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The Recent Progress of Natural Source and Manufacturing Process of Biodiesel: A Review

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Abstract: Biodiesel has caught the attention of many researchers because it has great potential to be sustainable fossil fuel substitute. Biodiesel has non-toxic and renewable nature and has been proven to emit less amount of environmentally harmful emissions such as hydrocarbons (HC), and carbon monoxide (CO), as well as smoke particles during combustion. Problems related to global warming caused by greenhouse gas (GHG) emissions could also be solved by utilizing biodiesel as a daily energy source. However, the expensive cost of biodiesel production, mainly because of the cost of natural feedstock, holds the potential of biodiesel commercialization. The selection of natural sources of biodiesel should be made with observations from economic, agricultural, and technical perspectives to obtain one feasible biodiesel with superior characteristics. This review paper presents a detailed overview of various natural sources, their physicochemical properties, as well as the performance, emission, and combustion characteristics of biodiesel when used in a diesel engine. The recent progress in studies about natural feedstocks and manufacturing methods used in biodiesel production were evaluated in detail. Finally, the findings of the present work reveal that transesterification is currently the most superior and commonly used biodiesel production method compared to other methods available.

Keywords: biodiesel; engine performance; emissions; natural feedstocks; production method

1. Introduction

Nowadays, as we live in the modern era where various aspects of human activity have been automated and run by fueled machines, the need for energy will continue to increase over time. According to the International Energy Outlook 2019, it has been predicted that world energy consumption will rise nearly 50% from 2018 to 2050 [1–5]. As of today, global energy consumption highly depends on fossil resources such as crude oil, natural gas, and coal, which make up about 80% of the total consumption. Oil is the most widely used type of fossil fuels and its demand will continue to increase and is projected to reach 109.1 million barrels per day by 2045 [6,7].

The problems caused by the use of fossil fuels are their finite resources and also the environmental pollution resulted from their combustion. Fossil resources have a very slow regeneration rate. Based on current daily fossil-usage data, it is only a matter of time until the fossil resources are completely depleted on earth [7]. Combined with global warming issues partly caused by greenhouse gases (GHG) emissions from fossil-fuel combustion, renewable energy development becomes a key and challenge for the world society to reduce fossil-fuel usage [8]. Bioenergy and biofuels could solve this problem due to their renewable nature. Carbon dioxide in the atmosphere absorbed by plants will

be released back during biofuel combustion, which means there is no extra carbon emission accumulated in the atmosphere from the use of biofuels [9]. Biodiesel is one of the widely used biofuels due to its considerably similar properties to fossil diesel [10–12].

Biodiesel is defined as a non-toxic, biodegradable, and renewable fuel made of vegetable oil, animal fat, and waste and produced by different techniques [13–17]. Biodiesel is considered the most carbon-neutral fuel with the ability to reduce carbon-dioxide emissions by 78% compared to petrodiesel. Moreover, the biodegradability of biodiesel has been proven to be really high, ranging from 80.4% to 91.2% after 30 days while fossil diesel only has 24.5% of biodegradability [9,18]. Another advantage of using biodiesel is that its emission content is considered less harmful to the environment. Although it widely varies according to study parameters in engine types and operating conditions, the dominant trend from some studies shows that combustion of biodiesel emits less content of CO, Particulate Matters (PM), Hydrocarbons (HC), and produces almost no sulfate emissions. However, an increase in NO_x emission is usually found from the usage of biodiesel [12,19,20].

The use of vegetable-based biodiesel (sunflower, soybean, grapeseed, corn, rice bran, olive) in the semi-industrial boiler has been studied by Bazooyar et al. [21]. The combustion performance, as well as emission characteristics of biodiesel is comparable to petrodiesel, especially for the lower A/F ratio and higher energy rates. Biodiesel application in boiler results in an increment of combustion efficiency and significantly reduces environmentally harmful emissions except for NO_x. Another comparative study of sunflower and soybean-based biodiesel in an experimental boiler showed different result patterns where the combustion of biodiesel was found to be more efficient in lower energy rates [22]. Combustion performance increased along with the content of vegetable oil in the fuel, but their high viscosity would be a problem when used in high percentage blends. So, it is recommended to blend vegetable oil up to 40% composition with diesel to prevent problems caused by their high viscosity as well as the need to modify the engine [23].

Palm oil biodiesel with B100 composition was tested on 14-hp Kubota RT140 DI diesel engine for 800 hours of engine operation under high load and low-speed conditions, ran 12 hours a day to aerate fish pond [24]. The experiment was conducted to determine the long-term mechanical durability and reliability of the usage of pure biodiesel on a small agricultural diesel engine. Based on the ferrographic analysis and visual inspection, the engine was found to develop the usual rate of wear. Therefore, it can be concluded that biodiesel B100 can be used as an alternate fuel for a small diesel engine without any serious mechanical durability problems. In an experimental study conducted by Shahir et al. [25], a turbocharged, CRDI engine was operated using several blends of animal fat-based biodiesel (B10, B20, B30, B40, B50) at a constant speed of 2800 rpm. B30 animal fat biodiesel was found to have optimum performance and emission characteristics, even better than diesel. Higher composition of biodiesel resulted in higher BSFC and lower thermal efficiency due to lower calorific value and higher viscosity. It also increased the emissions of CO2 and NOx due to higher oxygen content in biodiesel.

Economically speaking, some types of biodiesel are found to be feasible and suitable for commercial-scale production [26]. Bazooyar et al. [27] conducted a study in order to

compare the annual cost needed to utilize a boiler power plant fueled with vegetable oil, biodiesel, petrodiesel, and their blends (B5 and B20). They simulated and calculated both internal costs associated with fuel prices and external costs associated with gaseous emissions needed to run a boiler power plant within a year period. The results showed that vegetable oil and pure biodiesel were not economically feasible compared to conventional petrodiesel, but the blends B5 and B20 indicated the opposite results. Although the fuel prices of B5 and B20 are higher in the market, their external costs in the boiler are much lower. Thus, replacing petrodiesel with B5 and B20 could reduce the total costs of the power plant up to USD 1,452 and USD 1,878, respectively, in a year.

However, to be widely used, biodiesel must be able to be produced at a lower cost. The biodiesel industry currently depends strongly on the cost of feedstock as it accounts for most of the biodiesel production cost. Some feedstock types such as non-edible oil plants and waste cooking oil can provide cheaper cost, but these low-cost feedstock types are used to have a higher amount of impurities. Additional treatments are needed in the manufacture to produce standard quality biodiesel with low-cost feedstock to increase manufacturing cost such as by using recent technology in machine learning and computational analysis [28–30].

