its direct use as fuel in the engine [7].

Biodiesel generally has higher oxygen content, higher cetane number, higher viscosity, lower aromatic content, and almost no sulfur [8]. These special properties will affect engine performance, combustion and emission characteristics. In addition, biodiesel is non-toxic, harmless and also helps reduce carbon emissions. The carbon emissions of biodiesel produced from some crops can be partially reused by plants, which will reduce greenhouse gases [9]. It is no secret that biodiesel has a better

emission reduction effect than other fuels. Many studies have shown improvement of regulated emissions such as carbon monoxide (CO), hydrocarbon (HC), nitrogen oxide (NO_x) and particulate matter (PM) from diesel engines fueled with biodiesel. In most cases (except for NO_x), the emissions of several other gases will be reduced, even including some unregulated gases, such as volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). There are also full-cycle risk assessments of biodiesel that show few amounts of harmful gases are released before biodiesel feedstock is grown and produced [10,11]. Most components of VOCs and PAHs have a certain toxicity and may cause harm to the natural environment and organisms, but studies focused on these exhaust products produced by engines fueled with biodiesel are still limited [12,13]. The review of the impact of biodiesel on VOCs and PAHs emissions needs to be further summarized and supplemented.

The participation of biodiesel in combustion will both directly influence the engine operating performance and indirectly affect the noise and vibration of the engine, which is an important factor related to vehicle comfort [14]. Noise refers to the sound produced by irregular vibrations, which is another major health threat after air pollution. It may have adverse effects on various human daily behaviors, and even causes physical diseases such as neurological and cardiovascular disease [15]. Therefore, competitive alternative fuels should meet both exhaust and noise pollution requirements [16]. Many researchers investigated the noise and vibration of engines fueled with different biodiesels, but related retrospective work needs to be further improved.

Although the properties of biodiesel are similar to diesel, the compatibility between the fuel and fuel system will directly affect the normal operation and life of the engine. The lubricity of fuel is essential to fuel injectors and oil pumps, and it helps reduce the friction loss of the fuel system under high temperature, high pressure and high speed conditions [17]. In fuel injectors, good lubricity of the fuel ensures smooth movement of plungers, tappets, and needle valves. Although most researchers [18–20] have reported that the lubricity of biodiesel is excellent, it also has problems such as oxidative degradation and corrosion. The degradation of biodiesel may generate oxidation products such as acids, alcohols, aldehydes, and polymers, which will block the fine pores of filters and nozzles and can also challenge the corrosion resistance of fuel supply system materials. However, this also reflects the better degradability of biodiesel. At this stage, the specific impact of biodiesel compatibility on vehicle engines is mostly based on laboratory tests, and actual long-term road tests are still scarce.

This study refers to more than one hundred papers during the past ten years and summarizes their direct impacts, including engine performance, combustion and emission characteristics containing the analysis of VOCs and PAHs, and indirect effects including vibration and noise, compatibility along with the causes of these observations. The purpose of this work is to provide an exhaustive overview of the impact of biodiesel as an alternative fuel in diesel engines, highlight the advantages and disadvantages of biodiesel compared to traditional fossil diesel in application, which may provide a more complete picture of biodiesel as an alternative fuel.

2. Physicochemical Properties of Biodiesel

Biodiesel is slightly different when compared to traditional fossil diesel in composition and physicochemical properties, which will result in different conclusions on engine performance and combustion and emissions characteristics. Fossil diesel is mainly composed of straight-chain hydrocarbons with carbon number between 12 and 24, while biodiesel is mainly composed of intricate esters [21]. The composition of esters in different biodiesels is different, but it can be concluded that they have similar fuel properties as that of diesel. Different fatty ester properties in biodiesel will determine the properties of the fuel, thereby affecting the physicochemical properties of the fuel such as density, viscosity, and cetane number [22].

From the information mentioned in Table 1, most biodiesel has a higher density than fossil diesel, which means that higher quality fuel will be injected during the injection process. This is due to the higher degree of unsaturation of biodiesel, and its density increases with the number of double bonds [23]. The viscosity of vegetable oil is very high. Secondly, although the viscosity of biodiesel

after transesterification is greatly reduced, it is still higher than that of fossil diesel. It may affect the fuel injection accuracy and atomization effect. Regarding the calorific value, except for the higher value of Pongamia biodiesel shown in Table 1, the calorific value of most biodiesel is slightly lower than that of diesel. Both the oxygen content and the length of the ester chain will affect its energy density, which explains why the properties of biodiesel from different raw materials are different. The high cetane number is a major advantage of biodiesel, which directly affects the ignition performance of the fuel, especially under cold start conditions. The cetane number of biodiesel is related to the chain length and the number of branches of the ester [23]. Meanwhile, some scholars believe that different conversion scores in the transesterification process cause the difference between different types of biodiesel [24]. In addition, the oxygen content in biodiesel is generally higher, which may improve some performance of the engine.

Table 1. Comparison of physicochemical characteristics of biodiesel and fossil diesel (biodiesel/fossil diesel).

Biodiesel Types	Trends Compared to Conventional Diesel							Ref.
	Density (kg/m ³)	Kinematic Viscosity at 40 °C (mm ² /s)	Calorific Value (MJ/kg)	Flash Point (°C)	Cetane Number	Oxidation Stability (h) or (%)	Acid Value (mg KOH/g)	
Argemone mexicana biodiesel	870/830 (15 °C)	4.38/2.8	37.5/44.5	193/65.5				[25]
Moringa oleifera biodiesel	866.1/834.3 (40 °C)	4.03/3.63	39.9/45.21	189.0/71.5	54.3/52.4	10.8/0.1 h	0.24/-	[26]
Karanja biodiesel	881/831 (40 °C)	4.42/2.78	37.98/43.79		50.8/51.2			[27]
Jatropha oil biodiesel	865/841	5.2/4.5	34.5/42	175/50	51/49			[28]
Calophyllum inophyllum biodiesel	871.8/834.7 (40 °C)	4.9762/3.4926	39.17/45.6	92.6/68.5	56/48	2.53/35 h	0.41/0.072	[29]
Water hyacinth biodiesel	887/838 (15 °C)	3.96/2.76	36.9/42.7	212/68	52.5/48		0.42/-	[30]
Pongamia biodiesel	912/824 (15 °C)	10.29/2.3	912/824	175/53		2.3~11.6/- h	>1.53	[31]
Citrullus colocynthis L. biodiesel	886/830 (15 °C)	3.45/2.43	37.64/42.82	134/69	66.89/60.82		0.27/-	[32]
Fish oil biodiesel	885/850	4.741/3.05	40.057/42.8	114/56	52.6/52			[33]
Rice bran oil biodiesel	887/843	4.98/3.58	38.725/43.2		55.7/48	11.25%/0		[34]
Neem oil biodiesel	871/843	4.63/3.58	41/43.2		53.5/48	11%/0		[34]
Cottonseed oil biodiesel	864/843	4.14/3.58	36.8/43.2		52/48	~10%/0		[34]
Linseed oil biodiesel	924/842 (15 °C)	16.23/2.44	39.750/45.343	108/47	35/>50			[35]
Fleshing oil biodiesel	876.7/829 (15 °C)	4.7/3	37.3/43.2	168/63	58.8/56.8			[36]
Chicken fat biodiesel	889.7/829 (15 °C)	5.3/3	37.1/43.2	169/63	52.3/56.8			[36]
Canola-safflower biodiesel	884.3/831.7 (15 °C)	4.35/2.58	40.10/45.98	168/63				[37]
Rapeseed oil biodiesel	874/850	4.8/2.6	37.6/42	>140/68	54/51	10.2/- h		[38]

3. Engine Performance

3.1. Brake Specific Fuel Consumption

Brake specific fuel consumption (BSFC) represents the ratio of engine fuel consumption rate and brake power. BSFC is usually affected by some factors such as fuel calorific value, viscosity, density and volume fuel injection system [39]. BSFC is an important indicator to evaluate the fuel economy of the engine. Under the same operating conditions, a lower BSFC indicates better fuel economy. BSFC can be generally obtained by the formula [40]:

$$\text{BSFC} = \frac{\dot{m}_f}{2\pi NT_e} \quad (1)$$

Here, $\dot{m}_f$ is the fuel consumption flow rate, N is the operating speed, and T_e is the brake torque.

