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Effect of biodiesel on engine performances and emissions

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ABSTRACT

As a renewable, sustainable and alternative fuel for compression ignition engines, biodiesel instead of diesel has been increasingly fueled to study its effects on engine performances and emissions in the recent 10 years. But these studies have been rarely reviewed to favor understanding and popularization for biodiesel so far. In this work, reports about biodiesel engine performances and emissions, published by highly rated journals in scientific indexes, were cited preferentially since 2000 year. From these reports, the effect of biodiesel on engine power, economy, durability and emissions including regulated and non-regulated emissions, and the corresponding effect factors are surveyed and analyzed in detail. The use of biodiesel leads to the substantial reduction in PM, HC and CO emissions accompanying with the imperceptible power loss, the increase in fuel consumption and the increase in NO_x emission on conventional diesel engines with no or fewer modification. And it favors to reduce carbon deposit and wear of the key engine parts. Therefore, the blends of biodiesel with small content in place of petroleum diesel can help in controlling air pollution and easing the pressure on scarce resources without significantly sacrificing engine power and economy. However, many further researches about optimization and modification on engine, low temperature performances of engine, new instrumentation and methodology for measurements, etc., should be performed when petroleum diesel is substituted completely by biodiesel.

Contents

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1. Introduction

The resources of petroleum as fuel are dwindling day by day and increasing demand of fuels, as well as increasingly stringent regulations, pose a challenge to science and technology. With the commercialization of bioenergy, it has provided an effective way to fight against the problem of petroleum scarce and the influence on environment.

Biodiesel, as an alternative fuel of diesel, is described as fatty acid methyl or ethyl esters from vegetable oils or animal fats. It is renewable, biodegradable and oxygenated. Although many researches pointed out that it might help to reduce green house gas emissions, promote sustainable rural development, and improve income distribution, there still exist some resistances for using it. The primary cause is a lack of new knowledge about the influence of biodiesel on diesel engines. For example, the reduce of engine power for biodiesel, as well as the increase of fuel consumption, is not as much as anticipated; the early research conclusions have been kept in many people's mind, that is, it is more prone to oxidation for biodiesel which may result in insoluble gums and sediments that can plug fuel filter, and thus it will affect engine durability.

Although there are an increasing number of literatures to research engine performances and its emissions when using biodiesel, especially in this decade, only fewer people have analyzed and reviewed them. A previous review published by Graboski and McCormick [1] in 1998 could not reflect the new research achievements this decade, and the newer review finished by Lapuerta et al. [2] in 2008 did not include knowledge about engine durability, and about 20% literatures before 2000 year was cited to clarify the effect of biodiesel on engine performances and emissions. But the other newer one, written by Basha et al. [3] in 2009, seems unconvincing for professional (especially about the review on the long-term biodiesel engine test) and uneasy for non-professional to read.

In this work, the literatures indexed by highly rated journals in scientific indexes were cited preferentially since 2000 year, as well including some SAE technical papers. According to analysis and summary in this work, it is helpful (1) for researchers and engine manufacturers to develop the further researches related to optimize and readjust biodiesel engine and its relevant systems; and (2) for governments to design new energy policies to impel the use of biodiesel in the light of environmental costs; and (3) for private users to understand profits for using biodiesel, and enhance consciousness of environmental protection. Engine performances for biodiesel such as power performance, economy performance and durability are introduced and summarized at considerable length in Section 2. Then, the regulated emissions such as PM (particulate matter), NO_x (nitrogen oxides), CO (carbon monoxide), HC (hydrocarbon), and CO_2, and non-regulated emissions such as aromatic and polyaromatic compounds and carbonyl compounds, are listed to survey detailedly in Section 3. Finally, conclusions are drawn and further researches are pointed out.

2. Engine performances

2.1. Power performance

2.1.1. Effect of biodiesel on engine power

In this work, only the literatures illustrating the effect of biodiesel on engine power and/or torque are suveryed. It is shown in Table 1 that there are 27 literatures to study the effect of pure biodiesel on engine power, and 70.4% of them agreed that, with biodiesel (especially with pure biodiesel), engine power will drop due to the loss of heating value of biodiesel [4–22]. However, the results reported show some fluctuation. Some authors [4–20] found that the power loss was lower than expected (the loss of heating value of biodiesel compared to diesel) because of power recovery. Utlu and Koçak [8] found that the respective average decrease of torque and power values of WFOME (waste frying oil methyl ester) was 4.3% and 4.5% due to higher viscosity and density and lower heating value (8.8%). Hansen et al. [11] observed that the brake torque loss was 9.1% for B100 biodiesel relative to D2 diesel at 1900 rpm as the results of variation in heating value (13.3%), density and viscosity. And Murillo et al. [10] found that the loss of power was 7.14% for biodiesel compared to diesel on a 3-cylinder, naturally aspirated (NA), submarine diesel engine at full load, but the loss of heating value of biodiesel was about 13.5% compared to diesel.

The same range between power loss and the decreased heating value was reported in [22]. The authors found that the torque and power reduced by 3–6% for pure cotton seeds biodiesel compared to diesel, and they claimed that the heating value of biodiesel was less 5% than that of diesel. But they contributed to the difficulties in fuel atomization instead of the loss of heating value.

It was reported that there was no significant difference in engine power between pure biodiesel and diesel [23–28]. For instance, Lin et al. [23] found that the maximum and minimum differences in engine power and torque at full load between PD (petroleum diesel)

Table 1
Statistics of effects of pure biodiesel on engine performances and emissions.

	Total number of References	Increase		Similar		Decrease	
		Number	%	Number	%	Number	%
Power performance	27	2	7.4	6	22.2	19	70.4
Economy performance	62	54	87.1	2	3.2	6	9.7
PM emissions	73	7	9.6	2	2.7	64	87.7
NO_x emissions	69	45	65.2	4	5.8	20	29.0
CO emissions	66	7	10.6	2	3.0	57	84.4
HC emissions	57	3	5.3	3	5.3	51	89.5
CO_2 emissions	13	6	46.2	2	15.4	5	38.5
Aromatic compounds	13	–	–	2	15.4	11	84.6
Carbonyl compounds	10	8	80.0	–	–	2	20.0

The statistics on durability of biodiesel engine is shown in Table 2.

and 8 kinds of VOME (vegetable oil methyl ester) fuels were only 1.49% and −0.64%, 1.39% and −1.25%, respectively, due to higher viscosity, higher BSFC (brake specific fuel consumption), higher oxygen content and higher combustion rate of biodiesel. And Qi et al. [25] reported this trend, the explanation is that engine delivers fuel on volumetric basis and biodiesel density is higher than that of diesel, which supplies more biodiesel to compensate the lower heating value.

Of course, it was reported that there were surprising increases in power or torque of engine for pure biodiesel [29,30]. Song and Zhang [29] observed that the engine brake power and torque increased with the increase in biodiesel percentage in the blends. And they contributed to the higher oxygen content, the higher biodiesel consumption, an advance of injection timing and a shorter ignition delay time. But it is the most unbelievable that the increased power of the pure biodiesel could reach 70% relative to diesel fuel from Fig. 1 showed in the literature [30], as the results of the higher fuel mass flow of the denser and more viscous biodiesel and its blends.

2.1.2. Factors of effect on biodiesel engine power

2.1.2.1. Content of biodiesel. Content of biodiesel blended with diesel results in the difference in engine power performance, which has become the commonsense.

Engine power will decrease with the increase of content of biodiesel [4–7,10,11,13–15,31–35]. For example, Carraretto et al. [14] found that the increase of biodiesel percentage in the blends resulted in a slight decrease of both power and torque over the entire speed range for different blends (B20, B30, B50, B70, B80, B100) of biodiesel and diesel on a 6-cylinder DI diesel engine. Aydin et al. [4] reported that the torque was decreased with the increase in CSOME (cottonseed oil methyl ester) in the blends (B5 B20 B50 B75 B100) due to higher viscosity and lower heating value of CSOME. And Murillo et al. [10] observed that increasing the amount of biodiesel in the fuel decreased engine power on a single-cylinder, 4-stroke, DI and NA diesel engine.

Some authors [21,29,30,36,37] found that the use of biodiesel blends did not meet this trend. For instance, Gumus and Kasifoglu [36] found the power increased with the addition of biodiesel content in the blends until the B20 blend and reached a maximum value, when the biodiesel content continued to increase in the blends, the power would decrease below that of the diesel fuel and reached minimum value for B100, which was obtained on a single-cylinder, 4-stroke, DI, air-cooled (AC) diesel engine. Likewise, Usta et al. [37] showed that the power initially increased with the addition of biodiesel, reached a maximum value, and then decreased with further increase of the biodiesel content.

Of course, a small number of authors thought that the power between biodiesel blends appeared similar. Pal et al. [38] found the variation of brake power was almost negligible for all types of Thumba oil biodiesel blends (B10, B20, B30) within a whole engine speed range on a 4-cylinder, DI, water-cooled (WC) diesel engine. Lapuerta et al. [26] obtained that there were very small variations in effective torque among waste cooking oil methyl ester and ethyl ester (WCOM and WCOE) and their blends (WCOM30, WCOM70, WCOE30, WCOE70) on a 4-cylinder, 4-stroke, turbocharged (TU), intercooled, DI, 2.2 L Nissan diesel engine. Also, the similar results were obtained by Ghobadian et al. [24] who tested the waste cooking biodiesel blends (B10, B20, B30, B40, B50) at full load on a 2-cylinder, 4-stroke diesel engine.

2.1.2.2. Properties of biodiesel and its feedstock. Properties of biodiesel, especially in heating value, viscosity and lubricity, have an important effect on engine power.

Heating value of fuels is an important measure of its releasing energy for producing work. So, the lower heating value of biodiesel is attributed to the decrease in engine power, which is commonly agreed by the authors who reported that engine power reduced with biodiesel.

Higher viscosity of biodiesel, which enhances fuel spray penetration, and thus improves air–fuel mixing, is used to explain the recovery in torque and power for biodiesel related to diesel in some literatures [23,39,40]. However, a few authors [4,8] thought that the higher viscosity results in the power losses, because the higher viscosity decreases combustion efficiency due to bad fuel injection atomization.

High lubricity of biodiesel might result in the reduced friction loss and thus improve the brake effective power. Ramadhas et al. [41] used this argument to explain the recovery in the rated power, although they did not explain how this improvement occurred.

There may be no significant effect of biodiesel feedstock on engine power. Lin et al. [23] mentioned above, found that the maximum and minimum differences in engine power and torque at full load between the PD and VOMEs were only 1.49% and −0.64%, 1.39% and −1.25%, respectively, which indicates that using VOME yields the same engine power as PD at full load conditions as well as at average load conditions for various engine speeds. Additionally, Ozsezen et al. [6], who compared waste palm oil and canola oil methyl esters (WPOME and COME) with diesel on a WC, NA, DI diesel engine at 1500 rpm under full load, and Oğuz et al. [28], who compared biodiesel from soybean, rapeseed and palm on a 3-cylinder, 4-stroke, 30 kW diesel engine, all found that there were no significant differences in power.

2.1.2.3. Engine type and its operating conditions. Factors on engine type and its operating conditions, such as engine load, engine speed, injection timing and injection pressure, etc., have been studied to illustrate their effects on biodiesel engine power.

Karabektas [7] compared the naturally aspirated (NA) conditions to the TU conditions on a 4-stroke, DI diesel engine and found that the mean increase in torque for biodiesel with the TU conditions was determined as 18.7% with regard to the NA conditions.

Haşimoğlua et al. [42] observed that the engine power and torque were increased by the application of the low heat rejection (LHR) engine, mainly due to the increased exhaust gas temperatures before the turbine inlet in LHR engine. Similarly, the comparison of power between the coated engine (CE) and uncoated engine (UE) was conducted by Hazar [5]. The author reported that the increase values in power for the CE are 3.5% and 1.6% for pure biodiesel and its blend, respectively.

Although the basic trends of engine power performance with load or speed were similar for biodiesel engine and diesel engine, there existed offset of maximum value of torque and power for biodiesel compared to diesel [4,15,24,25,36].

Injection pressure and injection timing affect engine performance. Although the power and torque were not measured directly, Banapurmath et al. [43] compared the effect of three injection timings (19, 23 and 27 °CA) and the different injection of pressure (IOP) on the brake thermal efficiency (BTE) for HOME (Honge oil methyl ester). They found that there was an improvement in the BTE for biodiesel by retarding injection timing, and that the highest BTE occurred at 260 bar among all the IOPs tested because atomization, spray characteristics, and mixture with air were better with higher injection, which result in improved combustion. And, Sharma et al. [44] concluded that the difference of BTE between biodiesel and pure diesel tended to increase with the increase of fuel injection pressure. Carraretto et al. [14] observed that power and torque were increased up to almost pure diesel levels by reducing injection advance because it was possible to optimize combustion, and by improving performances especially at low and medium speed with respect to nominal injection advance operation.