2. Methods of Screening Paper

2.1. Criteria for selection of relevant literature

We searched for literature in the Google Scholar and ScienceDirect databases in December 2020 and January 2021 using the following criteria and boundaries: (1) written in English, (2) available as open access literature and free to download, and (3) related to ("biodiesel characteristics" OR "biodiesel emission" OR "biodiesel properties" OR "biodiesel performance") AND ("biodiesel production" OR "biodiesel method" OR "production cost"). Filters for the access type have been set to "open access", while for the article type have been set to "review articles", "research articles", and "patent reports". Subsequently, the literature obtained from the original search were screened manually by reading the abstract. To include as much relevant literature as possible, the literature was further expanded by reading the references of the articles encountered when reviewing other studies.

2.2. Extraction of useful information

The useful pieces of information of the selected literature were extracted by listing a set of questions.

- What problems does the article aim to solve?
- What methods were used?
- What are the results?
- What are the sources of biodiesel used?
- How did biodiesel samples be prepared?
- What engines were used for the experiment?
- How was the engine operation condition?
- Were the biodiesel samples able to run well in the engine?

- Was there any modification for the engine needed in order to run with biodiesel fuel?
- What are the effects of biodiesel on engine performance?
- What are the effects of biodiesel on engine emission characteristics?
- What challenges will be faced in future research?

3. Biodiesel Sources

In this part, various natural sources that have potential as biodiesel feedstock are discussed, especially related to previous studies about their engine performances and emission characteristics compared to diesel. The characteristic data were obtained by carrying out an engine test using biodiesel and biodiesel-diesel blends as fuel. Although the procedure of the test varies, they are usually with the general scheme of engine test as shown in Figure 1.

Performance and emission characteristics of biodiesel-fueled engine is influenced by various input parameters such as biodiesel blend composition, fuel injection pressure, and injection timing. Each parameter affects the characteristics differently, so it is important to investigate the best parameter for biodiesel with different natural feedstock [31]. The effect of injection parameter on thermal performance and emission characteristics of an oil burner fueled with B20 palm oil biodiesel-diesel has been studied by Abu-Hamdeh et al. [32]. An increase in injection pressure gives several advantages as it has been proven to be able to enhance the mixing rate and complete combustion and significantly reduce CO and soot particle emissions. However, NOx emission was found to increase with injection pressure.
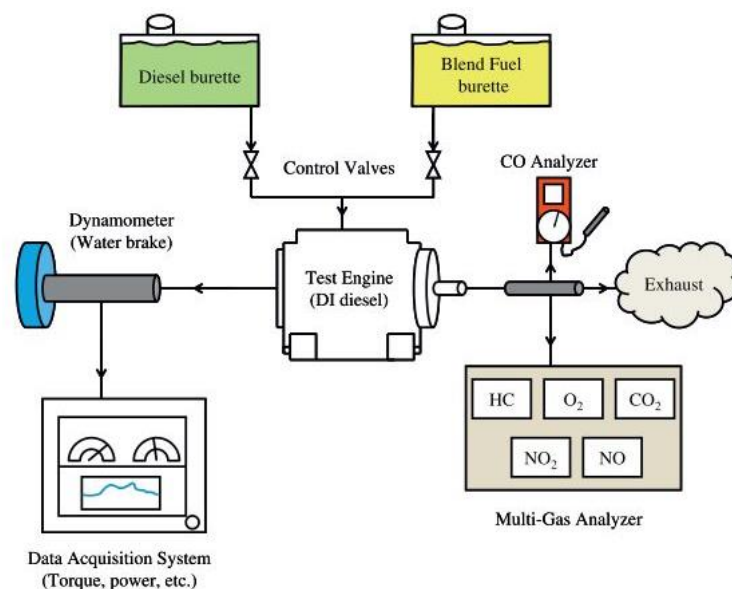

Figure 1. The basic scheme for engine performance and emission test [33].

Table 1. Performance characteristics of biodiesel from various natural sources.

Fuel type	Blend composition	Engine type	Test condition	BSFC	BTE	Exhaust gas temperature	Ref
Palm	B5	Mitsubishi 4D68 SOHC	variable speeds from	↑ 3.80% (1000 rpm)			[34]

		DI 4-stroke, 4-cylinder engine with EGR	1000 to 3000 rpm	↑ 4.22% (3000 rpm)		
Soy	B20, B40, B100	single cylinder, air cooled, vertical, DI diesel engine	variable loads at a constant speed of 1500 rpm	↑ 4.2% B20, ↑ 8.7% B40, ↑14.65% B100	↓ 2.61% B20, ↓ 4.95% B40, ↓ 8.07% B100	[35]
Corn	B10, B20, B30	single cylinder, 4-stroke, WC diesel engine	variable loads with maximum speed of 1500 rpm	↑ 4.13% B10 and B20, ↑ 2.48% B30	↑ 3.39% for B10, ↑ 2.07% for B20, ↑ 2.88% for B30	[36]
Canola	B10	DI, CI engine	variable loads at maximum speed of 2200 rpm	↑	↓	[37]
Jatropha	B100	double cylinder, DI, CI diesel engine	variable loads at constant speed of 1500 rpm	↑ 56.55% at full load	↓ 26.70% at full load	[38]
Jojoba	B20, B40	4-stroke, single cylinder CI engine	variable compression ratio (17:1, 17.5:1, and 18:1), variable loads at a constant speed	↑ (B40>B20) at full load	↓ (B20>B40) at CR 17:1 and 17,5:1 ↑ (B40>B20) at CR 18:1	[39]
Sun flower (hydrotreated, refined)	B25, B100	4-stroke, stationary DI diesel engine	variable loads at a constant speed of 1500 rpm	↓ 25% B25, ↓12,5% B100	↑ 10% B25, ↑ 38% B100	[40]
Peanut	B5, B20, B50, B100	3-cylinder Yanmar 3009D diesel engine	variable engine speeds (rated	↑ up to 9%, B100		[41]

			power = 14.2 kW)	(B100>B50> B20>B5)			
Flax	B10, B20, B30	an inline 4-cylinder, WC Mitsubishi Pajero engine	variable loads at a constant speed of 2000 rpm	↑ up to 13% at full load, B30 (B30>B20>B 10)	↓ up to 7.47% at full load, B20 (B20<B30<B 10)		[42]
Safflower	B100	a single cylinder, 4- stroke, CI engine	variable loads at a constant speed of 1500 rpm	↑ 16.87% (full load)	↓ 15.09% (full load)		[43]
Castor Seed	B10, B20, B30, B40	Techno-mate, TNM-TDE-700 machine	fixed load and speed	↑ 3.59% B10, ↑ 3.96% B20, ↑ 4.68% B30, ↑ 6.23% B40,			[44]
Cotton	B20	Kirloskar, single cylinder, 4-stroke diesel engine (CR 18:1)	variable loads at a constant speed of 1500 rpm	↑17.1%	↓ 4.13%		[45]
Avocado	B20, B40, B50, B60, B80, B100	single cylinder, 4-stroke, air cooled, direct injection-compression ignition engine (CR 20:1)	variable loads at a constant speed of 3600 rpm	↑ 6.06% B20, ↑ 12.12% B40, ↑ 15.15% B50, ↑ 18.18% B60, ↑ 27.27% B80, ↑ 33.33% B100 (at full load)	↓ 2.41% B20, ↓ 4.83% B40, d6.02% B50, ↓ 7.24% B60, ↓ 9.38% B80, ↓ 11.36% B100 (at full load)	↓ (B100<B80< B60<B50<B 40<B20)	[46]
Mahua	B5, B10, B15, B20	Kirloskar, twin cylinder diesel engine	variable loads at a constant	↓ 9.42% B5, ↑ 3.04% B10,	↑ 1.48 B5, ↓ 1.11% B10,		[47]