Most studies [4,7,8,25–27] have found that biodiesel and its blends have a larger BSFC compared to conventional diesel. Teoh et al. found that *Moringa oleifera* biodiesel–diesel blends have lower BSFC values than diesel at all speeds [26]. How et al. also obtained similar results [7]. They found that when the brake mean effective pressure (BMEP) is 0.34 MPa, the BSFC values of coconut biodiesel–diesel blends B10 (blends containing 10 vol% biodiesel), B20, B30, B50 are 0.8%, 2.1%, 3.5%, and 7% higher than diesel, respectively. The researchers also found that BSFC increases with the proportion of biodiesel in the fuel [7,28,32,41]. Meanwhile, a few studies showed that biodiesel has less BSFC than diesel. Monirul et al. tested fuel blends containing different concentrations of palm, jatropha and calophyllum inophyllum biodiesel at different speed conditions. They found that the CIB10 (fuel blended with 10% calophyllum inophyllum biodiesel) consumes less fuel, as shown in Figure 1 [29]. The higher BSFC of biodiesel is largely attributed to its lower calorific value, higher density and viscosity [7]. Due to the lower calorific value, more biodiesel is needed to compensate for the lower amount of heat released [4,7]. The greater density allows more biodiesel to be used than conventional diesel when the same volume is injected, while the larger viscosity affects the volumetric fuel injection rate [29]. The combined effect of these factors leads to a lower BSFC of biodiesel. Different fuels tested on different engines with different test conditions have different BSFC. However, most of the research results indicated that BSFC increases with an increase in the percentage of biodiesel in the biodiesel–diesel blends when it is used as a fuel in conventional CI engines compared to diesel. The BSFC of several common biodiesel–diesel blends is listed in Table 2.

Figure 1. Brake specific fuel consumption of diesel and biodiesel blends at various engine speeds [29].

Table 2. Different brake specific fuel consumption results using biodiesel–diesel blends compared to diesel fuel in diesel engines.

Engine	Test Condition	Test Fuels	Blend Ratio	Increase Rate of BSFC (%)	Ref.
Single cylinder, direct injection diesel engine, 582 cc	An average value for the three compression ratios (14, 16, 18), 2000 rpm	Diesel blend with wasted cooking oil	B10	2.72	[42]
			B20	2.3	
			B30	4.08	
			B50	7.12	
Single cylinder diesel engine-generating set of 5 kVA rating	Full load conditions	Diesel blend with eucalyptus biodiesel	B10	2.94	[43]
			B30	7.21	
			B50	12.04	
			B100	22.83	

Table 2. Cont.

Engine	Test Condition	Test Fuels	Blend Ratio	Increase Rate of BSFC (%)	Ref.
Single cylinder, direct injection diesel engine, 454 cc	Over the entire speed range under full load	Diesel blend with soybean biodiesel	B10	2	[4]
			B20	4	
			B50	7	
			B100	9	
Four-cylinder direct injection diesel engine, 1998 cc	A constant engine speed of 2500 rpm with 50% open throttle	Diesel blend with palm biodiesel	B10	1	[44]
			B20	2.1	
			B30	3	
Single cylinder, direct injection diesel engine, 638 cc	Over the entire speed range	Diesel blend with palm and coconut biodiesel	PB30	8.58	[45]
			CB30	9.03	
			PB15CB15	8.55	
Six-cylinder direct injection diesel engine, 12,822 cc	1400 rpm engine speed at full-load condition	Diesel blend with rapeseed oil biodiesel	B5	2.5	[46]
			B20	3	
			B70	5.5	
			B100	7.5	
Four-cylinder direct injection diesel engine, 2476 cc	Two idling conditions (1000 RPM 10% load and 1200 RPM 12% load)	Diesel blend with jatropha biodiesel	JB5	2.28–2.69	[47]
			JB10	3.98–5.39	
			JB20	8.83–9.29	

3.2. Brake Specific Energy Consumption

Brake specific energy consumption (BSEC) indicates the performance of fuel BSFC and calorific value, which can represent the energy input required to generate unit power. BSEC is more ideal than BSFC because it is not related to fuel type and takes into account the mass flow and heating value [48,49]. The formula for BSEC is as follows [50]:

$$\text{BSEC} = \frac{q\dot{m}_f}{2\pi NT_e} \quad (2)$$

where, q is the calorific value, $\dot{m}_f$ is the fuel consumption flow rate, N is the operating speed, and T_e is the brake torque.

In contrast to brake thermal efficiency (BTE), most biodiesel has a higher BSEC compared with conventional diesel. As shown in Figure 2, Alagu et al. mixed water hyacinth biodiesel with diesel at 0, 10, 20, 30, 40, and 100 vol%, and found that under different load conditions, the BSEC of the fuel increased significantly with the biodiesel content [30]. However, Gumus et al. found that under all load conditions, pure apricot seed kernel oil methyl ester biodiesel has the highest BSEC, while the BSEC of the B5 and B20 are less than diesel under all load conditions [48]. This shows that the single increase, decrease or a combination of both may occur for biodiesel. The change mechanism of BSEC is similar to BTE. There is more available oxygen in the biodiesel blend, which helps to improve combustion performance [7]. However, the lower calorific value and higher viscosity of biodiesel will have an adverse effect on atomization and combustion, resulting in an increase in BSEC [48].

Figure 2. Variation of brake specific energy consumption (BSEC) with different engine loads for different test fuels [30].

3.3. Brake Thermal Efficiency

BSFC is not an ideal choice when comparing different fuels with different heating values. Brake thermal efficiency (BTE) is a more suitable parameter under the same operating conditions. BTE refers to the efficiency at which diesel fuel combustion is converted into effective work output. That is, the ratio of power output to energy provided by fuel. BTE and BSEC are inversely related to each other. Therefore, the trends of the two are often opposite. The formula for BTE is as follows [51]:

$$\text{BTE} = \frac{2\pi N T_e}{q \dot{m}_f} \times 100 \quad (3)$$

Here, N is the operating speed, T_e is the brake torque, q is the calorific value, and $\dot{m}_f$ is the fuel consumption flow rate.