2.1.2.4. Additives. A few authors investigated the effect of additives on the power performance of biodiesel. Although Keskin et al. [27] found no significant effect of Mo and Mg as the additives into B60 biodiesel blend on engine torque and power tested on a single-cylinder, 4-stroke, AC, DI diesel engine, Gürü et al. [45] obtained the positive effect of a blend of 10% chicken fat biodiesel and diesel fuel with an additive 12 μmol Mg, which improved the performance of biodiesel in flash point, viscosity and pour point. And Kalam and Masjuki [46] found that B20X with 1% 4-nonyl phenoxy acetic acid (NPAA) additive produced higher brake power over the entire speed range in comparison to B20 and B0 (diesel), and the maximum brake power obtained at 2500 rpm is 12.28 kW from B20X followed by 11.93 kW (B0) and 11.8 kW (B20). They contributed to the increase of fuel conversion efficiency by improving fuel ignition and combustion quality due to the effect of fuel additive in B20 blend.

2.1.3. Summary

Based on analysis above, the following conclusions are available:

(1) The use of biodiesel will lead to the reduced engine power, which can be accepted commonly. Additionally, it can be concluded that, when using biodiesel, particularly for the blend fuel including a small portion of biodiesel, it is not easy for drivers to perceive power losses during partial load of practical driving.
(2) The main reason for power loss is based the reduced heating value of biodiesel compared to diesel, this viewpoint is agreed comprehensively. The high viscosity and high lubricity of biodiesel also have certain effects on engine power, but there is no unanimous conclusion. In addition, it seems that feedstock of biodiesel is not an important factor which affects engine power.
(3) In the case of no modification to an engine, the injection feature of biodiesel is influential to engine power. It is necessary to further research the relationship between injection pressure and injection timing and engine power in order to obtain the optimal match when using biodiesel.
(4) An additive used to improve ignition and combustion performances of biodiesel is advantageous to power recovery of biodiesel engine.

2.2. Economy performance

2.2.1. Effect of biodiesel on engine economy

Most of researches (up to 87.1%, shown in Table 1) [4,6–8,10–12,14,15,19–21,23–30,33,34,37,41,42,44–72] agreed that the fuel consumption of an engine fueled with biodiesel becomes higher because it is needed to compensate the loss of heating value of biodiesel.

Among of them, some authors [6,7,20,21,41,42,47,54,69,70] presented that the increase in fuel consumption is basically similar to the loss of heating value for biodiesel compared to diesel. For example, Armas et al. [47] found that the BSFC of B100 biodiesel, which the LHV (low heating value) was 12.9% lower than that of BP15, had increased approximately 12% compared to the BP15 on a 2.5 L, DI and TU, common-rail diesel engine operated at 2400 rpm and 64 N m. And Haşimoğlu et al. [42] obtained the higher BSFC 13% but LHV 13.8% for biodiesel compared to diesel on a 4-cylinder, TU and DI diesel engine. Lin et al. [23] investigated the BSFC of 8 kinds of VOME on a single-cylinder, 4-stroke, WC, DI diesel engine and found the diesel engine had a higher BSFC in the range of 9.45–14.65% than that of diesel, which was similar to the LHV (12.9–16%) of those VOMEs.

Some authors [4,14,15,52,71–72] found that the increased ratio of fuel consumption for biodiesel was more than the loss ratio of its heating value. For instance, Luján et al. [52] reported that the difference in fuel consumption between diesel and pure biodiesel was 18.5% in mass, and was reduced to 13.5% in volume because of higher density of biodiesel. Labeckas and Slavinskas [71] observed that the BSFC of pure biodiesel (lower 12.5% in LHV) increased by 18.7% at 1800 rpm and 23.2% at 2200 rpm. And it was obtained in [4] that the increased BSFC was above 18% for B100 biodiesel compared to diesel although the loss of heating value was about 8% for biodiesel.

Of course, a few literatures [22,36,44] reported that the increased fuel consumption was less than the loss of heating value for biodiesel. For example, Gumus and Kasifoglu [36] found that the brake specific energy consumption (BSEC) for B100 was higher than that of diesel maximal 4.8% due to the lower heating value (about 7.4%) and the higher viscosity.

On the contrary, it was reported in [9,13,16,29,38,73] that fuel consumption was decreased for biodiesel compared to diesel. For instance, Ulusoy et al. [16] observed that the fuel consumption of frying oil biodiesel was 2.43% less than that of diesel on a 4-cylinder, 4-stroke 46 kW diesel engine.

A few other authors [74,75] found no significant difference between pure biodiesel and diesel. Dorado et al. [74] experimented biodiesel from waste olive oil on a 3-cylinder 2.5 L engine with eight stable test models, and found no significant differences in BSFC compared with diesel. And it was observed by Sahoo et al. [75] that BSEC is slightly higher for B100 at lower loads and remains same at higher loads.

2.2.2. Factors of effect on biodiesel engine economy

2.2.2.1. Biodiesel content. Many authors compared the blends with different content biodiesel. In [14,15,32,41,47–49,51–54,69,71,76,77], authors believed that, with increasing the content of biodiesel, engine fuel consumption will increase. For example, Godiganur et al. [49] observed this trend after they tested B10, B20, B40, B60, B80 and B100 fuels on a 3-cylinder, 4-stroke, AC, DI and NA diesel engine. Raheman and

Phadatare [15] tested karanja methyl ester (B100) and its blends (B20, B40, B60 and B80) on a single-cylinder, 4-stroke, DI, WC diesel engine, and observed the same trend.

Although a few authors [13,24,30] agreed that there existed effect of biodiesel content on BSFC, they found no similar trend and observed that the effect of the blend(s) with certain content biodiesel might be highlighted. Reyes and Sepúlveda [13] found that B40 has the minimum SFC (specific fuel consumption) of all the blends (B20, B40, B60, B80 and B100) tested on a 6-cylinder, 4-stroke and WC diesel engine. Ghobadian et al. [24] reported that the mean value of engine SFC of 10%, 20%, 30%, 40% and 50% blends for various engine speeds are 4.0%, 0.8%, 0.6%, −2.2% and 1.4% higher than net diesel fuel respectively. Especially, it can be observed that there were big variation among the blends 75D, 50D, 25D and 100O (pure biodiesel) fueled on a single-cylinder, DI diesel engine tested by Al-Widyan et al. [30], although the reference fuel resulted in larger fuel consumption per unit energy output over the whole speed range compared to all other blends.

Of course, there are very few researches that showed an opposite trend [38,73]. This trend can be observed from results tested by Pal et al. [38], who compared the B10, B20 and B30 biodiesel from Thumba oil with the diesel on a 4-cylinder, DI and WC diesel between the engine speed ranges of 2000–4500 rpm. And Mahanta et al. [73] observed that B15 and B20 biodiesel from pongamia oil results in slight reduction in fuel consumption, compared with the diesel, and minimum fuel consumption was obtained with B20 throughout the entire loading range.

2.2.2.2. Biodiesel properties and its feedstock. The different biodiesel feedstock could cause the difference in engine economy [6,13,23,53]. Sahoo et al. [53] compared the BSFC of jatropha, karanja and polanga oil based methyl esters with diesel on a 3-cylinder WC tractor engine. They reported that an increase in BSFC for KB20, KB50 and KB100 was in the range of 2.68%, 5.84% and 13.31% with respect to diesel at rated speed, 2.86%, 6.0%, 12.37%, 2.59%, 5.84% and 13.31% for JB20, JB50, JB100, PB20, PB50 and PB100, respectively. Lin et al. [23], as mentioned above, found that PKOME (palm kernel oil methyl ester) and POME (palm oil methyl ester), which have particularly low volumetric calorific values and shorter carbon-chains, result in their BSFC being significantly higher than that of the other VOME fuels. Reyes and Sepúlveda [13] observed the essential differences between the crude biodiesel and refined biodiesel, and contributed to color residues and a possible small amount of unconverted glycerides in the crude biodiesel which may alter combustion properties with respect to the refined biodiesel.

As for the properties of biodiesel, the lower heating value, higher density and higher viscosity play primary role in engine fuel consumption for biodiesel. Most of authors, who agreed that fuel consumption increased for biodiesel compared to diesel, contributed to the loss in heating value of biodiesel. Of course, some authors [19,25,49,51,78] only explained the increased fuel consumption as the result of higher density of biodiesel, which causes the higher mass injection for the same volume at the same injection pressure. And this argument also cited by authors in [7,37,52]. However, some authors interpreted the increase in fuel consumption of biodiesel because of combination of properties of biodiesel. For example, it is attributed to lower heating value and higher density in [8,14,60], to the combined effect of higher viscosity and lower heating value of biodiesel in [4,41,77], and to the interaction of higher density, higher viscosity and lower heating value of biodiesel in literatures [23,29].

2.2.2.3. Engine type and its operating conditions. Biodiesel engine economy is affected by engine type and its operating conditions, such as load, speed, and injection timing and injection pressure.

Karabektas [7] found that the BSFC for biodiesel with the TU operation is averagely 17.7% lower than that of the NA operation on a 4-stroke, DI diesel engine. They explained that this reduction was mainly caused by improvement in fuel atomization, air–fuel mixing and combustion characteristics of the fuel due to the high air temperature and increased air charge in the cylinder of engine with the TU operation. Haşimoğlua et al. [42] observed that the SFC for the LHR diesel, which was modified by the coated cylinder head and valves, decreased approximately 4% compared to the standard engine and contributed to the increased in-cylinder temperatures due to heat insulation. Similarly, the comparison of BSFC between the CE and UE was conducted by Hazar [5]. The author reported that the decrease in BSFC was 4.9%, 5.8%, 4.7% and 8.0% for diesel, CME100 (100% cooking oil methyl ester), CME20 and CME35 in the CE compared with the UE, respectively.

With increase in load, the BSFC of biodiesel decreases [15,32,41,49,51,61,77]. One possible explanation for this trend could be the higher percentage of increase in brake power with load as compared to fuel consumption. But Gumus and Kasifoglu [36] showed that the BSEC initially decreased with increasing of engine load until it reached a minimum value and then increased slightly with further increasing engine load for all kind of fuels (B5, B20, B50, B100 and diesel). Further, it was reported in [57] and [37] that the increase in BSFC values at full load was higher than those at partial loads for biodiesel compared to diesel.

Pal et al. [38] compared three Thumba oil biodiesel blends (B10, B20 and B30) and diesel on a 4-cylinder, DI and WC diesel engine covering a wide range of engine speed. The BSFC initially decreased sharply with increase in speed up to 2000 rpm and then BSFC remains approximately constant between 2000 rpm and 4000 rpm. For the range more than 4000 rpm, the BSFC increased sharply with speed. Hazar [5] reported the similar trend, the BSFC increased at low speed, decreased at medium speed, and increased again at high speed in both the UE and the CE for all test fuels (CME20, CME35, CME100 and diesel). However, it was showed in [46,59] that the BSFC increased with the increase in engine speed.

The effect of injection timing and injection pressure on fuel consumption for biodiesel was investigated experimentally. Carraretto et al. [14] found that the fuel consumption was reduced by reducing injection advance because it is possible to optimize combustion, and by improving performances especially at low and medium speed with respect to nominal injection advance operation. Tsolakisa et al. [60] retarded injection timing by 3 °CA on a single-cylinder, NA, AC, DI diesel engine equipped with pump–line–nozzle type fuel injection system, and they observed that the BSFC was increased for both B50 and pure RME (rapeseed methyl ester), although the increase was not significant. Various aspects of engine performances using B20 were studied by Sharma et al. [44] on a single-cylinder DI diesel engine at different injection pressures. And they obtained that the BSFC was slightly higher at all loads for B20 compared with pure diesel but the same values of BSEC indicated that the efficiency which energy was utilized was the same at an injection pressure of 1.57 kN/cm^2.