Feedstock	Blends	Engine	Operating condition				Ref.
			speed of 1500 rpm	↑ 3.95% B15, ↑ 5.17% B20 (full load)	↓ 2.59% B15, ↓ 3.70% B20 (full load)		
Pongamia pinnata	B20, B40, B60, B80, B100	Kirloskar, single cylinder 4-stroke, WC, CI engine	variable loads at a constant speed of 1500 rpm	↓ slightly for B20, almost same for B40, ↑ for B60, B80, and B100 (B100>B80>B60)			[48]
Mustard	B10, B20	an inline 4-cylinder, WC, Mitsubishi Pajero engine (CR 21:1)	variable loads and speeds ranging from 1000 to 4000 rpm	↑8.5% B10 ↑ 13.4% B20			[49]
Coconut	B5, B15	a 1-cylinder, 4-stroke, DI diesel engine	100% load with variable speeds of 1500 to 2400 rpm (interval 100 rpm)	↑ 0.53% for B5 and ↑ 2.11% for B15		↑ 2.22% for B5 and ↑ 3.33% for B15 (2200 rpm)	[50]
Hemp	B10, B20, B30, B50, B100	Kirloskar TV1, single cylinder, 4-stroke, DI engine	variable loads at a constant speed of 1500 rpm	↓ 2.56% B10 & B20, ↑ 2.56% B30, ↑ 5.13% B50 & B100	↓ 0.35% B10, ↓ 1.06% B20, ↓ 10.28% B30, ↓ 14.54% B50, ↓ 16.31% B100	↑ (B30>B20>B50>B10>B100)	[51]
Camelina	B20, B100	4-cylinder, 4-stroke, DI diesel engine	variable speeds between 1200 and 2600 rpm (interval 200 rpm) at full load	↑ 0.86% B20, ↑ 3.84% B100			[52]

Feedstock	Blends	Engine	Conditions				Ref
Grease	B20, B100	4-cylinder, 4-stroke, DI Fiat diesel engine	variable loads at a constant speed of 1500 rpm	↑ significantly (B100>B20)	↑ slightly (B100>B20)		[53]
Waste cooking oil	B20	single cylinder, 4-stroke, DI Kirloskar diesel engine	variable loads at a constant speed of 1500 rpm	↑ 2.96% (at full load)	↑ 10.79% (at full load)		[54]
Beef (beef bone marrow)	B50, B100	4-stroke, 4-cylinder, direct-injection diesel generator engine	variable loads (3.6, 7.2, and 10.8 kW)	↑ (B100>B50) at all loads	↓ (B100>B50) at 3.6 and 10.8 kW ↓ (B50>B100) at 7.2 kW	↑ (B100>B50) at all loads	[55]
Sheep (sheep fat)	B25, B50, B75, B100	Kirloskar TV1, single cylinder, WC diesel engine	variable loads at a constant speed of 1500 rpm		↓ from 1.8% to 2.3% (B100<B75<B50<B25)		[56]
Pork (pork lard)	B100	single cylinder, WC, DI diesel engine	variable loads at a constant speed of 1500 rpm		↓		[57]
Algae (*Scenedesmus obliquus*)	B50	single cylinder, 4-stroke, WC diesel engine (CR 20:1)	variable loads at a constant speed of 1400 rpm	↑ 14.55%	↓ 4.75%	↓ 5.21%	[58]
Algae (*Spirulina platensis*)	B10, B20, B100	1-cylinder, 4-stroke, compression ignition engine	variable loads at a constant speed of 1500 rpm		↓ 1.48% B10, ↓ 4.49% B20, ↓ 2.50% B100 (full load)		[59]
Fish	B20, B40, B60, B80, B100	single cylinder, 4-stroke,	variable loads and speeds		↓ up to 12.68% (B100<B80<		[60]

		air-cooled diesel engine					B60<B40<B20)		

Table 2. Emission characteristics of biodiesel from various natural sources.

Fuel type	Blend composition	Engine type	Test condition	HC	CO	CO2	NOx	Smoke opacity	Ref
Palm	B5	Mitsubishi 4D68 SOHC DI, 4-stroke, 4-cylinder engine with EGR	variable speeds from 1000 to 3000 rpm	↓ insignificantly	↓ (↑ at 1500 rpm)	↓ insignificantly (↓ significantly at 3000 rpm)	↑ significantly		[34]
Soy	B20, B40, B100	single cylinder, air cooled, vertical, DI diesel engine	variable loads at a constant speed of 1500 rpm	↓ 15% B20, ↓ 27%, B40, ↓ 38.4%, B100	↓ 11.36 B20, ↓ 29% B40, ↓ 41.7% B100		↑ 7.5%, B20 (B100>B40>B20)	↓ 20.5% B20, ↓ 33.41% B40, ↓ 48.23% B100	[35]
Corn	B10, B20, B30	single cylinder, 4-stroke, WC diesel engine	variable loads with maximum speed of 1500 rpm	↓ 7.69% B10, ↑ 15.38% for B20, ↑ 30.77% for B30			↓ 1.48% B10, ↓ 2.79% B20, ↓ 4.07% B30		[36]
Canola	B10	DI, CI diesel engine	variable loads at maximum speed of 2200 rpm	↓	↓	↑	↑	↓	[37]
Jatropha	B100	double cylinder, DI, CI diesel engine	variable loads at a constant speed of 1500 rpm				↑ 37.70% at full load		[38]
Jojoba	B20, B40	4-stroke, single cylinder, CI engine	variable compression ratios (17:1,	B40>diesel>B20l (CR 17:1)	Various for different CR and	-	B20>diesel>B40 (CR	B40>diesel>B20 at full loads	[39]