According to relevant studies, researchers found that the BTE of biodiesel and its blends with diesel are slightly lower or similar to conventional diesel [31,33,41,52–55]. Asokan et al. tested the BTE of diesel and diesel-biodiesel blends with B20, B30, B40, B100 under different loads and found that the biodiesel blends showed lower BTE during combustion [52]. The maximum BTE of diesel oil measured by Nantha Gopal et al. under a full load condition was 30.03%, while the BTE of diesel is the lowest [31]. However, some researchers reached the opposite conclusion [27,32]. Alloune et al. found that fuel containing *citrullus colocynthis* L. biodiesel has a higher BTE than diesel. They also found that B10 has the highest BTE at lower loads and B30 at higher loads [32]. The BTE of diesel engines is often affected by ignition delay, reaction temperature, and fuel characteristics [55]. The viscosity and density of biodiesel is high relatively, so the blends of biodiesel in the fuel will deteriorate the atomization, evaporation and air-fuel mixing effects of the fuel, resulting in uneven combustion [29,54]. By definition, the lower heating value of biodiesel and generally higher BSFC do not improve BTE [29]. Fortunately, the problem of poor atomization will be greatly alleviated when the cylinder temperature is high, such as under high load [52]. In addition, a higher cetane number and higher oxygen content promotes combustion, while good lubricity reduces friction losses, and these improve BTE [34]. The comprehensive mechanism of positive and negative factors determines the BTE performance of biodiesel under various operating conditions. Figure 3 below shows the typical BTE trend of fish oil biodiesel blends.

Figure 3. Variation of brake thermal efficiency of fish oil biodiesel blends with load at 21°bTDC [33].

3.4. Coefficient of Variation in Indicated Mean Effective Pressure

During the operation of the engine, each cycle slightly varies due to changes in the initial temperature, pressure, fuel composition and thermodynamic conditions in the cylinder [56]. The indicated mean effective pressure ($IMEP$) represents the work done per unit cylinder volume per cycle [57]. It can reflect the extensive pressure information of the entire operating cycle, and is often used to evaluate the combustion changes of the engine each cycle [58]. The coefficient of variation in indicated mean effective pressure (COV_{IMEP}) is an important indicator reflecting this periodic change, which indicates the cyclic variability of operation. A smaller coefficient of variation indicates a more uniform the combustion process and more stable engine operating conditions. Generally, it is believed that $COV_{IMEP} < 10\%$ is the upper limit of stable combustion [59]. COV_{IMEP} is calculated by the expression [57]:

$$COV_{IMEP} = \frac{\sigma_{IMEP}}{IMEP} \times 100 \quad (4)$$

where, σ_{imep} is the standard deviation in $IMEP$, and $imep$ is the mean $IMEP$.

Most studies show that the COV_{IMEP} of biodiesel-diesel blends is similar to or smaller than diesel [35,36,44]. Uyumaz et al. tested linseed oil biodiesel and found that the COV_{IMEP} of biodiesel blends decreases as the concentration of biodiesel increases, and the advantages compared with diesel become more obvious [35]. Turkcan et al. compared the COV_{IMEP} of diesel, ethyl ester biodiesel, methyl ester biodiesel, chicken fat biodiesel, and fleshing oil biodiesel. It was found that under low and high load, diesel has a higher COV_{IMEP} , but that of the medium load is just the opposite [36]. As shown in Figure 4, the other blends are much smaller except that the COV_{IMEP} of B10 is similar to diesel [44]. These phenomena may be attributed to the higher cetane number and oxygen content of biodiesel, which can be burned quickly and smoothly [59]. Although biodiesel has a lower calorific value, higher oxygen content will make combustion more complete, so the COV_{IMEP} of biodiesel blends tends to be lower [56]. Of course, the lower calorific value is considered to be the cause of fluctuations at higher loads [50].

Figure 4. Coefficient of variation in indicated mean effective pressure (COV_{IMEP}) of palm biodiesel–diesel blended fuel and mineral diesel [44].

3.5. Exhaust Gas Temperature

Density, viscosity, calorific value, cetane number and other characteristics of biodiesel mainly affect the exhaust gas temperature (EGT) [60,61]. A lower EGT generally means good combustion and less heat loss, indicating the effective usage of thermal energy in the fuel. In general, the heat generated in the cylinder increases with an increase of the rotation speed and load, resulting in an increase in EGT [62].

Both higher and lower EGT may be observed when using biodiesel. Dhamodaran et al. compared the EGT of rice-bran-, neem-, and cottonseed-oil biodiesels, and the results showed that the EGT of biodiesels are higher [34]. Other studies [62,63] also reached similar conclusions. However, some researchers found that the EGT of pure diesel is lower [60,64–66]. Elkelawy et al. tested the changes in EGT of different concentrations of biodiesel at different loads, and found that the average EGR values of B30, B50, and B70 are 2.77%, 8.28%, and 7.17% lower than diesel under the same conditions [65]. EGT is affected by the physical and chemical characteristics of the fuel, such as density, viscosity, calorific value, and cetane number [60]. The higher EGT of biodiesel may be attributed to its higher oxygen content, which promotes combustion [67]. The results are shown in Figure 5. Poor atomization caused by high density and high viscosity will cause unburned fuel in the main combustion period to burn later, resulting in a higher EGT [34]. However, a higher cetane number in the fuel would result in a shorter ignition delay, resulting in an earlier start of combustion, thereby reducing EGT and shortening the cylinder power cycle [64]. The lower calorific value may also lower cylinder temperature [60]. Another study [68] also indicated that the EGT of biodiesel is directly related to its oxygen percentage.

Figure 5. Variation of exhaust gas temperature (EGT) with different engine loads for different test fuels [65].

4. Combustion Characteristics

4.1. Ignition Delay

Ignition delay (ID) is the one of important parameters in combustion process of fuels, it is defined as the period of time from the start of fuel injection to the start of combustion [69,70]. The crank angle is generally used as the measurement unit, and the crank angle corresponding to 10% of the combustion mass is regarded as the end point of the ignition delay. The rise of the injector needle means the start of the fuel injection. However, the standard to identify the start of combustion is not unique. The sudden change in the cylinder pressure, heat release rate gradient, or the photoluminescent signal detected by the photocell can be used as a means to identify the start of combustion [25]. The ID is functionally dependent on physical and chemical delays. After being injected, the fuel is atomized, evaporated, and mixed with air resulting in spontaneous combustion. This period is called physical delay. The chemical delay is the period from the beginning of the slow chemical reaction until combustion occurs [71]. The physical delay and chemical delay occur simultaneously and depend on conditions such as ambient temperature and pressure [72]. The chemical delay is generally longer, but if the ambient temperature increases, the rate of chemical reaction will be accelerated, and the chemical delay will be shorter [71].

ID directly affects the heat release rate and indirectly affects the formation of engine noise and exhaust emissions [70]. Shrivastava et al. found that the ID of the fuel containing karanja biodiesel or roselle biodiesel is shorter than that of diesel [73]. The results are shown in Figure 6. The ID is usually related to the type of fuel and the operating conditions of the engine. Factors such as fuel properties, fuel injection atomization, fuel injection pressure, equivalence ratio, and engine speed may all affect the rhythm of ignition. Most studies found that biodiesel has a shorter ID than that of diesel due to the higher cetane number of biodiesel. Because the high cetane number can reduce the scale of premixed combustion. In biodiesel, some polymer esters with a higher boiling point than diesel will decompose into low molecular weight gas during high temperature injection. This light compound easily evaporates and spreads at the edge of the spray, which ignites the volatile fuel in advance and shortens the ID [28]. Meanwhile, the high viscosity, high density, low calorific value and low volatility of biodiesel also affect the physical delay, although the effect on the chemical delay is not obvious [74]. When the engine load increases, the ID will be shortened as the oil and gas mix at a faster rate because of the higher cylinder temperature, diluted exhaust gas and the excess heat retained in the previous combustion cycle [8,30]. Alagu et al. also found that the ID decreases with an increase in biodiesel content that may be due to the degraded atomization effect, the improved cetane number, the reduced spray cone angle, and the higher oxygen content. The combined effect leads to shortened ignition delay [4,30]. In some studies, the ID period increases when the engine speed and load increases and this may be attributed to the higher combustion temperature and exhaust gas dilution at higher load and speed. Moreover, the chemical reaction of injected biodiesel at high temperature leads to the decomposition of high molecular weight esters into small molecular weight, which makes volatile compounds burn earlier and delay period shorter [70].