2.2.2.4. Additives. A few authors investigated the effect of additives on fuel consumption. Ryu [50] evaluated the effect of antioxidants in biodiesel on performances and emissions of an unmodified 4-cylinder, 4-stroke, WC, indirect-injection (IDI) diesel engine and found that the BSFC of biodiesel fuel with antioxidants decreased more than that without antioxidants, although no specific trends were detected according to the type or amount of antioxidants. Kalam and Masjuki [46] found that the lowest SFC was obtained from B20X with 1% 4-NPAA additive followed by B0 and B20 fuels and the average SFC values all over the speed range were 405, 426.69 and 505.38 g/(kWh) for B20X, B0 and B20 fuels, respectively. Gürü et al. [45] added 12 μmol Mg into a blend of 10% chicken fat biodiesel and diesel fuel (B10) to improve the performance of biodiesel in flash point, viscosity and pour point and found that the SFC was increased only by 5.2% at the maximum torque speed of 2200 rpm for biodiesel fuel. Additionally, Keskin et al. [27] found that the SFC of B60 with metal-based additives (Mo or Mg) slightly decreased and the SFC values obtained with B60-8Mo (8 μmol) were lower than the other test fuels. And they explained that this change is due to the catalyst effect of metal-based additives and better fuel properties of biodiesel which increase the thermal efficiency of the engine.

2.2.3. Summary

Based on analysis above, the following conclusions are available:

(1) The vast majority of authors agreed that fuel consumption increase when using biodiesel, but this trend will be weakened as the proportion of biodiesel reduces in the blend fuel with diesel.
(2) The increase in biodiesel fuel consumption is mainly due to its low heating value, as well as its high density and high viscosity. The different feedstock of biodiesel with different heating value and carbon chain length, or different production processes and quality, also have an impact on engine economy.
(3) The use of a turbocharged engine or a low heat release engine, will improve biodiesel engine economy. Engine operating conditions, such as load, speed, injection timing and injection pressure, etc., are also influential to biodiesel engine economy, and although these influences are not essential, the further study on these conditions should be executed to improve engine and its control systems in order to obtain the optimal match.
(4) Additives used to improve properties of biodiesel may further improve combustion performance of biodiesel engine, thus it will promote economy, and meanwhile this will also improve engine power.

2.3. Durability

2.3.1. Durability of biodiesel engine

Only a small portion of researchers dedicated to the durability tests of biodiesel engine, because it is more time-consuming and costly than those in engine power, economy and emissions. For durability studies, the following aspects were focused on: carbon deposit, engine wear and problems in fuel system. The overview on durability test for biodiesel and its blends was shown in Table 2.

Carbon deposits are related to soot formation during combustion of fuel in the engine and fuel oxidation. For biodiesel, it has lower soot formation, which is consistent to the reduced PM emissions of biodiesel. This argument has been verified by most of authors who have undertaken this research. Sinha and Agarwal [79] investigated the effect of B20 (20% rice bran oil methyl ester blend with mineral diesel) biodiesel on wear of in-cylinder engine components during 100 h tests. It was reported that carbon deposits on the cylinder head, injector tip, and piston crown of biodiesel engine was significantly lower compared with mineral diesel engine due to the lower soot formation during combustion of biodiesel. It is also reported in [80,81] that biodiesel improves carbon deposits in combustion chamber. Of course, Dorado et al. [82] found that there was no visual difference in carbon deposits between biodiesel from waste olive oil and No.2 diesel on a 3-cylinder, WC, DI, 2.5 L engine at 8–15 kW and 1800–2100 rpm for 50 h. And Pehan et al. [83] observed the similar carbon deposits in combustion chamber between the pute biodiesel from rapeseed oil and D2 diesel on a 6-cylinder, WC, DI, 11 L engine for 110 h.

Biodiesel is effective in reducing friction when used as an additive in diesel fuel at about lower level. The results are obtained in laboratory tests using the four-ball wear tester [46,84,85]. This conclusion was validated by the authors in [79,80,81,86,87]. For example, Agarwal [80], based on tribological investigations of the lubricating oil, found that the amount of various possible contaminants such as wear debris, soot, resinous compounds, oxidation products, and moisture content was lower in the case of lubricating oil drawn from the biodiesel-fueled engine compared with the diesel-fueled engine. The improved performance of the biodiesel-fueled system is possibly attributed to the inherent lubricity of biodiesel, resulting in lower wear of vital moving components. And all the tribological investigations at viscosity, flashpoint, pentane and benzene insolubles, ZDDP (a wear protection additive) deleption, ferrograms, except oxidation stability of lubricating oils, decisively proved that the lubricating oil from the biodiesel-fueled system reflected a better condition of the engine parts. Biodiesel thus proves to be a strong candidate for partial replacement of mineral diesel fuel in existing diesel engines. And, Agarwal et al. [81] illustrated that wear metals debris such as Fe, Cu, Al, Pb reduced with increasing biodiesel of palm oil into blends, which produced the lower level of wear concentration than that of the ordinary diesel, and the reason is the effect of the corrosion inhibitor in fuel and lube oil that control corrosion as well as oxidation in lubricating oil. Especially, Kaul et al. [88], who estimated the corrosion behavior of several biodiesel during long duration static immersion test, showed there are no corrosion on piston metal and piston liner for biodiesel from Mahua and Karanja. However, there is an exception. Fontaras et al. [54] reported that the wear of some vital parts seems to be higher for B50 and B100 than that of diesel fuel because iron and copper content appeared to be increased by 67% and 272%, respectively. But, the wear of piston was reduced by 34% according to the measurement of aluminium. The possible explanation given by the authors is that (1) high biodiesel concentrations partly dissolve the lubricant, resulting in the increased friction coefficient of engine moving parts; (2) some acidic components are formed possibly during combustion process and can be dissolved in the lubricant. Most of papers reported that the use of biodiesel or its blends can help to improve carbon deposit and engine wear.

Based on durability of biodiesel engine, biodiesel can overcome durability concerns existing with vegetable oils such as fuel filter plugging, injector coking [80,81]. Pehan et al. [83] verified that, when using biodiesel from rapeseed oil, it was cleaner for injectors than that of D2 fuel on a 6-cylinder WC, DI, 11 L engine after 110 h test.

2.3.2. Summary

Although there are the negative reports in wear, it is expectable that the use of biodiesel favors to improve durability of engine for biodiesel due to the lower soot formation and the inherent lubricity, compared with diesel. However, the further studies on biodiesel engine endurance tests need be executed to make clear the reason and mechanism of wears, because the studies on these aspects are not enough so far.

3. Emissions

3.1. PM

3.1.1. PM emissions of biodiesel

It is overwhelming argument (87.7%, see Table 1) that the use of biodiesel instead of diesel causes the reduce in PM emissions [5,6,8,9,12,13,15,16,19,20,23,25–29,31–33,36,38,41,44,45,48,50,52,53,55,56,60,61,63–65,68,70,72,75,76,78,89–111]. Wu et al. [89] investigated the emission performance for five pure biodiesels on a Cummins ISBe6 DI engine with turbocharger and intercooler, and found different biodiesels reduced PM emission by 53–69% on

Table 2
Overview on durability of biodiesel and its blends engine.

Content and feedstock	Ref. diesel	Engine tested	Operation conditions	Duration	Test results	References
20% Rice bran oil	Conventional	4-Cylinder, NA, WC, DI	Ten nonstop running cycles	100 h	CD: significantly lower; Wear: lower	[79]
20% Linseed oil	Agricultural	1-Cylinder, WC, portable	1500 rpm	512 h	IJ: no coking, no filter plugging; Wear: lower	[80,81]
20% Linseed oil	Agricultural	1-Cylinder, WC, portable	1500 rpm	512 h	Wear: lower	[86]
100%, 15%, 7.5% palm oil	Conventional	4-Cylinder, NA, WC, IDI, 1.8 L	2000 rpm	100 h	The reduction of wear with the increased content of biodiesel	[87]
100%, 50% soybean oil	No. 2 (EN 590)	TC, DI, 1.9 L	NEDC driving cycle	1350 km, 750 km	Wear: higher except piston	[54]
100% Waste olive oil	No. 2 (EN-590)	3-Cylinder, WC, DI, 2.5 L	8–15 kW and 1800–2100 rpm	50 h	CD: no visual difference; Wear: no visual difference	[82]
100% rapeseed oil	No. 2 (EN 590)	6-cylinder WC, DI, 11L	–	110 h	CD: similar; IJ: cleaner than that of D2	[83]
100% Mahua, Karanja oil	High speed diesel	–	Static immersion test at ambient temperature	300D	No corrosion on piston metal and piston liner	[88]

CD is the carbon deposit, IJ is the injector.

average compared with the diesel fuel. Lin et al. [23] also observed that there was significant reduction (ranging form 50% to 72.73%) in the smoke emission for 8 kinds of VOME fuels compared with PD. In addition, it was reported in [6,16,19,25,52,53,64,65,95] that the decreased PM value were over 50% for biodiesel in regard with diesel. Especially in the literature [105], there existed the extreme reduce in PM for biodiesel by 75% and 91%, respectively.

A small portion of authors found that there was no difference in PM emissions for biodiesel relative to diesel [67,77], or even there was a bit increase [4,47,112–114]. Most of the authors contributed these phenomena to higher viscosity of biodiesel which causes fuel atomization worse and combustion quality deterioration [4,67,77,112–114]. But Armas et al. [47] considered that the increased PM was due to the unburned or partially burned HC emissions. These HC will condense and be absorbed on the PM surface, thus result in the increase of SOF (soluble organic fraction) which is the main component of PM.

3.1.2. Factors of effect on PM emissions for biodiesel

3.1.2.1. Content of biodiesel. The contrast experiments were implemented with different contents of biodiesel blends, including 2 kinds blends compared in [31,48,54,65,72,76], 3 kinds in [5,26,52,53,60,97], and 4 or above 4 kinds in [4,13,15,29,41,57,61,75,93,106].

Generally, PM emissions decrease remarkably with increasing in biodiesel content in blends. Sahoo et al. [53] compared the effect of the blending ratio of 20%, 50% and 100% for 3 kinds of jatropha, karanja and polanga based biodiesel on smoke emissions, and found the use of KB20, KB50 and KB100 caused a reduction in smoke in the range of 28.96%, 44.15% and 68.83% with respect to diesel at a rated speed, respectively. Similarly, decrease in smoke for JB20, JB50, JB100, PB20, PB50 and PB100 are 28.57%, 40.9%, 64.28%, 29.22%, 44.15% and 69.48% was observed at the rated speed, respectively. Luján et al. [52] showed a reduction in PM emissions of 32.3%, 42.9% and 53% for B30, B50 and B100 respectively, which is obtained from after-treatment on a HSDI (high speed direct injection) 4-cylinder, 1.6 L, turbo diesel engine. Additionally, Canakci [65] showed that the smoke numbers of No. 2 diesel fuel, No. 1 diesel fuel, SME20 (20% soybean oil methyl ester), and SME100 were 1.09, 1.06, 0.89, and 0.42, respectively. Haas et al. [72] found that PM emissions reduced by 20% and 50% for 20% blends and 100% biodiesel, respectively.

However, several authors reported the reverse change with the increased proportion of pure biodiesel. Kalligeros et al. [97] experimented the effect of the blends of 10%, 20% and 50% for two biodiesel from sunflower and olive oil on a single cylinder, IDI, stationary diesel engine, and found the maximum PM emissions for the 10% blends and the minimum PM emissions for the 50% blends at the different loads. Also, it was reported in [54] that the PM emissions for B50 were higher than that of B100 at 7 kinds of driving cycles. Similarly, Aydin and Bayindir [4] found that the higher content of biodiesel in the blends caused the more PM emissions and contributed the reason to the higher density and the higher viscosity which deteriorates the fuel atomization. Lapuerta et al. [106] obtained that, there were higher reduce in PM for the 25% biodiesel blends than that of 50%, 70% and 100% biodiesel content.

However, a few literatures [15,29,75] showed there was no order for the effect of biodiesel content on PM emission, and authors did not give a convincing and reasonable explanation.

3.1.2.2. Properties of biodiesel and its feedstock. Many authors contributed the reduce in PM emissions to the higher oxygen content in biodiesel, which causes combustion more complete, and further promote the oxidation of soot. Particularly, Frijters and Baert [115] tested 14 biodiesel blends with oxygenates and found that it had a good relationship between PM emissions and fuel oxygen content.

The lack of aromatic and sulphur compounds further contribute to reduction in PM emissions [26,29,52,71,116,117]. Yoshiyuki [116] investigated the effects of fuel cetane number and aromatics on combustion process and emissions of a DI diesel engine, and reported that PM emissions increased at high load when the aromatic content was increased with constant cetane number.