Feedstock	Blend	Engine	Operating conditions						Ref
			17.5:1, and 18:1), variable loads at a constant speed	Diesel>B20>B40 (CR 17,5:1) B20>Diesel>B40 (CR 18)	loads, but generally Diesel>B20>B40		17,5:1 and 18:1) B20>B40>diesel (CR 17:1)		
Sunflower (hydrotreated refined)	B25, B100	4-stroke, stationary DI diesel engine	variable loads at a constant speed of 1500 rpm	↓ 42% for B25, ↓ 55% for B100 (at full load)	↓ 9% for B25, ↓ 37% for B100 (at full load)		↓ 10% B25, ↓ 18.18%. B100		[40]
Peanut	B5, B20, B50, B100	3-cylinder Yanmar 3009D diesel engine	variable engine speeds (rated power = 14.2 kW)	↑ for B20 and B100 (↑ 30%, B100), d for B5 and B50	↓ up to 29%, B50 (B50<B100<B5<B20)	↑ up to 18%, B100 (B100>B50>B5>B20)	↑ up to 30%, B100 (B100>B50>B20>B5)		[41]
Flax	B10, B20, B30	an inline 4-cylinder, WC Mitsubishi Pajero engine	variable loads at a constant speed of 2000 rpm	↑ up to 15.8% at full load, B30 (B30>B20>B10)	↓ up to 27.7% at full load, B20 (B20<B30<B10)		↑ up to 14.4% at full load, B30 (B30>B20>B10)		[42]
Safflower	B100	a single cylinder, 4-stroke, CI engine	variable loads at a constant speed of 1500 rpm	↓ 3.85% (full load)	↓ 4.21% (full load)		↑ 1.27% (full load)	↓ 2.57% (full load)	[43]
Castor Seed	B20, B40, B60, B80, B100	Technomate, TNM-TDE-700 machine	fixed load and speed	↓ 20% B20, ↓ 37% B40, ↓49% B60, ↓ 59% B80, ↓ 67% B100	↓ 13% B20, ↓ 24% B40, ↓ 33% B60, ↓ 40% B80,		↑2% B20, ↑4% B40, ↑6% B60, ↑8% B80, ↑ 10% B100		[44]

					↓ 48% B100				
Cotton	B20	Kirloskar, single cylinder, 4-stroke, diesel engine (CR 18:1)	variable loads at a constant speed of 1500 rpm	↓ 3.86%	↓ 18.4%	↑ 14.0%	↑ 8.0%		[45]
Avocado	B20, B40, B50, B60, B80, B100	single cylinder, 4-stroke, air cooled direct injection-compression ignition engine (CR 20:1)	variable loads at a constant speed of 3600 rpm	↓ (B100<B80<B60<B50<B40<B20)		↓ (B100<B80<B60<B50<B40<B20)	↑ (B100>B80>B60>B50>B40>B20)	↓ (B100<B80<B60<B50<B40<B20)	[46]
Mahua	B5, B10, B15, B20	Kirloskar, twin cylinder diesel engine	variable loads at a constant speed of 1500 rpm	↓ 6.56% B5, ↓ 11.48% B10, ↓ 16.39% B15, ↓ 21.31% B20 (full load)	↓ 21.05% B5, ↓ 31.58% B10, ↓ 36.84% B15, ↓ 42.11% B20 (full load)		↑ 11.11% B5, ↑ 15.24% B10, ↑ 22.33% B15, ↑ 26.98% B20 (full load)	↓ 12.5% B5, ↓ 22.92% B10, ↓ 37.5% B15, ↓ 50% B20 (full load)	[47]
Pongamia pinnata	B20, B40, B60, B80, B100	Kirloskar, single cylinder 4-stroke, WC, CI engine.	variable loads at a constant speed of 1500 rpm	↓ B20, almost zero for B40, B60, B80, and B100	↓ B80 and B100, zero for B20, B40, B60 (75% load)	↓ except for B20 (B60<B40<B100<B80<B20)	↓ (B60<B40<B80<B100<B20)		[48]
Mustard	B10, B20	an inline 4-cylinder, WC, Mitsubishi Pajero engine (CR 21:1)	variable loads and speeds ranging from 1000 to 4000 rpm	↓ 24% B10, 42% B20	↓ significantly (19-40% lower) (B20<B10<B0)		↑9% B10, ↑ 12% B20		[49]

Feedstock	Blends	Engine	Operating conditions						Ref
Coconut	B5, B15	a one-cylinder, 4-stroke, DI diesel engine	variable loads at a constant speed of 2200 rpm	↓ 13.89% for B5 and ↓ 22.88% for B15 (full load)	↓ 13.38% for B5 and ↓ 21.51% for B15 (full load)	↑ 2.54% for B5 and ↑ 4.64% for B15 (full load)	↑1.42% for B5 and ↑ 3.19% for B15 (full load)		[50]
Hemp	B10, B20, B30, B50, B100	Kirloskar TV1, single cylinder, 4-stroke, DI engine	variable loads at a constant speed of 1500 rpm	↓ 11.11% B10, ↓ 2.22% B20, ↑ 2.22% B30, ↓ 8.89% B50, ↓ 4.44% B100	↓ 0.13% B10, ↓ 0.14% B20, ↓ 0.17% B30, ↓ 0.18% B50 ↓ 0.21% B100	↑ 2.08% B10 and B50, unchanged for B20, ↓5.00% B30, ↑ 6.25% B100	↑ 4.17% B10, ↑ 10.42% B20, ↑ 19.79% B30 and B50, ↑ 20.83% B100	↓18.79% B10, ↓15.03% B20, ↓12.72% B30, ↓4.34% B50, ↑6.36% B100	[51]
Camelina	B20, B100	4-cylinder, 4-stroke, DI diesel engine	variable speeds between 1200 and 2600 rpm (interval 200 rpm) at full load		↓ 15.4% B100 (B100<B20)	↓13.8% B100 (B100<B20)	↑ 9.6% B100 (B100>B20)		[52]
Grease	B20, B100	4-cylinder, 4-stroke, DI Fiat diesel engine	variable loads at a constant speed of 1500 rpm	↓ slightly B20, ↓ significantly B100	↓ 11.26% B20 ↓ 43% B100 (full load)	↑1.8% B20, ↑ 0.7% B100 (full load)	↑ 12.28% B20 ↑ 20.52% B100 (full load)		[53]
Waste cooking oil	B20	single cylinder, 4-stroke, DI Kirloskar diesel engine	variable loads at a constant speed of 1500rpm	↓ 2.86% (at full load)	↓ 29.07% (at full load)	↑ 3.19% (at full load)	↑ 5.33% (at full load)		[54]
Beef (beef bone marrow)	B50, B100	4-stroke, 4-cylinder, direct-injection diesel generator engine	variable loads (3.6, 7.2, and 10.8 kW)	↓ 24% B50 ↓ 12% B100	Diesel>B100>B50 at all loads	↑ slightly for both B50 and B100	↓ slightly (B50>B100)	-	[55]