Figure 6. Effect of load on ignition delay of fuel blends [73].

4.2. Cylinder Pressure

Cylinder pressure (CP) is an important parameter usually measured by pressure sensors that reflects the combustion process and the degree of mixing of fuel and air. The ID, heat release rate, combustion mass fraction, cylinder pressure-volume and other information can be gleaned from the cylinder pressure [31]. Some researchers also use the CP to estimate the intake and residual mass of the engine [75] or to develop functions for calculating combustion noise simulation data [76].

Changes in CP will be affected by parameters such as fuel type, engine speed, engine load, fuel injection pressure and injection timing. According to research by Das et al., the CP of B10 (10% castor oil methyl ester + 90% diesel) tends to rise earlier, and the rise rate is slightly higher, and the peak pressure is also larger compared with diesel [8]. Other studies [34,77] reached similar conclusions. However, Gnanasekaran et al. found that at 1500 rpm, under full load, the released peak CPs of diesel are 70.7, 73.6 and 77.6 bar, respectively, at injection timings of 21, 24, and 27° bTDC. Pure fish oil biodiesel generated lower peak CPs that were 63.8, 67.1 and 73.8 bar, respectively, under the same conditions [33]. Sakthivel et al. also found that the maximum rate of pressure rise increases with retardation in injection timing, decreases with injection timing advance and increases with load, as shown in Figure 7 [67]. The trend variation of CP of the same biodiesel blends is not unique. Shehata et al. found that under the same operating conditions, the blends with 20 vol% corn biodiesel has the larger CP at an injection pressure of 190 bar, but at 200 bar, the CP of pure diesel was larger [78]. Other studies [4,37] also showed that the maximum combustion pressure did not change much when using biodiesel, and the peak positions were also very similar. Biodiesel and the blends mixed with diesel usually have a higher cetane number and a shorter ID, so CP tends to rise earlier than diesel. Higher oxygen content and earlier combustion will cause the peak pressure to increase. For stoichiometric flames, biodiesel-containing fuels are more reactive, which is also an important factor [8]. However, the lower calorific value of biodiesel also affects the peak CP. Similarly, the higher viscosity and density of biodiesel will affect the volatilization and atomization effect of the fuel, which may cause the peak CP to be even lower than diesel [26,78].

Figure 7. CP changes for biodiesel with loads at 21, 24 and 27° bTDC. Adapted with permission from [67]. Copyright © 2016, Fuel, published by Elsevier Ltd., Amsterdam, The Netherlands.

4.3. Heat Release Rate

The heat release rate (HRR) indicates the rate at which the fuel releases chemical energy during the combustion process in the diesel engine [31]. It can be used to determine the start of combustion, the difference in fuel fraction and combustion rate during the premix period [34]. The engine performance parameters can be well understood and controlled through HRR. According to the first law of thermodynamics, it can be calculated by [79]:

$$\frac{dQ_{\text{combustion}}}{d\theta} = \frac{dQ_{\text{net}}}{d\theta} + \frac{dQ_{\text{wall}}}{d\theta} = \frac{1}{k-1} V \frac{dP}{d\theta} + \frac{k}{k-1} P \frac{dV}{d\theta} + \frac{dQ_{\text{wall}}}{d\theta}, \quad (5)$$

where, $\frac{dQ_{\text{combustion}}}{d\theta}$ is the heat release rate, θ is the crank angle, k is the ratio of specific heat, and Q_{wall} means the heat exchange of the wall.

Toh et al. studied the combustion characteristics of moringa oleifera biodiesel-diesel blends at six engine speeds (1500, 2000, 2500, 3000, 3500, 4000 rpm) in a four-cylinder turbocharged diesel engine with total cylinder volume of 1.461 L. They reported that the peak HRR of MOB50 (50% moringa oleifera biodiesel + 50% petroleum diesel by volume) was 2.06% lower than baseline diesel at 3000 rpm, which was the largest difference across all engine speeds [26]. Studies [32,54] also showed that biodiesel decreased the HRR peak value, which is shown in Figure 8. However, a few studies [34,59] observed almost the opposite phenomenon. The HRR of fuel varies with engine test conditions, and the relative trends of diesel and biodiesel under different operating conditions are not unique. Most studies showed that fuels containing biodiesel components tend to start burning earlier than pure diesel and have a lower peak HRR [4,7,59]. This is because the shorter ID of biodiesel makes it burn earlier than diesel. In addition, biodiesel has a higher bulk modulus and viscosity. A higher bulk modulus results in lower compressibility, so the pressure response in the fuel injection system is more sensitive. A larger viscosity helps reduce losses during the fuel injection process, making it beneficial to spray early [80]. Although the HRR of diesel is slower than that of biodiesel, it is often observed that diesel has a higher peak HRR in the premixed combustion stage. Many results show that the peak HRR decreases with increasing biodiesel content [33,38,52]. This may be due to the greater density and viscosity of biodiesel, which results in slower vaporization of the fuel, which affects the release of premixed combustion heat. The lower heating rate peak of biodiesel may be attributed to its lower calorific value and density [26]. Some researchers also found that sometimes the peak HRR of biodiesel is greater, probably because the higher oxygen content promotes good air-fuel mixing [32,34,59]. Biodiesel and diesel have similar trends in the diffusion combustion stages, and the excess oxygen content of biodiesel allows the burn to continue in the later period [31].

Figure 8. Heat release rate of *Cymbopogon flexuosus* biofuel [54].

5. Emission Characteristics

5.1. Regulated Emissions

5.1.1. Hydrocarbon

Hydrocarbon (HC) is usually formed when the mixture of oil and gas is too lean or too rich and the temperature in the cylinder is low. Similarly, HC is also generated due to poor atomization and corresponding wall humidity caused by the higher viscosity of biodiesel [81]. In addition, the gap volume and the presence of flame quenching are also sources [82,83]. Unburned hydrocarbons exist in the exhaust gas in the form of a complex mixture of unburned and partially burned hydrocarbons [84]. Compared with traditional diesel, the combustion of biodiesel produces less HC in most cases [59,85,86]. Gharehghani et al. used waste fish oil biodiesel and diesel as a blended fuel in a single-cylinder engine having a variable compression ratio (Max. CR22) and displacements of 507 cc to test the emission characteristics. They found that biodiesel had lower HC emissions than traditional diesel at all loads [59]. Palash et al. also found that the average reduction rates of HC emissions of fuels with 5 vol% and 10 vol% of *aphanamis polystachya* biodiesel were respectively 9.86% and 22.32% of those of traditional diesel over the entire speed range as shown in Figure 9 [87]. Other studies [88,89] also confirmed this view. This phenomenon is mainly because biodiesel tends to have more oxygen, leading to an increase in the temperature of the gas and reducing possible incomplete combustion. Biodiesel may also provide some positive factors such as post flame oxidation and higher flame speed [4,54,59,87,90]. In addition, a higher cetane number will shorten the ID by reducing the probability of over-mixing and lean regions during the delay period, thereby reducing local fuel enrichment during combustion and reducing HC emissions [59,91]. However, a few studies have come to the opposite conclusion. Nabi et al. found that adding licella biodiesel to diesel will increase THC emissions. This may be related to the low volatility of licella biodiesel, while a lower cetane number results in longer ID, which may increase the amount of hydrocarbons in the exhaust [92]. There are also claims that the engine type also has an impact on the emissions [93].