As for the effect of cetane number of biodiesel, Yoshiyuki [116] showed that reducing cetane number resulted in the decrease of particulate at high load. Korres et al. [57] reported that biodiesel addition to JP-5 reduced PM emissions as compared to the JP-5 alone and this was attributed to the higher cetane number of biodiesel from soybean oil compared to the reference diesel and improved combustion efficiency. This argument was approved in [29,118].

Higher density and viscosity of biodiesel could affect the volatilization and atomization processes, and further deteriorate combustion in chamber. This viewpoint was applied to the explanation of the increased PM emissions for B75 and B100 fuels in [4], which also appeared in [29,89].

Advance in combustion for biodiesel, as a result of the higher cetane number [31], and advance of start of injection of biodiesel due to the higher density and viscosity and the lower compressibility [6,26,95], prolong the residence time of soot particle in the high temperature environment, and thus further promote the oxidation in the presence of oxygen [104]. It was reported by Kidoguchi et al. [116] that fuels with longer ignition delay by keeping the aromatic content constant, exhibited lower particulate emissions and higher NO_x at high loads. However, it is believed that this effect is small [115].

Although biodiesel has a higher distillation temperature, the lower boiling point of biodiesel enhances the probability of the lower soot or tar formed from the heavy HC compounds [98].

Some authors [13,23,26,53,76,89,97,105,113,114,119] investigated the effect of biodiesel feedstock on PM emissions. Lin et al. [23], mentioned above, compared 8 kinds of VOME fuels which had a significant reduction in PM emissions (ranging from decreases of 50–72.73%), but PKOME and POME were particularly effective in reducing PM emissions (by 72.73% and 59.09%, respectively) as the result of shorter fatty acid carbon-chain lengths. Likewise, Wu et al. [89] showed that the biodiesels, which reduced PM in descending order, were WME (waste cooking oil methyl ester), PME (palm oil methyl ester), CME (cottonseed methyl ester), RME (rapeseed methyl ester) and SME (soybean methyl ester) due to the interaction of different oxygen content, viscosity and cetane number. In literatures [26,76], the different authors compared the methyl ester and ethyl ester from Karanja oil and waste cooking oil, respectively. And they all concluded that the smoke emission from ethyl ester is more than that of methyl ester due to the presence of more oxygen for methyl ester. Although the PM emissions of 3 kinds of biodiesels JOME (jatropha methyl ester), SOME (sesame oil methyl ester) and HOME were higher than the reference diesel, Banapurmath et al. [113] reported that the smoke opacity for JOME was higher in comparison with other fuels due to its heavier molecular structure and higher viscosity.

Of course, a few authors found no relationship between PM emissions and biodiesel feedstock. Canakci and Van Gerpen [68] investigated two biodiesels from cooking oil and soybean oil and a traditional diesel on two same diesel engines. PM emissions all reduced for two biodiesels compared to the diesel, but there was no difference in PM emissions between the two biodiesel. Haas et al. [72] tested biodiesels with different saturation levels on a 6-cylinder DI engine. The PM emissions reduced by 50% for all biodiesel, and had nothing to do with their saturation levels. However, they all concluded that the main factors affecting PM formation is the oxygen content of biodiesel.

3.1.2.3. Engine type and its operating conditions. A few conferences collected studied comparatively the effect of engine types such as the NA and TU, STD and the LHR engines, but only the literature [114] presented clearly that all the fuels without LHR operation resulted in higher smoke emission due to relatively incomplete combustion, the others found no difference between PM emissions or did not do research in this area. The large amount of researches focused on the engine operating conditions, such as load, speed, EGR, injection timing, low temperature start.

Engine load plays a significant role in PM emissions of biodiesel. Many researches showed that PM emissions increase as load increases [12,19,26,28,56,61,71,78,93,95,106,120]. Raheman and Ghadge [61] tested mahua biodiesel and its blends at the different load on a single-cylinder, 4-stroke, WC Ricardo E6 engine, and found that the smoke level increased sharply with increase in load for all fuels tested. They explained that it was mainly due to the decreased air–fuel ratio at higher loads when larger quantities of fuel are injected in to the combustion chamber, much of which goes unburnt into the exhaust. Although it was reported in [26,71] that reductions in PM emissions became smaller at low and middle load, authors all agreed on the trend of PM emissions with load. However, some researchers observed the reverse trend [121–123]. Leung et al. [122] tested the biodiesel from rapeseed oil and diesel in a single-cylinder engine with different load conditions, and found the higher decrease in PM emissions for biodiesel at high load. The authors explained that, this trend is because particles are mainly formed during the diffusion combustion, and most of the combustion is diffusive at high load, which means that the oxygen content of biodiesel is more effective in reducing Durbin and Norbeck [123] also found a greater reduction at high load, but the sharp increase at low load when using biodiesels from grease and soybean oil. On the contrary, Lapuerta et al. [106] reported that a greater decrease in PM appeared at low load with the low and intermediate load operation mode.

The impact of engine speed on PM emissions is basically reached a consensus, that is, the higher the engine speed is, the lower PM emissions are [12,29,90,91]. It is because the improved combustion efficiency should be attributed to an increase in turbulence effects with an increase in engine speed, which enhances the extent of complete combustion. However, authors in [8] reported that the impact of engine speed appeared fluctuant. PM emissions reduced at low speed, and increased a bit in the range of 2000–4000 rpm, then decreased again after 4000 rpm. Additionally, it was reported in [27] that the reduction was higher at low and high engine speeds.

Usually, start of injection of biodiesel occurs earlier than diesel due to higher density and viscosity and lower compressibility [6,26,95]. Therefore, the effect of injection timing of biodiesel on engine performance and emissions was studied by a few authors [43,47,60]. Banapurmath et al. [43] showed that the smoke emission with HOME biodiesel generally increased when the injection timing was retarded. But the smoke level of the reference diesel falls firstly when the injection timing is advanced to 23° BTDC from 19° BTDC and then increases when the injection timing is advance further. The same trend was proved by Tsolakisa et al. [60]. These researches imply that the optimum parameter of diesel engine may not be suitable for biodiesel.

There are several literatures described the impact of EGR on PM emissions. Tsolakisa [60] and Agarwal et al. [63] illustrated that the smoke was increased for biodiesel blends with EGR addition from 0% to 20%, although the smoke levels were generally lower and kept at considerably lower values. They all contributed to the decreased availability of oxygen for combustion of fuel, which results in relatively incomplete combustion and increased formation of PM. Additionally, Zheng et al. [94] investigated the effect of EGR with the bigger change range from 0% to 100%. They found there are two distinct slopes which showed the effect of EGR on soot. In the first slope, the soot increased with increasing EGR up to 50–70%. After this point, the soot decreased with increasing EGR.

The advantage of biodiesel in PM emissions will be weakened or even reversed in low temperature tests. Fontaras et al. [54] investigated the influence of cold and hot starts on the emissions from a TU and DI diesel engine. All emission levels tended to significantly increase over the cold start of the urban part (UDC) of the NEDC. The respective increases in PM for B50 and B100 over the cold phase of the NEDC were 31% and 178% due to the fuel's higher kinematic viscosity and lower boiling point which make fuel atomization and evaporation more difficult under cold start conditions. The similar results and reason were obtained by Armas et al. [107], who carried out a few tests in load, speed and transient start conditions on a DI engine with two pure biodiesels from waste oil and sunflower oil and their blends mixed with diesel. Additionally, Martini et al. [124] tested three biodiesels from the different feedstock with NEDC cycle and found PM emissions reduced by 40% during city cycle stage due to the cold temperature.

3.1.2.4. Additives. Some studies investigated the effect of additives, such as oxygenates (ethanol or methanol), and metal-based additives, antioxidants, on engine performances and emissions [26,27,45,50,55,112,120]. In the literatures [26,55,120], the oxygenates such as ethanol, methanol and alcohol were added into biodiesel and they all caused the further decrease in PM emissions due to the enrichment of oxygen content in the fuel. Keskin et al. [27] concluded that the biodiesel blends with Mg and Mo had better effect on PM emissions due to catalyst effect of them, just like what Gürü et al. [45] reported. But Ryu [50] found that there were no differences in exhaust emission between biodiesel fuel with or without antioxidants which have a significant influence on fuel consumption.

3.1.3. Summary

Based on analysis above, the following conclusions are available:

(1) It is dominating argument that PM emissions of biodiesel are significantly reduced compared to diesel. Of course, this reduction will become smaller with the reduction of biodiesel proportion in the blended fuel, and abnormal variation may appear in the case of a certain content of biodiesel.
(2) The trend which PM emissions of biodiesel will be reduced is due to lower aromatic and sulfur compounds and higher cetane number for biodiesel, but the more important factor is the higher oxygen content. It should be noted that, the advantage of no sulphur characteristics for biodiesel will disappear as the sulfur content in diesel is becoming fewer and fewer.
(3) It can be accepted by the majority of researchers that, the larger engine load is, the greater PM emissions of biodiesel will be. And the trend is basically no objection, that is, the higher engine speed is, the lower PM emissions will be.
(4) The feature of injection advance of biodiesel is inappropriate to the diesel engine in optimal state, it is necessary to further study the matching characteristics of biodiesel and/or its blends with engine.
(5) The use of EGR might deteriorate PM emissions of biodiesel, although PM emissions level is still very low relative to diesel. But PM emissions of biodiesel compared to diesel will increase abnormally in the case of low temperature condition. This trend is worthwhile to further study.
(6) Oxygenates can improve PM emissions of biodiesel, but it would not be useful for power recovery. The metal-based additives may be effective to reduce PM emissions of biodiesel due to catalyst effect.

3.2. NO_x

3.2.1. NO_x emissions of biodiesel

It is found in Table 1, the 65.2% literatures believe that the use of pure biodiesel causes the increase in NO_x emissions [5–7,9–11,14,16,19,20,23,27,29–31,34,35,37,43,48,49,51–53,55–57, 59–63,65,71,89–95,118,120,125,126]. For example, a maximum of 15% increase in NO_x emissions for B100 was observed at high load condition as the results of 12% oxygen content of the B100 and higher gas temperature in combustion chamber [93]. Ozsezen et al. [6] employed the WPOME and COME on a 6-cylinder WC, NA, DI diesel engine and found that the NO_x emissions of the WPOME and COME increased by 22.13% and 6.48%, respectively. Especially, Lin et al. [23] compared 8 kinds of VOME mentioned above and observed that using VOME fuels in the diesel engine yielded higher NO_x emissions, ranging from an increase of 5.58% to an increase of 25.97%, when compared to PD.

Of course, no difference or small difference was found between biodiesel and diesel in [26,103,123,133]. In the literatures [26,133], it was reported that diesel and biodiesel had similar NO_x emissions. And Durbin and Norbeck [123] tested the diesel, pure biodiesel and their blends with 20% biodiesel on four different engines, which represent a large range of heavy-duty engines: TU and NA, DI and IDI. They found a small difference in NO_x emissions and concluded that the difference was not important. Wang et al. [103] drew the same conclusion when they investigated blends with 35% biodiesel from soybean oil and diesel on several vehicles.

The 29.0% literatures [4,8,15,25,33,44,47,55,58,64,74–76,78,97, 110–113,127] reported that NO_x emissions reduced when using biodiesel. Puhan et al. [78] found that the average reduction of NO_x in the case of MOEE was around 12% compared with the diesel fuel at the whole range of load. Dorado et al. [74] obtained that NO_x emissions reduced by over 20% for biodiesel from waste olive oil with an 8-mode test cycles. Banapurmatha et al. [113] reported that NO_x emission values were 970, 1000 and 990 ppm for three biodiesels JOME, SOME and HOME, respectively, compared to 1080 ppm with diesel operation at 80% load. In addition, in the literatures [8,25,64,75,110], it was reported that NO_x emissions decreased by no more that 5% for biodiesel.

3.2.2. Factors of effect on NO_x emissions for biodiesel

3.2.2.1. Content of biodiesel. Many comparative tests have been studied to perform the effect of content of biodiesel on NO_x emissions, including 2 blends fuel in [11,31,32,48,54,65,76,125], 3 blends fuel in [5,26,34,35,52,53,60,97] and more blends in [4,10,15,19,20,29,36,49,51,57,58,61,71,75,93,106].