Feedstock	Blends	Engine	Conditions						Ref.
Sheep (sheep fat)	B25, B50, B75, B100	Kirloskar TV1, single cylinder, WC diesel engine	variable loads at a constant speed of 1500 rpm	↑ slightly except for B100 (B100>B75>B50>B25)	↑ significantly (B100>B75>B50>B25)		↓ significantly at full load (B100<B75<B50<B25)	↑ (B100>B75>B50>B25)	[56]
Pork (pork lard)	B100	single cylinder, WC, DI diesel engine	variable loads at a constant speed of 1500 rpm	↓ slightly (less than 7.5%)	↓ 12.32%		↓ 3.74% (full load)	↓ 7.69%	[57]
Algae (*Scenedesmus obliquus*)	B50	single cylinder, 4-stroke, WC diesel engine (CR 20:1)	variable loads at a constant speed of 1400 rpm	↓ 2.84%	↓ 4.63%	↓ 4.46%	↑ 4.63%		[58]
Algae (*Spirulina platensis*)	B10, B20, B100	1-cylinder, 4-stroke, compression ignition engine	variable loads at a constant speed of 1500 rpm	↓ up to 33.33% (B100<B20<B10)	↓ 17.42% B10, ↓ 24.84% B20, ↓ 61.29% B100 (at full load)		↑ 1.75% B10, ↑ 6.25% B20, ↑ 23.31% B100	↓ (B100<B20<B10)	[59]
Fish	B20, B40, B60, B80, B100	single cylinder, 4-stroke, air-cooled diesel engine	variable loads and speeds	↓ up to 20.45% (B100<B80<B60<B40<B20)	↓ up to 43.94% (B100<B80<B60<B40<B20)		↑ up to 55.03%, (B100)		[60]

3.1. Plant oils

3.1.1. Palm

Palm oil, like other vegetable oils, can be used to produce biodiesel for an internal combustion engine. An experimental study using palm oil biodiesel/diesel fuel with a composition of 5:95 (B5) was conducted on a Mitsubishi 4D68 SOHC DI, 4-stroke, 4-cylinder diesel engine. The results on engine performance showed an increase in BSFC up to 4.22% compared to the data obtained when using straight diesel at an engine speed of 3000 rpm. It was also found that the utilization of palm oil B5 could reduce the CO emission level and insignificant amount of HC and CO_2 emissions, while NO_x emission was found to be higher compared to that of diesel [34].

3.1.2. Soybean

Soybean oil is a vegetable oil extracted from the seeds of soybean. It is commonly used as cooking oil and natural feedstock in biofuel production. Soybean biodiesel-diesel blends with 20% (B20), 40% (B40), and 100% (B100) proportions of biodiesel were tested on a single cylinder, air-cooled, vertical, DI diesel engine [35]. Several performances and emission parameters of each blend were noted when running a diesel engine under variable loads and constant speed of 1500 rpm condition, then the results were compared to that of diesel. Soybean biodiesel-diesel blends was indicated having poor performance compared to diesel as it had a higher value of BSFC by 4.2%, 8.7%, and 14.65% and lower brake thermal efficiency by 2.61%, 4.95%, and 8.07% for B20, B40, and B100 blends, respectively. On the other side, biodiesel-diesel blends showed better characteristics in terms of emission as the use of these blends could significantly reduce HC, CO, and smoke emission levels. The greater amount of emission cut gained from the blend, the higher the composition of soy biodiesel. However, up to a 7.5% increase in NO_x emission was observed from the use of biodiesel blends sourced from soybean.

3.1.3. Corn

Corn oil methyl ester biodiesel was mixed with diesel fuel into B10, B20, and B30 biodiesel-diesel fuel blends which were used to ran a single-cylinder, 4-stroke diesel engine in an experimental test conducted by Balaji et al. [36]. As shown in Table 2, an increase in both BSFC and BTE values was observed. Hydrocarbon emissions were reported higher than when the engine was fueled by neat diesel (up to 30.77%), while nitrogen emissions were slightly lower. These results are contrary to most of the other studies about biodiesel emission characteristics where biodiesel utilization in diesel engine tends to produce more NO_x emission compared to diesel.

3.1.4. Canola

Canola is a crop with plants from three to five feet tall that produce pods from which seeds are harvested and crushed to produce canola oil and food. A recent study conducted by (author) et al. investigated the engine performance and emission of B10 canola biodiesel-diesel fuel on a DI diesel engine under various load conditions. A reduction in engine performance was observed as an increase in BSFC and a decrease in BTE were found from B10 canola biodiesel fuel. However, the use of canola biodiesel gives a significant improvement in emission characteristics such as lower amounts of HC, CO, and smoke emissions. Besides, NO_x and CO_2 emissions were found to be higher compared to diesel [37].

3.1.5. Jatropha

Jatropha curcas seeds contain 27–40% oil that can be processed to produce high-quality biodiesel fuel that is usable in a standard diesel engine. Shehu et al. reviewed and evaluated *Jatropha* as natural feedstock for biodiesel related to its ecological requirements and land suitability in Nigeria. It was found that the choice of *Jatropha* for biodiesel production in Nigeria is seen to be beneficial considering that suitable ecological conditions exist to support the cultivation of the crops in most parts of the country. *Jatropha* has less rigid ecological requirements that make it easy and cheap to be produced [61]. Paul et al. [38] ran an experimental test on a double cylinder, DI, CI diesel engine using pure *Jatropha* biodiesel (B100) as fuel, and so was tested straight diesel fuel as a

comparison. The test was carried out in variable engine loads and a constant speed of 1500 rpm conditions. The use of B100 *Jatropha* biodiesel has resulted in a significant loss for engine performance as BSFC value was found 56.55% higher and BTE was 26.70% lower at full load than that obtained from straight diesel. It was also found that combustion of *Jatropha* pure biodiesel in diesel engine emitted a 37.70% higher amount of NO_x emission.

3.1.6. Jojoba

Jojoba has promising potential as an alternative biofuel source. Oil extracted from jojoba seeds contains a long chain of ester compounds and has a very high boiling point of nearly 400°C that makes it suitable to be used as fuel. Hariram et al. compared performance and emission characteristics between straight diesel and jojoba biodiesel (B20 and B40) when used as fuel on a single-cylinder, 4-stroke, CI engine [39]. At full load condition, the BSFC of jojoba biodiesel blends was higher and the BTE was lower compared to diesel, except at the compression ratio of 18:1 where the BTE was found to be higher. The emissions from B20 and B40 jojoba biodiesel at full engine load condition were generally lower for HC, CO, and smoke particles and higher for NOx parameters, but it was noted that B40 fuel emitted less amount of NOx emission at a compression ratio of 17.5:1 and 18:1.

3.1.7. Sunflower

Sunflower oil is a vegetable oil extracted from the seeds of sunflowers. Refined sunflower oil which has been hydrotreated was tested on 4-stroke, stationary DI diesel engine by Hemanandh et al. [40] The engine performance and emission parameters obtained from utilizing the hydrotreated refined sunflower oil and its blend by 25% proportion with diesel was indicated as a favorable mix. From the engine performance improvement observed, there were 10% and 38% increase in BTE and 25% and 12.5% decrease in BSFC for B25 and B100 fuels, respectively. Decreases in all emission parameters were also observed at full load conditions with a maximum reduction of 55% found in HC emission for B100 fuel. However, CO_2 and smoke emissions were not determined in this experiment.