Figure 9. Hydrocarbon (HC) emissions of diesel and biodiesel fuels at different speeds at full load [87].

5.1.2. Carbon Monoxide

Carbon monoxide (CO) is one of the main gases emitted from vehicles. CO is formed because of incomplete oxidation of carbon in the fuel-rich zone due to an inappropriate air–fuel ratio [84]. Generally, CO emissions are affected by fuel type, combustion chamber design, air–fuel equivalent ratio, atomization parameters, injection timing start, injection pressure, engine load and speed [4]. Similar to HC, using biodiesel as alternative fuel can generally reduce CO emissions from internal combustion engines. The higher oxygen content in biodiesel may lead to lean combustion in the cylinder and effectively improve the combustion efficiency [4,59]. Fewer carbon monoxide emissions are generated when biodiesel converts CO to CO₂, thus reducing the formation of CO [86,89,90,94]. Besides, researchers pointed that CO emissions decrease as the proportion of biodiesel or engine load increases [56,86,89,90,95]. Research from Can et al. showed that CO emissions remained basically unchanged at low and medium loads as shown in Figure 10, but under high load conditions, the reduction in emissions after adding canola biodiesel reached about 32% [91]. Al-Iwayzy et al. also found that the average values of CO (1.7%) and CO₂ (7.24%) produced by 100% *Chlorella protothecoides* biodiesel were the lowest, being 28% and 4.2% lower than petroleum diesel [96]. This is because the oxygen concentration in the combustion chamber decreased as the load increases [56]. Although most of the studies on the emission effects of biodiesel have indicated that biodiesel can reduce CO emissions, even up to 90% in these literatures. However, An et al. found that CO emissions increased with the increase of biodiesel blend ratio and the decrease of engine speed at lower engine loads. These experiments were performed on a four cylinder, four-stroke, common rail fuel injection diesel engine fueled with waste cooking oil biodiesel and its blends. They pointed out that the above results were mainly related to the high oxygen content and high viscosity of biodiesel. High oxygen content promoted the development of fuel–air ratio to a leaner mixture under low load, and high viscosity affected atomization, resulting in incomplete combustion and more CO emissions [97].

Figure 10. Effects of canola biodiesel blends on CO emissions (adapted with permission from [91], Elsevier, 2017).

5.1.3. Particulate Matter

Particulate matter (PM) has three components: dry soot (DS), soluble organic fraction (SOF) and sulfate. Soot accounts for about half of the PM component [98]. Soot formation usually occurs in fuel-rich areas at high temperatures without sufficient oxygen concentrations [99]. Hydrocarbon-containing fuels are pyrolyzed in a high-temperature and anoxic environment in the cylinder, which will generate soot precursor materials as well as unsaturated hydrocarbons, polyacetylene, and polycyclic aromatic hydrocarbons. The small-molecule carbon-hydrogen phase reactants form a large-molecular aromatic structure through the addition of free radicals, and they serve as a soot core in the early stage of combustion [98]. In the later stage of combustion, the particle nucleus continues to physically and chemically adsorb dehydrogenated gaseous hydrocarbons, which greatly increases the quality of the particle [100]. Particles also combine and collide to form larger spherical or chain-like structures, and soot is formed during subsequent oxidation. Subsequently, the semi-volatile or low-volatile substances such as unburned hydrocarbons, sulfates, and moisture condensed on the surface due to the decrease in ambient temperature and formed PM [98]. Excessive PM emissions can affect human health. They can cause cough and wheezing, and worsen various respiratory and cardiopulmonary diseases, and even cause death [101].

Most studies show that fuels containing a certain proportion of biodiesel can effectively reduce PM generation. Nabi et al. investigated the effects of biodiesel derived from waste cooking oil on PM emissions in a six-cylinder turbocharged diesel engine with a high-pressure common rail injection system in compliance with a 13-mode European stationary cycle (ESC). They found that there was significant reductions in PM emissions with biodiesel blends relative to those of the reference diesel at all modes, a maximum of 84% PM reduction was observed with the biodiesel blends, as shown in Figure 11 [102]. Many researchers reached a similar conclusion for PM [54,56,90,103]. The higher oxygen content resulting in less oxygen demand is considered to be an important factor, which will easily promote more stable and complete combustion of fuels in oil-rich areas [104,105]. In addition, there are fewer aromatic compounds and very few sulfur atoms, which form soot precursors, so less PM can be generated [83,104,106]. Biodiesel is mainly composed of long-chain hydrocarbon groups, which will lead to a higher cetane number [107].

Figure 11. Particulate matter (PM) concentrations for all tested fuels under different speeds and loads [102].

5.1.4. Nitrogen Oxides

Compared with gasoline engines, diesel engines have significant nitrogen oxides (NO_x) emissions. Most studies suggest that there are three main sources of NO_x whose main ingredients are NO (95%) [108]. They are described in the following: (1) thermal NO: N_2 and O_2 in air can react through a series of chemical steps called the Zeldovich mechanism at high cylinder temperatures. The increase in the residence time and the temperature of the mixture in the cylinder may lead to an increase in NO_x emission; (2) prompt NO: under oil rich conditions, the intermediate products containing hydrocarbons are produced first in fuel combustion. CH and CH_2 can react with N_2 , and the substances containing CN compounds continue to oxidize to NO_x ; (3) N_2O pathway: in this mechanism, N_2 directly reacts with oxygen to produce N_2O [108]. For diesel engines, the formation of NO_x is mainly influenced by the mechanism affected by the local temperature in the combustion mixture, the residence time at high temperatures, and the local air/fuel ratio in the cylinder [59,88,109]. NO_x is both harmful to the human respiratory system, and contributes to the formation of photochemical smog [84].

Many researchers have found that NO_x emissions from biodiesel are greater than that from traditional diesel under different loads [4,56,59,89]. Can et al. tested the combustion and emission characteristics of canola biodiesel blends on a four-stroke naturally aspirated single-cylinder stationary DI diesel engine. It was found that the average NO_x emissions of all loads of each fuel B20, B15, B10 and B5 increased by 8.9%, 7.8%, 6.3% and 3.3%, respectively [91]. When testing rapeseed oil biodiesel, Raman et al. found that the NO_x emissions of B25, B50, B75, and B100 were 14.4%, 21.6%, 28.5%, and 32.9% higher than that of diesel at maximum braking power, as shown as Figure 12 [38]. The effect on NO_x formation seems to be mainly due to the effect of molecular structure on the spontaneous ignition delay that occurs after the fuel is injected into the combustion chamber, and the flame temperature during fuel combustion is relatively low [104]. In addition to the higher cetane number, the higher oxygen content in biodiesel is an important factor in NO_x formation. Excessive hydrocarbon oxidation and high oxygen content of biodiesel lead to excessive local temperature and corresponding excess air in the cylinder, which increases NO_x emissions [56,59,88,91,95]. Moreover, as more fuel is injected, an oil-rich core is generated, which may combine with oxygen in the oil to affect NO_x emissions, especially under high load conditions [59]. Sanjid et al. also pointed out that the higher percentage of unsaturated fatty acids in biodiesel fuels, which have higher adiabatic flame temperatures, lead to higher NO_x emissions [88]. Longer hydrocarbon chain lengths promote higher adiabatic flame

temperatures [104]. The double bonds of fatty acids promote the formation of hydrocarbon free radicals [91,94]. However, a few scholars have reported some cases of NO_x reduction. NO_x emission characteristics were evaluated in a four-stroke, single-cylinder air-cooled diesel engine fueled with microalgae *chlorella protothecoides* biodiesel-diesel blends by Al-lwayzy et al. [96]. They found that that the biodiesel blends reduced NO_x emissions by an average of 7.4%. The main factors to reduce the NO_x were the exhaust gas temperature, the O₂ content, cetane number and biodiesel chemical structure. The emissions characteristics for regulated gases are shown in Table 3.