Many literatures [5,10,11,29,31,35,36,48,49,51–54,57,60,61,65, 93,125] showed that NO_x emissions increase with the increase in content of biodiesel. Luján et al. [52] tested on a HSDI, 4-cylinder, 1.6 L, TU diesel engine fueled by biodiesel and its blends B30, B50 and B100. The authors observed that the increase in NO_x emissions for B30, B50 and B100 could be scored at 20.6%, 25.9% and 44.8%, respectively. Lertsathapornsuka et al. [125] obtained that the respective NO_x emissions were about 12.62% and 1.84% higher for B100 and B50 than diesel on the John Deere 6076TF030 engine at 1500 rpm speed. Additionally, Gumus and Kasifoglu [36] and Godiganur et al. [49], who employed at least 4 kinds of biodiesel and its blends to test engine performance and emissions, all concluded that the increasing proportion of biodiesel in the blends causes the increased NO_x emissions.

On the other hand, Aydin and Bayindir [4] investigated engine performances and emissions of CSOME and its blends (B5, B20, B50 and B75) on a single-cylinder DI and AC diesel engine. It could be observed that the increasing content of biodiesel in the blends resulted in the reduced NO_x emissions, and all blends except for B5 decreased the NO_x emissions in the study. Kalligeros et al. [97] also found this trend for the biodiesel blends, containing 10%, 20%, and 50% of two types of sunflower oil and olive oil methyl esters, on a stationary single-cylinder, IDI diesel engine.

Of course, some others literature showed that there are no regularity with the increased content of pure biodiesel. For example, Labeckas and Slavinskas [71] found that the B35 blend (4.075% oxygen) produced the maximum NO_x values than the other blends including the pure biodiesel RME (10.9% oxygen), as the results of the indigenous feature of not containing any aromatic compounds, slower evaporation and lower heating value. And Sahoo et al. [75] observed that the NO_x emissions from B20 were increased to be 2% higher but 100% biodiesel blend gave 4% lower NO_x emissions and explained that the difference might be due to the difference in engine geometry, compression ratio, less reaction time and temperature in the case of biodiesel. Additionally, Sahoo et al. [53] compared three kinds of biodiesels from jatropha, karanja and polanga oil and their blends (B20, B50 and B100) and found that the biodiesels from karanja and polanga oil and their blends had the trend of the NO_x increase with the increased content of biodiesel, but there was variation for jatropha oil biodiesel because the NO_x emissions value for JB100 was lower than that of JB20.

3.2.2.2. Properties of biodiesel and its feedstock. Properties of biodiesel such as cetane number, advance in injection and combustion, especially higher oxygen content, and feedstock of biodiesel have important effect on NO_x emissions for biodiesel according to the literatures collected in this work.

Higher cetane number of biodiesel shortens ignition delay and thus combustion advances. Al-Widyan et al. [30] applied this argument to explain why NO_x emissions increase for biodiesel, and this argument was also showed in [9,26,32,64,89,97,118]. However, the argument above is questionable. Higher cetane number will not only lead to burn early, but also lead to lower premixed combustion, which will lead to softer changes in pressure and temperature, thus it causes lower NO formation. Wu et al. [89] agreed the argument and contributed it to the difference in NO_x emissions between PME and WME biodiesels, which have almost the same oxygen content. In fact, many authors [9,26,64,97,117] believed that, with cetane number increasing, NO_x emissions reduced. Likewise, this trend was proved by US EPA [100].

Advance in injection and thus advance in combustion for biodiesel affect NO_x emissions, as discussed above. Tat et al. [95] found that the start of injection (SOI) for biodiesel from soybean oil was advanced about 0.7° relative to No. 2 diesel fuel on a 4-stroke, 4-cylinder, TU, DI John Deere 4045T diesel engine, and Ozsezen et al. [6] observed that the SOI timing advanced 0.75 °CA and 1.25 °CA for WPOME and COME, respectively, compared to the PBDF. And they all concluded that the advanced SOI caused the increase in NO_x emissions. Other authors also agreed that NO_x emissions increased due to advance in injection [6,29,48,70,97]. Monyem and Gerpen [101] and Szybist et al. [128] even found that, there existed a good correlation between starting point of injection and NO_x emissions, which has nothing to do with fuel used.

Higher oxygen content in biodiesel enhances formation of NO_x, which is accepted generally. Labeckas and Slavinskas [71] investigated experimentally the relationship between NO_x values and mass percent of fuel oxygen on a 4-stroke, 4-cylinder, WC, DI, NA diesel engine. The results showed that the maximum NO_x emissions increased proportionally with the mass percent of oxygen in the RME-Diesel blends. However, a few authors [109,110] thought oxygen content in biodiesel has no obvious influence in NO_x emissions increase. And Canakci [66] found that there is no significant difference in the oxygen amounts in the exhaust between the fuels, No. 2 diesel fuel (no oxygen), No. 1 diesel fuel (no oxygen), SME (10.97% oxygen in mass) and its 20% blend, and the NO_x emissions of the SME and 20% blend were increased by 11.2% and 0.6%, respectively, compared to the No. 2 diesel, but the NO_x emissions less 6% for No. 1 diesel fuel than for No. 2 diesel fuel. Therefore, they suggested that more researches are required regarding the other properties of biodiesel and their effects on combustion and fuel system to give better explanations about NO_x increase.

Some authors [6,9,23,26,48,62,76,89,91,102,119,129] reported the difference in NO_x emissions of biodiesels from different feedstock. Lin et al. [23], as mentioned above, found that POME and PKOME had a less increase in NO_x emissions and a significant reduce in smoke emissions, to the more saturated carbon bonds for PKOME and POME compared to the other 6 VOME fuels. Wyatt et al. [129] found the same trend when they tested 3 animal fat biodiesels. Graboski et al. [102] tested the different pure methyl esters and ethyl esters on a 11.1 L engine with a transient test cycle. The results showed that, NO_x emissions increase, because the average carbon chain length lowers and the unsaturated compounds increase. But, Lin and Lin [62] contributed the different NO_x emissions among a commercial biodiesel from soybean oil, sample 1 biodiesel (processed to remove impurities from the commercial biodiesel) and sample 2 biodiesel (further reacted by using the peroxidation process) not only to the difference of weight proportion of saturated carbon bonds but also to the different air–fuel equivalence ratio. The different air–fuel equivalence ratio, residual amount of methanol, injection delay and ignition delay are attributed to the different NO_x emissions between WPOME and COME (corn oil methyl ester) biodiesels in the literatures [6]. Of course, the different viscosity and oxygen content and cetane number in [26,48,89] were used to explain the different NO_x emissions in the different biodiesels.

3.2.2.3. Engine type and its operating conditions. Engine type and its operating conditions have something to do with NO_x emissions of biodiesel.

Karabektas [7] compared the difference of NO_x emissions for rapeseed oil biodiesel in NA and TU conditions, and found the NO_x emissions with biodiesel were higher on an average of 21% in the TU operation, compared to the NA operation, due to more air to the engine and the higher combustion temperatures. McCormick et al. [130] carried out the different tests of the pure biodiesel and 20% blends mixed with ULS diesel on the two high injection-pressure engines (one equipped with Common Rail). They concluded that, when using common-rail engine, the reduction in NO_x emissions of biodiesel was less significant than that of old engine. In addition, Haşimoğlua et al. [42], Banapurmath and Tewari [114] and Hazar [5] compared the NO_x emissions from an original engine and a LHR engine. They all reported that NO_x emissions increased in the LHR engine compared with the original engine due to a higher combustion temperature.

According to mechanism of NO_x formation, engine load plays very important role in NO_x formation. Therefore, many papers [10,19,26,29,35,36,48,49,51,55,56,61,71,75,76,78,93,95,106,120,125,131] studied the effect of engine load on NO_x emissions of biodiesel.

NO_x formation increases as load is increased [10,19,26,29,35,36,48,49,51,55,56,61,71,75,76,78,93,120,131], which is as the results of higher combustion temperature due to higher engine load. Particularly, it was reported successively in [44,49,51] that the NO_x concentration varies linearly with load, on a 3-cylinder, 4-stroke, AC, NA, DI diesel engine with fish oil biodiesel and its blends (B10, B20, B40, B60 and B80), and on a Cummins 6BTA 5.9 G2-1, 158 HP rated power, TU, WC, DI diesel engine with mahua oil biodiesel and its blends (B20, B40, B60 and B80). As load is increased, the overall fuel-air ratio increased which resulted in an increase in the average gas temperature in the combustion chamber and hence NO_x formation which is sensitive to temperature increases. This trend also was illustrated in literatures [48,56,61]. However, Tat et al. [95] found that the NO_x emissions increased at light loads, although the NO_x emissions increased with the increased load at middle and high loads. The authors contributed the phenomenon to the timing changes made by the light-load advance mechanism on the fuel injection pump.

Of course, the literatures [26,125] showed that there is no significant effect of engine load on NO_x emissions, and there is no further explanation. Incredibly, Murillo et al. [10] found that NO_x emissions decreased as load was increased on a single-cylinder, 4-stroke, NA, DI diesel outboard engine during ISO C-3 test cycle. They explained that this is probably due to the increase in turbulence inside the cylinder, which may contribute to a faster combustion and to lower residence time of the species in the high temperature zones. Kazunori et al. [121] observed that NO_x emissions lower slightly at low load and increased at high load for three different biodiesels from waste oil at 2000 rpm and different loads on a single cylinder engine.

Engine speed also affects NO_x emissions. Some authors [59,62,91] agreed that NO_x emissions reduced with an increase in engine speed. They analyzed that this trend was primarily due to the shorter residence time available for NO_x formation, which may be as the results of an increases both in the volumetric efficiency and flow velocity of the reactant mixture at higher engine speeds. However, Utlu and Koçak [8] found that the increasing in NO_x was between maximum torque and maximum power speeds for WFOME and the reference diesel fuel, which depends on exhaust temperatures and rising of volumetric efficiencies. It was reported in literature [27] that the NO_x emissions increased at light load, and reach the maximum value at medium load, then reduced with the increasing in engine speeds when the B60 biodiesel blend was fueled at full load on a single-cylinder, 4-stroke, AC, DI diesel engine. But Usta [34,35] illustrated that the different effect of engine speed on NO_x emissions at the different load conditions without explanation, that is, as engine speed is increased, the NO_x emissions increased at full load, and slightly increased at 75% load, but gradually reduced at 50% load.

As discussed above, advance in injection and combustion for biodiesel have an impact on NO_x emissions. Therefore, some authors investigated the effect of changes in injection timing and injection pressure. Carraretto et al. [14] found that NO_x emissions increased as the injection advance reduced. And, Tsolakisa et al. [60] found that the retardation of injection timing resulted in reduced NO_x emissions and increased smoke, CO and HC emissions. On the other hand, Sharma et al. [44] observed variation of NO_x as a function of injection pressure at full load and concluded that there was a significant effect of injection pressure on NO_x emissions.

Of course, there were researchers who found NO_x emissions increase for biodiesel when keeping starting of injection. For example, Cheng et al. [132] tested the biodiesel from soybean oil and diesel by keeping starting of injection and premixed combustion rate unchanged. Under these conditions, they measured the increased NO_x emissions for biodiesel.

Effect of EGR was studied in a few literatures. Tsolakis et al. [60] found that the use of EGR was more effective (higher reduction of NO_x with lower increase of smoke) for B20, B50 and RME compared to ULSD. They contributed the higher reduction to the increased H_2O and CO_2 and the retardation of combustion for RME. Zheng et al. [94] investigated the effect of EGR on a single-cylinder, 4-stroke, NA, DI diesel engine, and found that there were slight differences of NO_x emissions between biodiesels and diesel, but NO_x emissions for all fuels decreased with the increasing EGR. Although Agarwala et al. [63] showed that all biodiesel blends (B10, B20 and B50) had lower NO_x emissions than the baseline data for diesel without EGR, they did not investigate the difference with and without EGR. Nabi et al. [133] operated a single cylinder engine with different EGR ratio and found that, there was no significant difference between diesel and neemoil biodiesel with the 5–30% EGR ratio, although they obtained the increase in NO_x emissions without EGR.

3.2.2.4. Additives. Some additives, such as metal-based additives [27,45,46,50], alcohol (methanol and ethanol) [11,55,118,120], cetane number improver [31] and emulsifiers [59], was added into biodiesel to improve NO_x emissions.

In the literature [45], the effect of chicken fat biodiesel with the synthetic Mg additive on engine performances and emissions was studied on a single-cylinder, DI diesel engine. The authors reported that the NO_x emissions increased by 5% for a blend of 10% biodiesel with regard to diesel at full load and different engine speeds from 1800 to 3000 rpm. Keskin et al. [27] studied the effect of Mg and Mo as combustion catalysts on engine performances and emissions for B60 biodiesel blends on a single-cylinder, 4-stroke, AC, DI diesel engine, and found that lower NO_x emissions were measured with Mg at low engine speed and with Mo at high speed. Kalam and Masjuki [46] found that 1% 4-NPAA additive is helpful to improve NO_x emissions for B20.