3.1.8. Peanut

Santos et al. [41] carried out an experimental study to investigate the performance and emission parameters of peanut oil biodiesel and its blends when performed on a 3-cylinder Yanmar 3009D diesel engine. Different blends based on the proportion of biodiesel in sample fuels were made consist of B5, B20, B50, and B100 biodiesel-diesel fuels. From the experiment, relatively unsatisfactory parameters were obtained from peanut oil biodiesel fuels as it indicated up to 9% higher of BSFC and significantly increased CO_2 and NO_x emissions by 18% and 30% maximum, respectively for B100 fuel and straight diesel. HC emission levels were found to be increased on B20 and B100, while it was decreased on B5 and B50. Finally, a maximum 29% decrease in CO emission obtained by B50 fuel was also observed from the experiment.

3.1.9. Flax

An experimental study using B10, B20, and B30 flax oil biodiesel was carried out on an inline 4-cylinder, Water Cooled Mitsubishi Pajero engine. The engine was operated under variable loads at a constant speed of 2000 rpm conditions and data related to engine

performance and emission parameters were recorded. Compared to parameters obtained when the engine ran by diesel fuel, higher BSFC (by up to 13%, B30) and lower BTE (by up to 7.47%, B20) values were gained from flax oil biodiesel blend samples when the engine was running at maximum load. Less favorable parameters were also found in terms of emission. The uses of flax biodiesel blend fuels resulted in a higher amount of HC and NOₓ emissions by up to 15.8% and 14.4%, respectively, for B30 fuel at full load condition. The only positive parameter came from CO emission as the combustion of all biodiesel blend fuels emitted significantly less amount of CO emission (by up to 27.7% for B20 at full load) compared to that of diesel [42].

3.1.10. Safflower

Balasubramanian et al. [43] ran an experimental test utilizing pure safflower biodiesel (B100) and straight diesel as fuel to run a single-cylinder, 4-stroke, CI engine. The test was carried out in variable engine loads and a constant speed of 1500 rpm conditions. A slight decrease in engine performance was observed when running the engine with B100 safflower biodiesel as BSFC value was found 16.87% higher and BTE was 15.09% lower than that obtained from straight diesel at full load condition. An insignificant decrease in HC, CO, and smoke emission levels, as well as a slight increase in NOx emission, were observed when using B100 safflower biodiesel fuel with less than 5% change in every parameter compared to emission from straight diesel. This result could make safflower biodiesel one of the most comparable fuels with diesel, even utilizing safflower biodiesel in a lower proportion of biodiesel-diesel blend could possibly result in a renewable fuel with better characteristics than diesel.

3.1.11. Castor seed

Biodiesel fuel derived from castor seed was produced using the transesterification method, they were then blended with diesel into B10, B20, B30, and B40 fuels. An engine test was carried out on a Techno-mate, TNM-TDE-700 machine to obtain performance and emission characteristics resulted from utilizing these biodiesel-diesel blended fuels in the diesel engine. In terms of BSFC, the castor biodiesel blends were found to have slightly higher yet acceptable values compared to that of diesel with the BSFC values which increased along with biodiesel composition in the fuel blend. Promising results were also found from the investigation on emission characteristics using different variations of biodiesel-diesel blends (B20, B40, B60, B80, and B100). The utilization of castor biodiesel in a diesel engine could reduce HC and CO emission by up to 67% and 48%, respectively, compared to diesel. But, the slight increase in NOx emission by less than 10% was observed, making it one challenge to be solved in the future [44].

3.1.12. Cotton

Sundar et al. [45] carried out an engine test using cotton oil biodiesel/diesel fuel with a volume ratio of 20:80 (B20) on a Kirloskar single-cylinder, 4-stroke diesel engine equipped with 18:1 compression ratio. The engine was run at a constant speed of 1500 rpm and some engine performance and emission parameters were noted. The BSFC of B20 cotton biodiesel was 17.1% higher and the BTE was 4.13% lower compared to that of diesel. In terms of emission, combustion of B20 cotton oil biodiesel on the diesel engine emitted

higher levels of CO2 and NOx by 14% and 8%, respectively, and lower amounts of HC and CO by 3.86% and 18.4%, respectively.

3.1.13. Avocado

Anawe et al. [46] studied performance and emissions on a single-cylinder, compression ignition engine fueled with six different compositions of avocado biodiesel-diesel blends (B20, B40, B50, B60, B80, B100). They analyzed engine performance parameters such as BSFC, BTE, and exhaust gas temperature as well as parameters for emission. The results showed that BSFC and NOx emission were higher, whereas BTE, exhaust gas temperature as well as HC, CO2, and smoke emissions were lower than pure diesel. It was also noted that the amount of the increase or decrease in all parameters observed was proportional to the amount of biodiesel in the blend composition.

3.1.14. Mahua

Raman et al. [47] tested a Kirloskar twin cylinder diesel engine with B5, B10, B15, and B20 compositions of mahua biodiesel-diesel blends. They reported a slight increase in Brake Specific Fuel Consumption (BSFC) except for B5 fuel which was noted to have 9.42% lower BSFC than diesel. An increase of 26.98% in NOx emission and reduction of 21.31% in HC, 42.11% in CO, and 50% in smoke particles during engine operation using B20 fuel were observed as the maximum or minimum value of the mentioned emission parameters compared to diesel and other biodiesel blends.

3.1.15. Pongamia pinnata

Pongamia pinnata or also known as Karanja is a non-edible plant species capable of growing in almost all types of lands. It can even grow in an extreme environment such as saltwater and withstand extreme weather conditions. A single tree of *Pongamia pinnata* could yield about 25 to 100 kg of seeds containing around 27% to 50% of oil annually. Raw *Pongamia* oil has relatively lower kinematic viscosity (37.12 mm2/s at 40°C) compared to other raw vegetable oils which should give advantages to its fuel properties. Sureshkumar et al. [48] experimented on the engine performance and emission parameters of a single-cylinder, 4-stroke, water-cooled diesel engine running with blends of Karanja biodiesel (B20, B40, B60, B80, B100). They found out that B20 blend gave the best results in terms of engine performance. It has lower BSFC even when compared to diesel. In emission characterization, all blends of Karanja biodiesel were found to emit a lower amount or similar amount of harmful emissions such as HC, CO, CO_2, and even NO_x with an exception for B20 blend which indicates an increase in CO2 emission compared to diesel.

3.1.16. Mustard

Engine performance and emission characteristics of mustard biodiesel-diesel blends of B10 and B20 compositions were evaluated in an experimental study using an inline 4-cylinder, Water Cooled Mitsubishi Pajero engine with compression ratio of 21 as experimental engine. The value of BSFC, as well as emission parameters such as HC, CO, and NO_x were analyzed in the experiment. The results from the test of mustard biodiesel blends showed that BSFC and NOx emissions were 8.5% and 9% higher for B10, respectively. Meanwhile, for B20, BSFC and NOx emissions were 13.4% and 12% higher, respectively. However, HC and CO emissions were reduced by up to 42% and 40%, respectively, compared to that of diesel [49].