Figure 12. Effects of rapeseed oil biodiesel on nitrogen oxide (NO_x) emissions [38].

Table 3. Emission characteristics of different fuels with biodiesel. (“↑” means the emissions increase, “↓” means the emissions decrease, and “↑↓” means emissions vary with operating conditions).

Raw Materials	Blends	Trends Compared to Conventional Diesel				Reference
		HC	CO	NO _x	PM	
Waste cooking-oil biodiesel	D100, B10, B20, B30	↓	↓	↑	↓	[103]
Soybean biodiesel	D2, B10, B20, B50, B100	↓	↓	↑	↑	[4]
Palm oil	D100, B20, B100, PO20	↓	↓	↑		[94]
Waste fish oil	D, B25, B50, B75, B100	↓	↓	↑		[59]
Mixed inedible feedstocks	B0, KB5MB5, KB10, MB10, KB10MB10, KB20, MB20	↓	↓	↑		[88]
Pongamia biodiesel	D, B20, B40, B60, B80, B100	↓	↓	↑		[86]
Castor biodiesel	D, B20, B40, B60, B80, B100	↓	↓	↑	↑↓	[89]
Mustard oil biodiesel	D100, M10, M20, M30	↓		↑	↓	[56]
Spirulina microalgae biodiesel	B0, B20, B40, B60, B80, B100	↓	↓	↓	↓	[90]
Citrus sinensis biodiesel	D, B5, B10, B20		↓	↑		[95]
Camelina biodiesel	D, B7, B100		↓	↑		[93]
Canola biodiesel	D, B5, B10, B15, B20	↓	↓	↑	↑	[91]
Cymbopogon flexuosus biofuel	DF, C10, C20, C30, C40, C100	↓	↓	↑	↓	[54]
Microalgae Chlorella protothecoides biodiesel	PD, B20, B50, B100		↓	↓	↓	[96]
Licella biofuel	R0, R5, R10, R20		↑	↑	↓	[92]
Aphanamixis polystachya oil	Diesel, APME5, APME10	↓	↓			[87]
Jatropha biodiesel	D100, JME5, JME10, JME20, JME30, JME100	↓	↓	↑	↓	[110]
Argemone biodiesel	D, AB10, AB20, AB30, AB50	↓	↓	↑↓	↓	[25]
New series of non-edible biodiesel	D, MD, WD, MWD	↓	↓	↑	↓	[111]

On the other hand, to address the increased NO_x emissions of biodiesel, appropriate nano additives can be used to decrease NO_x emission of biodiesel. Pimenidou et al. reported that nanosized CZA2 (Ce_{0.6}Zr_{0.2}Al_{0.26}O₂) catalysts absorb heat, catalyze combustion and release oxygen under a higher load, reducing the amount of NO_x release (and also decreasing the emissions of HC and

CO) [112]. Another study [113] also indicated that the amidated CeO₂-MWCNTs (Multi-Walled Carbon Nano-Tubes) additive obtained by hybridization of nano-cerium oxide and MWCNTs by a solvent-aided method can reduce the four main regulated gases to varying degrees, where HC is reduced the most, as shown in Figure 13. Proper nanoparticles or oxygen-containing additives can both improve the engine performance and optimize the physicochemical properties of biofuels such as viscosity, density and flash point, which can make up for some of the shortcomings of biodiesel [114].

Figure 13. Overall decrease in emissions of carbon monoxide (CO), hydrocarbon (HC), soot and NO_x achieved by addition of the CeO₂-MWCNTs nanocatalyst compared to catalyst-free fuels [113].

5.2. Unregulated Emissions

5.2.1. Volatile Organic Compounds

Volatile organic compounds (VOCs) usually refer to organic compounds with an atmospheric boiling point ranging from 50 °C to 260 °C. The most common chemical structures include aldehydes, ketones, alkanes, aromatics, alkenes and halogenated hydrocarbons [12,115]. Vehicle emissions are an important source of VOCs. VOCs emitted by vehicles generally come from the natural volatilization and incomplete combustion of fuel, and the components emitted from these are very similar [116]. Volatile organic compounds can easily form photochemical smog and secondary aerosols that damage the environment. They can also affect the normal metabolism of the human body and cause acute symptoms such as headaches and allergies [117].

Most researchers have observed experimental results that the total emissions of VOCs by biodiesels have decreased. Peng et al. tested diesel and waste soybean oil biodiesel blend B20 in three driving modes to simulate engine VOCs emission characteristics under various operating conditions and loads. It was found that B20 releases an average of 61% less total VOCs than conventional diesel, which has more emissions and more types of substances. In addition, there are 27 kinds of volatile organic compounds with emissions exceeding 1 mg kW h⁻¹ in diesel, and only 13 kinds in B20 [118]. Ge et al. performed experiments and found that combustion of fuels containing canola oil biodiesel fuel can release fewer VOCs as shown as Figure 14, and benzene is the highest emission component in all fuels, reaching 41% [119]. This trend may be due to the higher cetane number and higher flash point of biodiesel, which can reduce the ignition delay. In addition, the increased oxygen content in biodiesel helps the fuel to burn more completely, thereby reducing hydrocarbon emissions [118,120,121]. In addition, diesel is mainly composed of linear alkanes, and the conversion into emissions requires a series of complex reactions involving alcohols, carbonyl compounds, acids, and esters. In contrast, biodiesel is dominated by short-chain compounds, which make it easier to directly oxidize esters to carbon dioxide [121,122].

Meanwhile, the composition of the released VOCs gases from different fuel blends is also different. For example, Lopes et al. found that benzene (25.9%) is the most abundant in B0, nonane (16.0%) is the most abundant in B7, and butanal (18.3%) is the most abundant in B20 [120]. The increase or decrease in VOCs will also change under different loads and operating speeds. Generally, the reduction of VOCs is more pronounced at higher engine speeds [121]. Some conclusions point out that there is a

positive correlation between VOCs emissions and load, which may be due to higher injection pressure, good atomization and inlet turbulence intensity [12]. Of course, the oil–gas mixture is likely to be thicker due to the large injection volume under high load, which may show the opposite result [121].

Figure 14. Volatile organic carbon (VOC) emissions from a diesel engine fueled with conventional diesel fuel, B20, and canola oil biodiesel fuel (adapted with permission from [119], Elsevier, 2018).

5.2.2. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are organic substances composed of carbon and hydrogen atoms. They are composed of at least two condensed or molten aromatic ring structures [123]. Low molecular weight compounds containing no more than four rings are mostly distributed in the gas phase, and higher molecular weight compounds containing more than six rings are mainly found in the particles [124]. Their distribution between the two phases depends on their molecular weight, ambient temperature, PAH concentration and particle composition [13]. Although PAHs are unregulated gases, the emissions can be harmful to humans. The American Conference of Governmental Industrial Hygienists (ACGIH) indicates that short-term exposure to PAHs can lead to impaired lung function, and certain patients may even show a thrombotic effect. Prolonged exposure to PAHs may cause cancer, cell malformations and even inheritance of toxicity. At a certain concentration, adverse symptoms such as vomiting and dizziness may also occur [123].