Methanol and ethanol were added in a small amount to improve NO_x emissions for biodiesel [11,55,118,120]. Hansen et al. [11] concluded that ethanol could act as an effective NO_x emissions reducing additive, because they found that the addition of only 5% ethanol to biodiesel in the BE5 experimental fuel drastically suppressed the increase (2.6%) in NO_x compared to B100 (12% increase). And Bhale et al. [120] compared that the engine performances and exhaust emissions of MME (mahua methyl ester), MME E20 (MME with 20% ethanol), MME E10 on a single-cylinder, 4-stroke, WC, NA, CI engine. Low NO_x emissions were shown for biodiesel blended with ethanol, and lowest for MME E20 blend, as the result of the very high value of latent heat of vaporization of ethanol. Additionally, Cheung et al. [55] observed that increasing the methanol mass fraction in the biodiesel fuels led to a decrease of NO_x emissions due to the lower heating value and higher latent heat of evaporation of methanol, which reduce the combustion temperature and the lower exhaust gas temperature.

Lastly, Lin and Lin [59] found that the NO_x emissions were most effectively reduced by burning the O/W/O three-phase biodiesel emulsion that contained aqueous ammonia, particularly at lower engine speeds on a four-stroke, four-cylinder, NA, DI diesel engine.

3.2.3. Summary

Based on analysis above, the following conclusions are available:

(1) The vast majority of literatures reported that NO_x emissions will increase when using biodiesel. This increase is mainly due to higher oxygen content for biodiesel. Moreover, cetane number and different injection characteristics also have an impact on NO_x emissions for biodiesel.
(2) The content of unsaturated compounds in biodiesel could have a greater impact on NO_x emissions. The larger the content of unsaturated compounds is, the more NO_x emissions will reduce, which is a matter of concern.
(3) The larger engine load is, the higher the level of NO_x emissions for biodiesel will be, which is in line with the mechanism of NO_x formation.
(4) A further study is needed to perform the effect of injection timing and injection pressure on NO_x emissions of biodiesel.
(5) The use of EGR will reduce NO_x emissions of biodiesel, but due to the change of combustion characteristics for biodiesel, EGR rates which are optimized to mach the operating conditions of diesel may not fit well with the same conditions of biodiesel engines. This research area needs refinement.
(6) Metallic additives, oxide additives, emulsifier, etc. seem to be useful to improve NO_x emissions of biodiesel, but the comprehensive assessments on other emissions and engine performances (especially about power) are required in the future.

3.3. CO

3.3.1. CO emissions of biodiesel

According to most of literatures (up to 84.4% in Table 1), it is common trend that CO emissions reduce when diesel is replaced by pure biodiesel [4–8,10,14–16,19,20,24,25,27, 31–36,41,44–47,49,51,52,56,57,59–65,71,73,75–78,89–95,120,125, 134–138]. Krahl et al. [135] obtained about 50% reduction in CO emissions for biodiesel from rapeseed oil compared to low and ultra low sulphur diesel. A higher reduction in CO emissions was shown by Raheman and Phadatare [15], who observed that the reducing range of CO emission was 73–94% for the karanja methyl ester (B100) and its blends (B20, B40, B60 and B80) compared to diesel, and by Ozsezen [6], who found that the CO emissions decreased by 86.89% and 72.68% for WPOME and COME, respectively. However, some literatures [8,14,16,25,41,45,61,78,89] showed the less reduction. For example, Puhan et al. [64] obtained the reduction of around 30% compared to diesel. And the average decrease was determined as 17.13% less than diesel fuel in [8]. Meanwhile, Wu et al. [89] found that five biodiesels mentioned above reduce CO emissions by 4–16% on average.

However, some authors reported that there was no difference in CO emissions between biodiesel and diesel [26,29]. This is mainly attributed to too low emissions so that it can not be identified.

It was most surprising that some authors reported the significant increase in CO emissions for pure biodiesel [52–54,58,112–114]. Banapurmatha et al. [113] compared the CO emissions for JOME, SOME and HOME with that of diesel on a single-cylinder, 4-stroke, DI, WC, and CI engine at a rated speed of 1500 rpm. CO values were 0.155%, 0.12% and 0.145% for JOME, SOME and HOME, respectively, compared to 0.1125% with diesel operation at 80% load. Sahoo et al. [53] found that there was deterioration in CO emissions for the pure biodiesel from jatropha oil, but there was an improvement for the pure biodiesel from karanja and polanga oil. Especially, Fontaras et al. [54] reported that use of B50 and B100 led to CO increases over NEDC, in the order of 54% and 95%, respectively. The primary reasons given by the authors include the higher viscosity and the poor spray characteristic for biodiesel, which lead to poor mixing and poor combustion.

3.3.2. *Factors of effect on CO emissions for biodiesel*

3.3.2.1. Content of biodiesel. With content of pure biodiesel increasing in blends fuel, CO emissions of blends reduce due to increasing in oxygen content. This trend was reported in [4,10,31,32,36,41,60,93]. Murillo et al. [10] obtained that, at full load, the CO emissions of diesel were the highest (15.2 g/(kWh)), with the other fuels recording lower emissions: BD-10 (12.8 g/(kWh)), BD-30 (11.7 g/(kWh)), BD-50 (10.7 g/(kWh)), and BD-100 (11.4 g/(kWh)). But at full load, in literature [53] mentioned above, this trend did not appear only for the pure biodiesel from karanja and its blends instead of the other two biodiesels. And it was reported in [15,29,75] that there was variation in CO emissions of the blends with the increase of biodiesel content. Furthermore, Song and Zhang [29] found that, with increase in biodiesel percentage in the blends, there was no obvious difference in the CO emission at partial loads, but it fluctuated at full load. And the explanation was due to the interaction of the low-volatility polymers and the higher oxygen content.

Incredibly, Luján et al. [52] and Fontaras et al. [54] reported the opposite trend, that is, the higher the biodiesel content was, the greater the CO emissions were. The authors did not give an explanation on this trend.

3.3.2.2. Feedstock and properties of biodiesel. Feedstock of biodiesel affects CO emissions. Wu et al. [89] found the difference in CO emissions for five biodiesels (CME, SME, RME, PME and WME) and contributed to the different oxygen content and cetane number between them. The difference was also reported in [113] where waste palm oil and canola oil biodiesels were tested, and in [6] where HOME, JOME and SOME were tested. And Kalligeros et al. [97] compared the blends (10%, 20% and 50%) of two types of biodiesels from sunflower oil and olive oil and also illustrated the difference, just like Sahoo et al. [53] who experimented three types biodiesel from jatropha, karanja and polanga oil and their blends (20% and 50%). Additionally, Baiju et al. [76] concluded that methyl esters emited less CO compared to ethyl esters. Knothe et al. [119] tested on an engine with lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl ester, and reported that CO emissions reduced much higher with the increasing of chain length.

The extra oxygen content of biodiesel promotes complete combustion, and thus leads to the reduction in CO emissions [4,7,19,20,25,27,30,34,45,49,56,63,64,78,89,125,136]. In the literature [89] mentioned above, authors contributed the difference in CO emissions for five types of biodiesels and diesel fuel at high load to the oxygen content, but at low load only to the cetane number, and concluded that CO decreased consistently for both biodiesels and diesel fuel as cetane number increased. Biodiesel has a higher cetane number, which results in the lower possibility of formation of rich fuel zone and thus reduces CO emissions. This viewpoint was admitted in [7,27,31,45,89,125,136,137].

Advance in injection of biodiesel also have an effect on CO emissions. It was reported in [14,43,47] that CO emissions reduced when the injection timing was advanced for biodiesel fuel, which leads to the advance of ignition timing. Tsolakisa et al. [60] tested the effect of the use of retarded ignition timing by 3 °CA on emissions of biodiesel from rapeseed oil, and found that the retardation resulted in increased CO emissions.

Of course, it should be pointed out that the lower carbon content for biodiesel compared to the diesel yielded diminished CO emissions [7,62].

3.3.2.3. Engine type and its operating conditions. Different engine affects CO emissions. Karabektas [7] tested biodiesel and diesel fuel on a DI diesel engine with NA and TU conditions. CO emissions in the NA conditions for both biodiesel and diesel all were higher than those of the TU conditions, which increases air to the diesel engine and enable mixing of fuel and air easily in the combustion chamber. Hazar [5] and Banapurmath and Tewari [114] modified the engines by coating the vital components with ceramic materials to examine the effects of biodiesel on performances and exhaust emissions. They all reported that CO emissions reduced when this low heat loss engine was used.

Engine load has been proven to have a significant impact on CO emissions. The literatures [34,36,37,41,63,90,125] all reported that CO emissions increased with engine load increasing. The main reason for this increase is because the air–fuel ratio decreases with increase in load, which is typical for all internal combustion engines. The literatures [29,76] agreed on this view, but they pointed out that no obvious change in low and intermediate loads. On the contrary, it was reported in [55,58,95] that CO emissions reduced with the increased load, this trend was be explained because the increase in combustion temperature lead to more complete combustion during the higher load. Authors in [44,89] also found that CO emissions decreased as load increased, but they increased slightly at heavy load or full load. Some other authors [10,73,120] found that CO emissions was lower in the intermediate load, but was higher in low load or no load, heavy load and full load. The similar trend was also found in [61,71,118], but CO emissions increased greater in a high load than that of no load or small load.

There is a largely unanimous conclusion about the effect of engine speed on CO emissions, that is, CO emissions for biodiesel decrease with an increase in engine speed, as the result of the better air–fuel mixing process and/or the increased fuel/air equivalence ratio with the increased engine speed [25,27,34,59,62,91].

The oxidation converter might play an important role on CO emission for biodiesel. Luján et al. [52] found that the oxidative catalytic converter reduced CO emissions greater than that without the converter, but the conversion efficiency of converter declined slightly. This trend also was observed by Päivi et al. [139] and Munack et al. [140].

3.3.2.4. Additives. The decreased CO emissions of biodiesel with metal based additives were reported. Kalam and Masjuki [46] compared the CO emissions of B20, B20X (added 1% 4-NPAA additive into B20) and diesel B0, and found that the B20X fuel produced the lowest level of CO emissions, which was 0.1%, followed by B20 (0.2%) and B0 (0.35%). Keskin et al. [27] observed that CO emission of biodiesel fuel decreased with Mg and Mo based additives.

As additives, alcohol (methanol and ethanol) also have an impact on CO emissions of biodiesel. Cheung et al. [55] tested the exhaust emissions of the pure biodiesel and its blends with 5% (BM5), 10% (BM10) and 15% (BM15) methanol. For BM5, the CO emissions were even lower than that of biodiesel, with a reduction of 6% on average, based on different engine loads. However, the CO emissions of BM10 and BM15 were higher than that of biodiesel at light and medium engine loads, while lower than that of biodiesel at high engine loads. Bhale et al. [120] also reported the decreased CO emissions when operated with Mahua biodiesel blended with ethanol. Furthermore, it was reported that the reduction in CO emission level with the addition of oxygenates (ethanol) was obvious when performance and emissions were compared with MME, MME E20, MME E10 and MME E10 D10 (MME with 10% diesel and 10% ethanol). However, Kwanchareon et al. [118] tested the emissions of diesel, biodiesel and the blends with diesel fixed at 90%, 85% and 80% by volume and biodiesel and ethanol addition. The result showed that the blend of 80% diesel, 15% biodiesel and 5% ethanol produced the smallest amount of CO at full engine load. And it was shown that the impact of diesel–biodiesel–ethanol on CO emissions varies with engine operating conditions.

3.3.3. Summary

Based on analysis above, the following conclusions are available:

(1) It is accepted commonly that CO emissions reduce when using biodiesel due to higher oxygen content and lower carbon to hydrogen ratio in biodiesel compared to diesel.
(2) With content of pure biodiesel increasing in blends fuel, CO emissions of blends reduce.
(3) CO emissions for biodiesel are affected by its feedstock and other properties of biodiesel such as cetane number and advance in combustion.
(4) Engine load has been proven to have a significant impact on CO emissions. There is a largely unanimous conclusion about the effect of engine speed on CO emissions, that is, CO emissions for biodiesel decrease with an increase in engine speed. An oxidative catalytic converter, which is designed for diesel engine, play an important role on CO emissions for biodiesel, but its conversion efficiency may become weak.
(5) CO emissions of biodiesel reduce with metal based additives, and methanol and ethanol also further improve CO emissions.