3.1.17. Coconut

B5 and B15 blends of coconut oil biodiesel were utilized on a single-cylinder, 4-stroke, DI diesel engine under variable engine speeds. Performance and emission parameters of these samples were recorded and compared to that of diesel. The BSFC and exhaust gas temperature were noted slightly higher than diesel by less than 3.33% differences which make these blends comparable as diesel fuel. The engine emissions when using the B15 blend were 22.88% and 21.51% lower for HC and CO emissions, respectively, but 4.64% and 3.19% higher for CO2 and NOx emissions. The emission characteristics of the B5 blend were noted similar as that of B15, with higher emission in B15, but both were lower than that of diesel [50].

3.1.18. Cannabis sativa

Cannabis sativa or hemp is a crop plant grown in temperate zones cultivated annually from seeds. Hemp seeds have high oil content ranging from 26% to 42% which makes them suitable as a biofuel feedstock. Different biodiesel blends consisting of diesel and biodiesel produced by alkali base transesterification of *Cannabis sativa* oil in B10, B20, B30, B50, and B100 compositions were tested on Kirloskar TV1 single-cylinder, 4-stroke DI diesel engine. The BSFC of B10 and B20 fuels were noted lower than diesel, while an acceptable increase was observed for other blends. The results also showed that, for emission characteristics, the use of hemp biodiesel promotes lower emission levels of HC, CO, and smoke particles in general, comparable emission of CO2, and higher emission of NOx compared to that of diesel [51].

3.1.19. Camelina

Camelina sativa or also known as false flax is a plant that is commonly cultivated as an oilseed crop in Europe or Northern America. Engine performance and emission characteristics of false flax biodiesel (B100), diesel, and their blend (B20) were evaluated in an experimental study using a 4-cylinder, 4-stroke, direct injection diesel engine as an experimental setup. The value of BSFC, as well as emission parameters such as CO, CO2, and NOx were determined from the experiment. The results from the test using B100 false flax biodiesel showed that BSFC and NOx emissions were 3.84% and 9.6% higher, respectively, but CO and CO2 emissions were reduced by 15.4% and 13.8%, respectively, compared to those using diesel [52].

3.2. Waste cooking oils

3.2.1. Grease

Grease is thickened oil having a solid or semi-solid phase, which is also a dispersion of thickening agent in liquid lubricant oil. There are several types of grease such as brown and yellow grease, both sourced from the waste of food industry but having different oil content and characteristics. A study of biodiesel fuel produced from yellow grease collected from restaurant waste was conducted by Chaichan et al. [53] Yellow grease biodiesel was prepared using the base transesterification method, then the product was blended with diesel into B20 fuel. Diesel (B0), pure yellow grease biodiesel (B100), and B20 blend were tested on a single-cylinder, water-cooled, DI diesel engine to investigate its performance and emission characteristics. They reported an increase in both BSFC and BTE parameters, significant decrease in HC and CO emissions, slight increase in CO2

emission, and significant increase in NOx emission from the use of B20 and pure yellow grease biodiesel.

3.2.2. Waste Cooking Oil

Waste cooking oil (WCO) is a potential source of relatively cheap feedstock for biodiesel production, but it has high free fatty acid (FFA) contents which can be a serious bottleneck for the process of transesterification. Avase et al. [54] in their study, made biodiesel fuel from the transesterification of waste cooking oil (WCO) mixed with diesel in the proportion of 2:8 (B20). The utilization of B20 WCO biodiesel could reduce the amount of HC and CO emissions by 2.86% and 29.07%, respectively, but slightly increased the amount of NO_x and CO_2 emissions by 5.33% and 3.19% compared to that of diesel. An increase in both BSFC and BTE parameters by 2.96% and 10.79%, respectively, at full load was also observed from the experiment.

3.3. Animal fats

3.3.1. Beef

Beef bone marrow contains fat that could be potentially converted into biodiesel fuel. An experimental study has been done by Erdoğan et al. [55] to test engine performance and emission run with beef bone marrow fat biodiesel and its blend with straight diesel in the proportion of 1:1 (B50). The engine used in the study was a 4-cylinder, 4-stroke, DI diesel generator engine, and the test was carried out under various load conditions. The results showed that the use of beef bone marrow biodiesel and its blend caused a reduction in engine performance due to higher BSFC and lower thermal efficiency. However, positive effects were shown in the form of a significant amount of reduction in HC, CO, and NO_x emissions. Only a slight increase in CO_2 emission was reported.

3.3.2. Sheep

Oil and fat contained in sheep meat could also be used as a source of biodiesel. Ultrasonic-assisted transesterification process was carried out to convert sheep fat into biodiesel and then several proportions of biodiesel were blended with diesel to obtain B25, B50, and B75 fuels. Sheep fat biodiesel (B100) and its blends were tested on a Kirloskar TV1, single-cylinder, water-cooled diesel engine at a constant engine speed of 1500 rpm. The brake thermal efficiency of sheep fat biodiesel and biodiesel blend fuels by amounts was slightly lower compared to diesel, ranging from 1.8% to 2.3%. The sheep fat biodiesel and its blends were also found emitting a higher amount of harmful emissions except for NOx, on contrary to other data from other natural source biodiesels [56].

3.3.3. Pork

Pork lard, like other animal fats, has a high cetane number, rich oxygen content, and very close lower heating values when compared to standard diesel. An experimental study utilizing pure biodiesel (B100) derived from waste pork lard on a single-cylinder, water-cooled, DI diesel engine has been done to observe the performance and emission characteristics of pork lard biodiesel. Although using pork lard biodiesel in the engine indicated a reduction in brake thermal efficiency, the emission parameters obtained were satisfactory. Using pork lard biodiesel has been proven able to reduce all emission

parameters observed in this study, including NO_x by a maximum 12.32% reduction found in CO emission compared to diesel [57].

3.4. Other oils

3.4.1. Algae

Algae have become a popular biofuel feedstock as it is known to store a high amount of lipid and oil contents. Algae could also produce biomass very rapidly; some species even have a doubling time for only six hours. The engine performance and emission when running with algae biodiesel have been studied utilizing various species of algae. B50 fuel derived from *Scenedesmus obliquus* mixed with diesel fuel has been tested on a single-cylinder, 4-stroke, water-cooled diesel engine [58]. The B50 fuel has a 14.55% higher BSFC, and 4.75% and 5.21% lower BTE and exhaust gas temperature, respectively. Reduction of HC, CO, and CO2 emissions by 2.84%, 4.63%, and 4.46% was also observed, while NOx emission was found higher by 4.63% compared to diesel. In the other study, another algae species, *Spirulina platensis*, was converted into biodiesel and biodiesel-diesel blends of B10 and B20 [59]. The engine test on a diesel engine has been done, and the results showed a similar trend on BTE and emission parameters to what has been found in *Scenedesmus obliquus* biodiesel. For B100 *Spirulina platensis* biodiesel, the BTE, HC, and CO emission levels were found lower by 2.5%, 33.33%, 61.29%, respectively, while NOx emission was increased by 23.31% compared to diesel.