Most experimental studies have found that biodiesel can reduce the release of some PAHs. Ballesteros et al. tested rapeseed methyl esters, waste cooking oil methyl esters and waste cooking oil ethyl esters biofuels in urban and extra-urban modes [13]. The results showed that the emissions of heavy PAHs are generally higher than that of light PAHs, and biodiesel can reduce total PAH emissions as shown in Figure 15. Lin et al. investigated the PAH emissions of waste cooking oil biodiesel (WCO) on Cummins heavy-duty engines and found that the average reduction rates of total PAHs of WCOB5, WCOB10, WCOB20 and WCOB30 were 8.1%, 24.0%, 32.0% and 37.7% compared with ultra-low sulfur diesel [125]. Some researchers also tested blends of ultra-low sulfur diesel and soybean biodiesel in different concentrations and combined them with the SCR (Selective Catalytic Reduction) system to analyze diesel engine emissions results. After replacing diesel with biodiesel, total PAHs emissions were reduced by 28% [126]. This conclusion is similar to findings of other studies [127–129].

The PAHs produced by diesel engines mainly come from PAHs formed from fuel during combustion, PAHs accumulated from fuel to lubricating oil, release of PAHs deposited by the engine, and PAHs generated from the fuel pyro-synthesis process [130]. Biodiesel itself has fewer polycyclic aromatic hydrocarbons, which can reduce granular phase aromatics generated during combustion and indirectly reduce the release of lubricants and sediments [126,130]. The higher oxygen content in biodiesel is more likely to result in complete combustion, thereby reducing PAH emissions [130].

Figure 15. Polycyclic aromatic hydrocarbon (PAH) emissions in urban mode (a) and extra-urban mode (b) for rapeseed methyl esters fuels (adapted with permission from [13], Elsevier, 2010).

6. Noise and Vibration

There are three main sources of engine noise: combustion noise, mechanical noise and aerodynamic noise. Combustion noise is caused by the cyclically sharp rise in pressure in the combustion chamber. Mechanical noise comes from the periodic mechanical movement of engine components. Aerodynamic noise generally comes from the intake and exhaust process and fan rotation [131]. Combustion characteristics such as in-cylinder pressure and heat release rate have a great influence on the generation of noise.

Most researchers found that noise coming from the engine fueled by biodiesel is lower. Patel et al. pointed out that both the combustion noise and engine noise of fuel with soybean biodiesel is lower than conventional diesel under almost all loads [132]. As shown in Figure 16, the engine external noise is always higher than the combustion noise, and the external noise of biodiesel blends is about 1–3 dB lower than that of diesel. Uludamar et al. found that engine noise increases with speed, but combustion produces lower noise for most biodiesel blends [14,133]. The engine noise level is often related to the cylinder pressure variation and the maximum heat release rate. The fuels that produced larger HRRmax generally showed a higher noise level. This may be because the higher cetane number of biodiesels shorten the ignition delay time, resulting in a lower pressure increase rate and HRRmax, which produces a lower noise level [132,134,135]. Meanwhile, the properties of biodiesel such as viscosity and volatility may lead to poor atomization and the appearance of large liquid beads. This is not conducive to the combustion of fuel in the premixed state, but to the reduction of the maximum in-cylinder pressure [16]. In addition, the higher bulk modulus of biodiesel will extend the injection timing and increase the noise radiation, but the impact is limited [134]. Redel-Macías et al. also found that biodiesel blends improved noise levels while they also improved acoustic roughness [135].

Engine vibration is caused by the reciprocating and rotating mass of the engine, and the operation of other accessories, which can affect the smoothness and stability of the engine. Vibration in the vertical direction (z-axis) is particularly obvious among the three orthogonal directions due to the vertical movement of the piston caused by the pressure variation generated when the fuel burns. In addition, torsional vibration of the crankshaft, vibration of the valve train, and vibration of the oil pump and fan are also important components of engine vibration.

Çalık et al. tested waste cooking oil biodiesel and conventional diesel at 1200, 1500, 1800, 2100, 2400 rpm and found that the vibration performance of biodiesel is better than conventional diesel at all speeds, as illustrated in Figure 17 [136]. Studies [7,14,132,137] also reported the great damping function of biodiesel. However, some researchers observed that the vibration damping effect of biodiesel is not absolute [138,139]. Taghizadeh-Alisaraei et al. tested nine biodiesel-diesel blends and found that in most cases, the fuel with the lowest vibration is B20 or B40, while the largest appeared in B15, B30, and B50 [138]. Vibration performance depends on the net effect of characteristics such as oxygen content, viscosity and calorific value of the fuel mixture. The lower heating value of biodiesel and the

undesirable atomization caused by the larger viscosity will reduce the power of the engine and alleviate vibration [138]. Meanwhile, the higher oxygen content of biodiesel also brings better combustion quality [14,133]. The larger cetane number of biodiesel shortens the ignition delay time, resulting in a shorter mixing-controlled combustion phase, making the pressure peak point closer to the top dead center, which will help reduce vibration [136]. In addition, others [132,134] discovered the vertical (z-axis) vibration levels, and the noise of the engine was positively correlated with the trend of HRR.

Figure 16. (a) Combustion noise and (b) engine external noise of different fuels [132].

Figure 17. a_{total} (total vibration acceleration) of diesel, biodiesel and their hydrogen enriched blends [136].

7. Compatibility

7.1. Lubricity

Lubricity is the ability of a fluid to reduce friction and adhesion between two contact surfaces. Fuel lubricity is of great significance to the life of the engine, especially for components such as fuel pumps and fuel injectors that require fuel self-lubrication [18]. Most studies show that, compared with diesel, biodiesel often has better lubricity under the same conditions. Fazal et al. tested the lubrication of palm biodiesel-diesel blends with different concentrations through the four-ball wear test, and found that the diameter of the steel ball wear marks decreased with an increase in the concentration of biodiesel [17]. High quality jatropha biodiesel was tested by Tongroon et al., who found that the blend with 15 vol% biodiesel has the best lubricity. However, the lubrication effect cannot continue to improve due to the increase in biodiesel concentration [140]. Figure 18 shows the effect of biodiesel on fuel lubricity and viscosity. In some studies, biodiesel has also been used as an additive to improve lubricity [19].

Figure 18. Effect of biodiesel blends on WS1.4 (wear scar 1.4) and viscosity of different concentrations [140].

Better lubricity depends on the main components of biodiesel such as fatty acid methyl ester, and a few other ingredients such as glycerides, antioxidants, and sterols, which can effectively improve the lubricity of the fuels [20,141]. The ester molecules in biodiesel form a relatively stable protective film on the metal surface, which helps to prevent the sliding surface from contacting [17]. In addition, the residual polar compounds such as free fatty acids and monoacylglycerol in the production process of biodiesel can also enhance the lubricating effect, and the O atoms in the fatty compounds have a strong polarizing effect [141]. Some scholars found that the oxidation process of biodiesel affects the lubrication. During this process, the ester is oxidized to various fatty acids, which will cause fuel degradation and corrosion of the materials, thereby deteriorating the lubrication effect [17].