3.4. HC

3.4.1. HC emissions of biodiesel

It is predominant viewpoint (89.5%, as shown in Table 1) that HC emissions reduce when pure biodiesel is fueled instead of diesel [6,9,16,19,20,23–26,29–33,36,44,46,47,49–53,55–58,19,60,63–65, 73,75,76,78,89,92,94,95,97,101,118,120,125,127,135,136,138,141, 142]. Wu et al. [89] mentioned above reported that the 5 different biodiesels reduced HC emission by 45–67% on average compared with diesel fuel. Some others researchers [6,19,65,78,135,141,142] reported the considerably similar decrease. For example, Puhan et al. [78] reported that the HC emissions reduced average around 63% for biodiesel compared with diesel. Alam et al. [142] found that the HC emissions reduced by 60% for biodiesel regarding ULSD. But some authors reported the lower decreases [9,23,25,49,51,52,53,95,120,125]. For example, Lin et al. [23] found the THC emissions reduced in the range of 22.47–33.15% for the 8 kinds of VOMEs mentioned above. And Sahoo et al. [53] compared the biodiesels from jatropha, karanja and polanga and their blends compared with diesel on a 3-cylinder WC tractor engine during 8 mode cycle tests, and reported that HC emissions for the pure biodiesels reduced by 20.73%, 20.64% and 6.75%, respectively.

Of course, several researches [67,71,139] showed that there was no significant difference between biodiesel and diesel. And an amazing trend, which the THC emissions increased for biodiesel, was found in several literatures [54,112,113]. The 10% increase in HC emissions was obtained for methyl ester of jatropha oil with regard to diesel in [112]. And Fontaras et al. [54] observed that use of biodiesel negatively affects HC emissions over the legislated cycles (UDC, EUDC and NEDC), and HC emissions for pure biodiesel increase by 58% over the NEDC. Banapurmatha et al. [113] found that HC emissions with JOME, SOME and HOME all were higher compared to the standard diesel fuel on a single-cylinder, 4-stroke, DI, WC, CI engine at a rated speed of 1500 rpm. They contributed this trend to relatively poor atomization and lower volatility of biodiesels.

3.4.2. Factors of effect on HC emissions for biodiesel

3.4.2.1. Content of biodiesel. Many authors [24,29,31,36,49,51,60,73,97] agreed that HC emissions decreases with increasing biodiesel percentage in the blend. Godiganur et al. [49] found that the reduction in HC was linear with the addition of biodiesel for the blends. Although Song and Zhang [29] showed the same trend, they pointed out that the higher reduction in CO emissions appeared with the low content of biodiesel, that is, the lower biodiesel concentration is more effective than the higher one. This interesting trend was also accepted in [24].

However, there are exceptions. Sahoo et al. [53] found that the reduction of THC was of the order of 32.28%, 18.19% and 20.73% for JB20, JB50, JB100, respectively. Especially, Luján et al. [52] found that HC emissions results by 22.9%, 17.7% and 16.4% for B30, B50 and B100 respectively, compared with diesel. And they explained that, the lower heating value of the pure biodiesel implies higher fuel consumptions and therefore it could produce high local fuel-to-air ratios which caused an increase in HC emissions, and the high catalyst efficiency reduced the biodiesel advantage in terms of HC emissions.

3.4.2.2. Feedstock and properties of biodiesel. Some studies have shown that the sources of biodiesel have an effect on HC emissions, although Canakci and Van Gerpen [68] found that there are no difference in THC emissions between cooking oil and soybean biodiesels on a TU, DI engine. Sahoo et al. [53] reported that the significant difference in HC emissions between jatropha and karanja biodiesels (20.73% and 20.64%) and polanga biodiesel (6.75%). Also, Ozsezen et al. [6] found that the difference in HC emissions between WPOME (14.29%) and COME (9.52%). As mentioned above, the variation of THC emissions in the range of 22.47–33.15% for eight VOME biodiesels in [23]. Wu et al. [89] reported that five typical methyl ester biodiesels reduced HC emissions by 45–67% on average mentioned above, and contributed the difference in HC emissions with different biodiesels to a combined effect of oxygen content and cetane number.

Although Graboski et al. [102] reported that there was no difference in THC emissions for the methyl and ethyl ester, Lapuerta et al. [26] found shown that the alcohol used had a significant impact on the HC emissions, because the ethyl ester showed the lower HC emissions than methyl ester in medium load conditions, and no clear trend in low load condition due to the lower volatility of ethyl esters.

The properties of biodiesel are related to HC emissions. Graboski et al. [102] showed that the increase in chain length or saturation level of several biodiesels led to a higher reduction in THC emissions on an 11.1 L engine. Similarly, Knothe et al. [119] reported that, THC emissions reduced with the increasing in chain length when they tested lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl esters on a 6-cylinder engine, and THC reduced by 50% for pure biodiesel instead of diesel.

However, more researches focus on the effect of oxygen content, cetane number and advance in injection and combustion of biodiesel on HC emissions. Biodiesel involves higher oxygen content, which leads to more complete combustion [6,14,19,20,24,29,30,36,52,55,56,60,63,75,112,136]. Additionally, in the literatures [30,78,89], it was explained that the decrease in THC emissions was caused not only by the oxygen content but also by the cetane number. Higher cetane number of biodiesel could reduce the burning delay, which results in the THC emissions reduction [40,143].

Injection and combustion timing will advance for biodiesel compared with diesel. Ozsezen et al. [6] found that the SOI timing advanced 0.75 and 1.25 °CA with the use of WPOME and COME, respectively. Armas et al. [47] and Banapurmath et al. [43] all observed that, the more advanced injection was, the lower THC emissions were. And Tsolakisa et al. [60] observed that the injection delay, THC emissions increased.

3.4.2.3. Engine operating conditions. Effect of engine load on HC emissions for biodiesel was studied primarily, but there are inconsistent conclusions. Some authors [36,63] showed experimentally the increase in HC emissions with load increase. And Lertsathapornsuka et al. [125] also reached the same conclusion, and the explanation given was due to high fuel consumption in high load. However, Tat et al. [95] found that the BSHC for biodiesel reduce as load increases. In addition, authors in [26,29,55] all agreed that the HC emissions of biodiesel had a greater decrease in HC emissions at low load observed, but it was reported that a greater decrease occurred at intermediate load than low and high load [97,118].

An oxidative catalytic converter have an impact on HC emissions, but its function seems be weakened. Päivi et al. [139] tested three biodiesels from rapeseed, soybean and cooking oil and diesel on a heavy duty engine with the ECE R49 test cycle. THC emissions were decreased for biodiesels, but the decrease was sharper without the catalytic converter with the increase of biodiesel percentage. The same conclusion was reached by Munack et al. [140] when they experimented on an agricultural engine fueled by rapeseed oil biodiesel.

3.4.2.4. Additives. Metal based additives were employed to improve biodiesel emissions in the literatures [27,45,46,50], but it was reported only in [25] that using of B20X including 1% 4-NPAA additive improved HC emissions when comparing with B20.

In some researches, ethanol and methanol was added to biodiesel to study their effect on HC emissions. Bhale et al. [120] compared emission of MME, MME E20, MME E10 and MME E10 D10 on a single-cylinder, 4-stroke, WC, NA, CI engine. The HC emission for MME on average was 12.4% lower than that of diesel. The reduction in HC emission for ethanol blended biodiesel (E20 and E10) was lower than 9.15% and 5.25%, respectively. Likewise, Kwanchareon et al. [118] tested the emissions in the blends containing diesel at 90%, 85% and 80% by volume mixed with biodiesel and ethanol and found that a higher percentage of ethanol would have higher HC emission at low and medium load. But, Kim and Choi [31] reported that BD15E5 mixed fuel (15% biodiesel, 5% bioethanol and 80% diesel) yielded the lower THC emissions than that of B20 (20% biodiesel and 80% diesel) on a common rail direct injection (CRDI) diesel engine. Additionally, Cheung et al. [55] found that the HC emissions of BM5 (5% methanol) and BM10 (10% methanol) were lower than that of biodiesel, except at the lowest engine load of 0.08 MPa while the HC emissions of BM15 (15% methanol) were higher than those of biodiesel except at the highest engine load of 0.70 MPa. They explained that the small amount of methanol for BM5 could increase the oxygen content of the blended fuel and reduce the viscosity and density of the blend so that HC emissions were reduced. But the cooling effect of methanol for BM15 dominates the increase of HC emissions.

3.4.3. Summary

Based on analysis above, the following conclusions are available:

(1) It is predominant viewpoint that HC emissions reduce when pure biodiesel is fueled instead of diesel.
(2) Most of researches showed that HC emissions for biodiesel reduce with the increase of biodiesel content.
(3) The feedstock of biodiesel and its properties have an effect on HC emissions, especially for the different chain length or saturation level of biodiesels. The advance in injection and combustion of biodiesel favors the lower HC emissions.
(4) There are inconsistent conclusions about effect of engine load on HC emissions for biodiesel. Although an oxidative catalytic converter has a positive impact on HC emissions for biodiesel, its function seems be weakened.
(5) Metal based additives have less efficiency to improve HC emissions for biodiesel than the others emissions. And a small proportion of ethanol and methanol added into biodiesel and its blends with diesel may be advantageous to HC emissions.

3.5. CO_2

Because the contribution rate of traffic on CO_2 emissions is as high as 23% [144], some authors studied CO_2 emissions of biodiesel. In the literatures [6,8,27,59,75], it was reported that, biodiesel resulted in fewer CO_2 emissions than diesel during complete combustion due to the lower carbon to hydrogen ratio. While the literature [62] compared the CO_2 emissions between three kinds of biodiesels and ASTM No. 2D diesel using CO_2 emission index, which is defined as the CO2 emission (%) divided by the corresponding fuel consumption rate (in unit of g/h). Three kinds of biodiesels had lower CO2 emission indices than ASTM No. 2D diesel. This is attributed to the fact that biodiesel is a low carbon fuel and has a lower elemental carbon to hydrogen ratio than diesel fuel.

But, it was reported that CO_2 emissions rise [16,41,54,65,71,78] or keep similar [29,37], this is due to more efficient combustion. Of course, it was pointed out in the literatures [71,75] that, in the case of biodiesel, the higher carbon dioxide emission should cause less concern because of Nature's recovery by raising biodiesel crops. While the literatures [14,26] evaluated the effect of biodiesel on global greenhouse gas emissions through the life cycle of CO_2 emissions. And they pointed out that, biodiesel will cause 50–80% reduction in CO_2 emissions compared to petroleum diesel.

3.6. Other non-regulated emissions

3.6.1. Introduction

Previous studies have been focused on emissions of regulated pollutants, however, there is increasing interest on the non-regulated emissions such as formaldehyde, acetaldehyde, 1,3-butadiene, benzene, toluene, and xylene, which are air toxics. Emissions in aromatic and polyaromatic compounds and carbonyl compounds, which were studied massively as non-regulated emissions, will be introduced with emphasis below.

3.6.2. Aromatic and polyaromatic compounds

Aromatic compounds and derivatives are toxic, mutagenic and carcinogenic. The decrease in aromatic and polyaromatic emissions of biodiesel is reported by most of researches [20,55,67,104,127,136,145–149]. Sharp et al. [145] found that PAH and nitro-PAH emission reduced with 50–75% on three different engines fueled by biodiesel. Lin et al. [20] tested pure palm oil biodiesel and the blend fuel with 20% biodiesel and ULS diesel on the NA2.84 L engine. They observed that PAH reduced 43% for the blend fuel and 90% for pure biodiesel. He et al. [147] carried out an experimental study on a DI and TU diesel engine, and found that, comparing with diesel, using B100 and B20 could greatly reduce the total PAHs emissions by 19.4% and 13.1%, respectively. In EPA review [100], it was inferred that some aromatic emissions with biodiesel, such as ethylbenzene, naphthalene and xylene, were consistent reduction, while others such as styrene, benzene and toluene had different results. And the National Biodiesel Board (NBB) [150] estimated that PAH and nitro-PAH reduced to about 80% and 90%, respectively.

Some authors [67,136] explained that the reduction in PAH emission was usually due to the enhanced absorption of PM to these components. Correa and Arbilla [148] pointed out that biodiesel had lower benzene emissions than Euro V diesel fuel due to the characteristics of non-light-aromatics. And Agarwal [149] agreed that the lack of aromatic hydrocarbon (benzene, toluene, etc.) in biodiesel reduces non-regulated emissions as ketone, benzene, etc.

Some authors found that there was no significant differences in PAH emissions between diesel and biodiesel, and even some authors reported a slight increase in aromatic emissions. Turrio-Baldassarri et al. [67] only found an obvious reduction in toluene, rather any of the analyzed PAH or nitro-PAH. Munack et al. [140] verified that the increase of rapeseed biodiesel content in the blend fuel caused the increase in benzene emissions on a single-cylinder 4.2 kW engine. They also tested on a 52 kW engine and observed that aromatic emissions increased slightly.

Engine operating conditions (load, cycle, etc.) play a noticeable role in aromatic and polyaromatic emissions of biodiesel. Cheung et al. [55] measured benzene, toluene and xylene (BTX) emissions on a diesel engine under five engine loads at a steady speed of 1800 rpm with Euro V diesel fuel, pure biodiesel and biodiesel blends with 5%, 10% and 15% methanol. Compared with the diesel fuel, the BTX emissions of biodiesel were lower, and with increase of methanol in the blends, benzene emissions decreased due to an increase of oxygen in the biodiesel which improves combustion and promote the degradation of benzene. They also observed that the BTX emissions decreased with engine load. Similarly, Di et al. [151] found higher benzene emissions at lower engine loads. Takada et al. [152] also showed higher benzene emissions at lower engine loads and lower exhaust gas temperatures, and concluded that benzene could be easily degraded at high exhaust gas temperature. Ballesteros et al. [127] reported that there are significant reductions in aromatic and oxygenated aromatic emissions with the use of biodiesel in the urban mode. In the extra-urban mode, the amount of aromatics emitted with biodiesel fuel blends was negligible.

3.6.3. *Carbonyl compounds*

It was reported that carbonyl compounds emission increased when using pure biodiesel [54,55,127,131,147,150,153,154] or its blends. He et al. [153] analyzed 14 carbonyl compounds emissions, mainly including formaldehyde, acetaldehyde, acrolein and acetone, etc., and found that biodiesel-fueled engine almost had triple carbonyls emissions of diesel-fueled engine and emitted a comparatively high content of propionaldehyde and methacrolein. Fontaras et al. [54] identified 13 carbonyl compounds in the exhaust gases and measured their concentrations over the various driving cycles with B100 biodiesel and the petroleum diesel. The experimental results demonstrated a significant increase of carbonyl emissions with the use of pure biodiesel, probably due to the oxygen atoms in the ester molecule. Turrio-Baldassarri et al. [67] found that, when the 20% blend fuel from rapeseed oil biodiesel was tested in a 6-cylinder engine, there existed a marked increase in formaldehyde, but no significant differences in acrolein, acetaldehyde and propionaldehyde. But, it was reported in [154], all 7 carbonyls, except benzaldehyde which showed a reduction on the emission (−3.4% for B2, −5.3% for B5, −5.7% for B10, and −6.9% for B20), showed a significant increase: 2.6%, 7.3%, 17.6%, and 35.5% for formaldehyde; 1.4%, 2.5%, 5.4%, and 15.8% for acetaldehyde; 2.1%, 5.4%, 11.1%, and 22.0% for acrolein + acetone; 0.8%, 2.7%, 4.6%, and 10.0% for propionaldehyde; 3.3%, 7.8%, 16.0%, and 26.0% for butyraldehyde.

Discordant results were reported by Sharp et al. [145] who found a substantial reduction in carbonyl emissions with pure biodiesel and a smaller reduction with B20 blend. Krahl et al. [150] tested diesel and soybean oil biodiesel in three engines (119, 205 and 276 kW). They concluded that, aldehydes and ketones reduced approximately 0–30% for biodiesel. Peng et al. [155] found that B20 (20% waste cooking oil biodiesel and 80% diesel) generated slightly less emissions in total aldehyde compounds than that of diesel. In the review of EPA [100], it was reported that, formaldehyde and acetaldehyde emissions showed a slight decrease of approximately 10% when using pure biodiesels.

It is widely accepted that, biodiesel increases these emissions because of higher oxygen content [104,154,156–158]. In addition, Fontaras et al. [54] found that the quality of biodiesel regarding the fatty acid profile, iodine number, and purity level played a role on the formation of certain carbonyl emissions. Some authors reported that acrolein concentration in the emissions was strongly related to the higher glycerine content of biodiesel used [159]. Arapaki et al. [157] found that acetaldehyde emission increased sharply with biodiesel–diesel blend, compared with Euro V diesel fuel, and concluded that the acetaldehyde emissions could be caused by a higher free glycerol or total glycerol content of the methyl ester. But in literature [154], authors contributed the increase in formaldehyde of 2%, 5%, 10% and 15% of biodiesel from waste cooking oil to the formation of formaldehyde during the frying or cooking process and the esterification process, and many short chain chemicals of biodiesel which favor the formation of formaldehyde during combustion.

Corrêa and Arbilla [154] found that all carbonyl emissions exhibited a strong correlation (correlation coefficients better than 0.96) with the biodiesel content, which indicates that carbonyl emissions are strongly influenced by the biodiesel content and that the biodiesel ester molecules are probably the source of these carbonyls. However, Liu et al. [131] reported that the total concentration of emitted carbonyls did not increase with the biodiesel content.

Of course, engine operating conditions and engine types also have an effect on these emissions. Liu et al. [131] elucidates the carbonyl compound emissions increased when the engine was run on biodiesel and its blends (10%, 30%, 50%, 75%, and 100% of biodiesel by volume) at idling, 10%, 33%, and 55% loads. Cheung et al. [55] reported that formaldehyde emissions increased when the engine load was increased from 0.08 MPa to 0.38 MPa, but decreased when the engine load was increased from 0.38 MPa to 0.70 MPa. Formaldehyde emissions attained the peak value at medium engine load, which were similar to that of the total hydrocarbon emissions. Cheung et al. [160] obtained continuous increase of formaldehyde emissions with the engine load. Zhang et al. [158] concluded that both engine speed and engine load affect formaldehyde emissions and showed that formaldehyde emissions increased with engine load under medium and high engine loads at the engine speed of 1200 rpm, while decreased with engine load under medium and high engine loads at the engine speed of 1400 rpm. Fontaras et al. [54] observed that some of the carbonyl compounds were also influenced by the driving cycle. Comparing the NEDC and the Artemis urban, most carbonyls were found in higher concentrations than over Artemis road and motorway. However, acrolein was significantly increased especially over Artemis urban and road cycles.

Munack et al. [140] tested two different engines using five operation modes from an agricultural cycle. In one engine fueled with pure diesel and rapeseed oil biodiesel, biodiesel had higher formaldehyde emissions than diesel. In another engine, 40% blend fuel was added to test. Results showed that, the emissions for pure biodiesel were lower than that of diesel, however the emissions for 40% blend fuel was the highest.

Some researches showed the effect of alcohol (methanol content). Cheung et al. [55] found that the formaldehyde and acetaldehyde emissions increased with increase of methanol fraction in the biodiesel blend fuel compared with diesel fuel. Zervas et al. [161] reported that the formaldehyde emissions increased with the methanol fraction, and concluded that exhaust formaldehyde was mainly produced from methanol. But they reported that acetaldehyde emission was produced from ethanol or straight-chain hydrocarbons, and methanol had no significantly effect on its emission. Chao et al. [162] observed that the formaldehyde emissions increased when methanol increased from 5% to 15%. Meanwhile, they showed an increase of acetaldehyde emissions with 8%, 10% and 15% methanol in the blended fuel, while a decrease with 5% methanol. Arapaki et al. [157] pointed out that, although methanol itself has no effect on acetaldehyde emissions, the addition of methanol in biodiesel could increase the oxygen content leading to the increase of acetaldehyde emissions, and simultaneously the contents of straight chain hydrocarbons will change after the addition of methanol. Thus, methanol tends to increase acetaldehyde emissions.

3.6.4. Summary

Based on analysis above, the following conclusions are available:

(1) There is increasing interest on the non-regulated emissions which are air toxics when biodiesel is fueled instead of diesel.
(2) Most of researches showed that aromatic and polyaromatic compounds emissions for biodiesel reduce with regard to diesel and it depends on engine operating conditions (load, cycle mode, etc.).
(3) Carbonyl compounds emissions have discordant results for biodiesel, but it is widely accepted that, biodiesel increases these emissions because of higher oxygen content. In addition, engine operating conditions (load and cycle mode), engine types also have an effect on these emissions, and methanol tends to increase acetaldehyde emissions.

4. Conclusions and further researches

Biodiesel, produced from renewable and often domestic sources, represents a more sustainable source of energy and will therefore play an increasingly significant role in providing the energy requirements for transportation. Therefore, more and more researches are focused on the biodiesel engine performances and its emissions in the past 10 years. Although there have always been inconsistent trends for biodiesel engine performances and its emissions due to the different tested engines, the different operating conditions or driving cycles, the different used biodiesel or reference diesel, the different measurement techniques or instruments, etc., the following general conclusions could be drawn according to analysis and summary of the massive related literatures in this work:

(1) The use of biodiesel will lead to loss in engine power mainly due to the reduction in heating value of biodiesel compared to diesel, but there exists power recovery for biodiesel engine as the result of an increase in biodiesel fuel consumption. Eespecially for the blend fuel including a portion of biodiesel, it is not easy for drivers to perceive power losses during practical driving.
(2) An increase in biodiesel fuel consumption, due to low heating value and high density and viscosity of biodiesel, has been found, but this trend will be weakened as the proportion of biodiesel reduces in the blend.
(3) It can be concluded from the limited literatures that the use of biodiesel favors to reduce carbon deposit and wear of the key engine parts, compared with diesel. It is attributed to the lower soot formation, which is consistent to the reduced PM emissions of biodiesel, and the inherent lubricity of biodiesel.
(4) The majority of studies have shown that PM emissions for biodiesel are significantly reduced, compared with diesel. The higher oxygen content and lower aromatic compounds has been regarded as the main reasons.
(5) The vast majority of literatures agree that NO_x emissions will increase when using biodiesel. This increase is mainly due to higher oxygen content for biodiesel. Moreover, the cetane number and different injection characteristics also have an impact on NO_x emissions for biodiesel.
(6) It is accepted commonly that CO emissions reduce when using biodiesel due to the higher oxygen content and the lower carbon to hydrogen ratio in biodiesel compared to diesel.
(7) It is predominant viewpoint that HC emissions reduce when biodiesel is fueled instead of diesel. This reduction is mainly contributed to the higher oxygen content of biodiesel, but the advance in injection and combustion of biodiesel also favor the lower THC emissions.
(8) There exist the inconsistent conclusions, some researches indicated that the CO_2 emission reduces for biodiesel as a result of the low carbon to hydrocarbons ratio, and some researches showed that the CO_2 emission increases or keeps similar because of more effective combustion. But in any event, the CO_2 emission of biodiesel reduces greatly from the view of the life cycle circulation of CO_2.
(9) Most of researches showed that aromatic and polyaromatic compounds emissions for biodiesel reduce with regard to diesel. Carbonyl compounds emissions have discordant results for biodiesel, although it is widely accepted that, biodiesel increases these oxidants emissions because of higher oxygen content.
(10) It can be concluded that the blends of biodiesel with small content by volume could replace diesel in order to help in controlling air pollution and easing the pressure on scarce resources to a great extent without significantly sacrificing enigne power and economy.

Overall, biodiesel, especially for the blends with a small portion of biodiesel, is technically feasible as an alternative fuel in CI engines with no or minor modifications to engine. For environmental and economic reasons, their popularity may soon grow. However, more researches and development in biodiesel resources and engine design are needed.

(1) The further improvement in production of biodiesel should be performed in the future to promote biodiesel properties and quality. And the further development in additives which improve consumption of biodiesel should be needed to favor power recovery, economy and emissions especially for NO_x emissions.
(2) It should be done to readjust or redesign engine or/and its control systems for biodiesel, especially for optimizing ignition and injection, and EGR control to achieve a more efficient combustion and thus meet the needs of biodiesel engine.
(3) The further studies on biodiesel engine endurance tests should be executed to make clear the reason and mechanism of wears, because the studies on these aspects are fewer so far due to the time-consuming tests.

(4) The further studies on the low temperature performance of biodiesel engine should be fulfilled because biodiesel presents higher viscosity than diesel, which could affect the emissions due to the different size of droplets and the different primary-zone equivalence ratio for biodiesel and diesel without any change in fuel nozzle.
(5) The further studies on non-regulated emissions of biodiesel should be carried out to obtain conclusive trend, especially for the carbonyl compounds emissions.
(6) The methodology or the instrumentation used for measurements need be improved to fulfill the expected requirements.

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