7.2. Oxidation Stability

The oxidation stability of a fuel indicates the tendency of the fuel to react with oxides at normal temperatures and its relative sensitivity to degradation due to oxidation. Because of the differences in composition, biodiesel is often more prone to oxidative deterioration than fossil diesel. Fossil diesel is a complex hydrocarbon blend containing alkanes, olefins, and aromatics obtained through a series of processes from petroleum crude oil such as fractionation. Unlike fossil diesel, long-chain fatty acid esters undergo a transesterification reaction with alcohols under the action of a catalyst to produce fatty acid monoalkyl esters as the main component of biodiesel [142]. The special structure of esters in biodiesel is very sensitive to its oxidation and thermal degradation [143], which are affected by the degree of unsaturation in the fuel. As shown in Figure 19, the influence of the compound structure of fatty ester and the number of double bonds is very important for fuel degradation, and there is a strong inverse relationship between oxidation stability and unsaturated fatty acid content. The auto-oxidation of biodiesel is a free radical chain reaction, which usually starts from the allyl site and includes three steps: initiation, propagation, and termination. The free radicals generated during the initiation phase interact with oxygen and form peroxides during the propagation phase. The peroxide then extracts hydrogen from the methylene group to form hydroperoxide and carbon radicals to promote chain reactions. Carbon radicals will continue to react with oxygen until termination [144]. The peroxides accumulate and eventually decompose to produce secondary oxides such as alcohols, aldehydes, acids, and oligomers, which will unfavorably affect fuel quality.

The oxygen concentration, temperature, light and other factors affect the degree of oxidation, which is generally measured by indexes such as iodine value, peroxide value, acid value, and fluidity. One study [145] found that most of the biodiesel from different feedstocks will increase in acid value, peroxide value, density and viscosity due to its oxidative degradation under permissible oxidation conditions, especially at higher temperatures. The problem of poor oxidation stability can be solved by controlling the material in which the biodiesel is stored, the ambient temperature and

light, and also by adding the appropriate antioxidants. Almeida et al. simulated the effect of storage containers on fuel oxidation by immersing copper sheets in biodiesel [146]. It was found that the induction time of biodiesel with antioxidant tert-butylhydroquinone was extended from 6.5 h to 24 h, which improved the oxidation stability of the fuel. Similarly, pyrogallol, gallic acid, propyl gallate, catechol, nordihydroguaiaretic acid, butylated hydroxyanisole and other antioxidants have also been found to have nice effects on the stability of biofuels [147].

Figure 19. The changes recorded on the oxidation stability of the nine biodiesel samples [142].

7.3. Corrosion

Fuel is stored, transported and injected through a fuel system containing a fuel tank, fuel pumps, fuel filters, fuel injectors and pipelines. Most components made of iron (cast iron), steel and non-ferrous metals (copper, alloy, etc.), and sealing elements made of elastic materials (rubber, polymer, etc.) are generally in direct contact with fuel. Therefore, the corrosion characteristics of the fuel will directly affect the service life of engine components. Generally, biodiesel is more corrosive than fossil diesel under similar conditions. The composition of biodiesel, moisture content, conductivity, temperature and contact time may all be factors that affect corrosion [148]. Fazal et al. tested the corrosion of copper (Cu), brass (BS), aluminum (Al) and cast iron (CI) in diesel and palm biodiesel [149]. The results showed that the corrosion order for these metals is copper, brass, aluminum, cast iron. The TAN (Total Acid Number) value of biodiesel in the corrosion process exceeded the ASTM D6751 standard. The corrosion of various metals can be seen in Figure 20. Ahmad et al. tested the corrosion rate of jatropha biodiesel on copper, aluminum and stainless steel [150]. They found that the corrosion rate of copper was the fastest, and the acid content, density, and water content of biodiesel increased. Another study [151] also reached similar conclusions with metals, especially copper. The corrosion situation of metal in biodiesel is related to the atmosphere and fuel composition. Taking copper as an example, the corrosion process may follow the following mechanisms [149,152]:

Figure 20. SEM (Scanning Electron Microscopy) micrographs of metal surfaces before and after exposure to diesel and biodiesel at room temperature for 2880 h. (a–l) in this figure indicate the tested metals: (a,e,i) Cu, (b,f,j) BS, (c,g,k) Al and (d,h,l) Cl [149].

To alleviate the corrosion of biodiesel, more and more attention has been paid to anti-corrosion additives. Fazal et al. found that tert-butylamine (TBA) and butylhydroxyanisole (BHA) additives can greatly delay metal degradation under the same conditions [152]. As shown in the Figure 21, copper corrosion rate is significantly reduced. In addition, other additives such as tert-butylamine (TBA), propyl gallate (PG), pyrogallol (PY), and butylated hydroxytoluene (BHT) effectively improve metal degradation [153].

Figure 21. AFM (Atomic Force Microscopy) images of copper surface after exposure to biodiesel and biodiesel with tert-butylamine (TBA) additives [152].

Some scholars have also explored the compatibility of biodiesel with elastomers. Kass et al. used the Hansen solubility parameter method to evaluate the compatibility between main degradation products of biodiesel (methyl hydroperoxide and acetaldehyde) and five common elastomers containing acrylonitrile butadiene rubber, fluorocarbon, neoprene, ethylene propene diene monomer and silicone rubber [154]. The partial degradation of biodiesel will increase the volume expansion of the elastomers and affect the compatibility of the two. Zhu et al. pointed that the degradation of biodiesel also deteriorated the mechanical properties of the elastomers, whose mass has also increased accordingly [155]. Other studies reached similar conclusions, but these are not absolute results.

As Hence et al. pointed out, most existing test methods (immersion, LPR and rotating cage etc.) and test standards (ASTM G31, ASTM G184, ASTM G59 and ASTM D471) cannot appropriately simulate the real engine operating conditions, and the factors that affect the deterioration of metals and elastomers in the test may not appear in actual situations [156]. Specific corrosion mechanisms also require further analysis of specific components of fuels, metals and elastomers to draw more systematic conclusions.

8. Conclusions

The characteristics of biodiesel as an alternative fuel are somewhat different from those of conventional diesel. This paper mainly discussed the impact of biodiesel on diesel engines based on combustion characteristics, performance, emission characteristics, vibration and noise, and compatibility with fuel systems. A summary of this study can be discussed as follows:

- ◆ In most cases, the BSFC and BSEC of biodiesel are slightly higher than that of diesel, and BTE may be slightly lower. COV_{IMEP} is generally low, which will help the engine run smoothly. The increase and decrease of EGT both occur, depending on the specific operating conditions.
- ◆ The effect of biodiesel on emissions is more obvious. The emissions of HC, CO and PM are significantly reduced due to the addition of biodiesel, but NOx increases. Biodiesel also has a very good reduction effect on VOCs and PAHs emissions.
- ◆ The ignition delay of biodiesel is generally shorter than that of diesel, and the maximum cylinder pressure would be reduced accordingly. As for the heat release rate, a downward trend in the peak value is usually observed, but the corresponding crank angle seems earlier.
- ◆ The addition of biodiesel helps reduce engine noise and improve noise quality. At the same time, it would significantly reduce the vibration of the engine in the vertical direction. These changes may be related to the exothermic characteristics of biodiesel.
- ◆ Biodiesel is generally highly corrosive, which would cause corrosion and deterioration on some metals and elastomers. However, the impact of biodiesel on the fuel system is still poorly understood, and more scientific and detailed investigations are needed.
- ◆ As for the increased NOx emissions caused by biodiesel, weak oxidation stability, and strong corrosiveness, these problems can be solved by adding special additives. In the future, a multifunctional additive can also be explored to optimize the multiple properties of biodiesel simultaneously.

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