3.4.2. Fish

Some species of fish considered as oily fish store high content of oil in their tissues. Fish oil is commonly used by people as a supplement, but it is also possible to use fish oil as material for biodiesel production. Performance and emission tests of Fish Oil Methyl Ester (FOME) and their blends (80%, 60%, 40%, 20%) with diesel were carried out on a single-cylinder, 4-stroke, CI engine at variable load conditions. The results indicated a reduction in engine performance as up to 12.68% decreases in BTE were observed from B100 fuel. The HC and CO emissions were reduced by up to 20.45% and 43.94%, respectively, while NO_x emission was increased by up to 55.03% compared to that of diesel [60].

4. Manufacturing process of biodiesel

The manufacturing process of biodiesel is one of the most important factors in biodiesel development. The common methods of biodiesel production that are currently used to yield biodiesel from crude oil are direct use and blending, microemulsion, pyrolysis, and transesterification. The choice of production method determines not only the quality of biodiesel yielded but also the cost and duration of the manufacturing process. In this section, the recent studies about biodiesel production related to their efficiency, stability, cost, factors that affected the process, and quality of the products are evaluated in detail.

Recently, waste from biodiesel production and combustion also has been reused to produce other forms of bioenergy or useful materials, making biodiesel even more environmentally friendly. A study conducted by Yin et al. [62]   showed huge potential from ash produced from the combustion of oil palm biomass waste to be reused for

several purposes. Its composition and toxicity were assessed by observation with electron microscope and toxicity characteristic leaching procedure (TCLP). It is concluded that oil palm ash should not be considered as toxic material and have the potential to be used as crude fertilizer and cement mixture. Other waste from oil palm production such as empty fruit bunches (EFBs) also has reusability potential as a fuel for oil palm mill boiler after being processed through the torrefaction process to reduce its moisture content [63]. The use of torrefied EFBs in the boiler as alternative fuel offers cleaner combustion and additional revenue for palm oil processing.

4.1. Direct use and blending

The direct use of natural oils especially those sourced from vegetables to run diesel engines has been applied since the 1900s. Vegetable oil offers numerous advantages over diesel fuel such as liquid nature-portability, heat content which is about 80% diesel fuel, availability, and renewability. Higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains are some disadvantages of vegetable oil which cause many inherent problems when they are used as fuel on diesel engines. Thus, crude vegetable oils are often mixed directly or diluted with diesel fuel to improve the viscosity [64,65].

Experiments related to the direct use of vegetable oil as fuel for diesel engines and their performance and emission characteristics have been done by many researchers. Almeida et al. [66] tested pure palm oil to run a diesel generator engine (4-stroke, NA, DI) for 350 hours of operation. Palm oil was heated at 50°C and 100°C before the fuel pump to promote smooth flow, then the effect of oil temperature was observed. A high level of deposits was found in the combustion chamber when it was operated with palm oil heated at 50°C due to incomplete combustion, but the use of oil heated at 100°C successfully reduced the deposits to an acceptable level and presented better combustion. In term of engine performance, diesel engine fueled by pure palm oil has higher ignition delay and specific fuel consumption compared to that of diesel. Investigation of the emission characteristics also showed unsatisfactory results where there were higher amount of CO, CO_2, and HC emissions. However, the emission of NOx was noted to be significantly lower than diesel. This result made a good agreement with the experiment using other sources of vegetable oils (raw sunflower oil, raw cottonseed oil, raw soybean oil, refined corn oil, distilled opium poppy oil, and refined rapeseed oil [67] as well as Karanja oil investigated in another study [68]), except the fact that some of these oils emitted less CO_2 emission than diesel.

Rapeseed oil (RSO) and its blend with standard low sulfur diesel with various compositions were tested using 2.0 L, 4-cylinder, 16-valve, direct injection diesel engine [69]. The NOx emission for RSO and its blend was lower than diesel, but they produced a much higher amount of soot emissions. Further reduction of NOx emission by 22% was achieved on 30% RSO blend by retarding the injection timing up to 3° bTDC and increasing the injection pressures up to 1200 bar, but the concentration of soot particles was still higher compared to diesel under this condition. Reduction of NOx emission at retarded injection timing also occurred when lemongrass oil (LGO) and its blends were run in diesel engines [70]. However, advanced injection timing (27° bTDC) is considered

to be an optimal condition for LGO-diesel blends as it indicated better performance and emitted a lower amount of HC and smoke emissions.

A mixture of sesame oil and diesel fuel in the ratio of 1:1 was tested in Lombardini 6 LD 400, one cylinder, 4-stroke, air-cooled, direct injection diesel engine to investigate its performance and emission characteristics [71]. The results were satisfactory as this mixture could successfully produce and maintain power and torque close to that produced by diesel, also emitted less amount of CO and NOx emissions. The only disadvantage reported was the higher number of BSFC due to the lower heating value of the blend compared to diesel. The direct use and blending of *Jatropha* oil were studied by Forson et al. [72] Diesel fuel, *Jatropha* oil, and blends of *Jatropha* oil-diesel with the proportion of 20%:80%, 50%:50%, and 2.6%:97.4% were used to operate an air-cooled, direct-injection, single-cylinder, 4-stroke diesel engine. The unmodified engine ran well on all fuels tested. The results on investigation of performance and emission characteristics put 2.6%:97.4% of *Jatropha* oil-diesel blend as the best even when it was compared to straight diesel, making *Jatropha* oil recommended for use as an additive for diesel fuel in the low amount.

A study conducted by Roy et al. [33] compared emission characteristics between the blends of canola oil-diesel and transesterified canola oil-diesel as fuels on a 4-stroke, 2-cylinder, naturally aspirated DI diesel engine. The canola oil-diesel fuel had a higher viscosity and a lower oxygen content compared to canola oil-diesel fuel at the same proportion which contributed to the lower fuel conversion efficiency of canola oil-diesel fuel. It was concluded that canola oil-diesel fuel generally emitted a higher amount of CO, HC, and NOx emissions compared to biodiesel-diesel, except for CO emission at canola oil-biodiesel proportion of up to 5% and HC emission at canola oil-biodiesel proportion of up to 5% and low-speed condition.

Although for a short-term use with low ratios of vegetable oil-diesel blends have been found to be successful, the direct use of vegetable oil in diesel engines has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engine. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening are obvious problems that cannot be ignored. Some significant engine modifications are required for enabling vegetable oil to be used as diesel fuel, including changing of piping and injector construction materials. Otherwise, engine running times are decreased, maintenance costs are increased due to higher wear, and the danger of engine failure is increased [64,65].

4.2. Microemulsion

Micro-emulsification is a potential method to solve the problem of the high viscosity of crude natural oil. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. The three components that make up a microemulsion are usually acted as an oil phase, an aqueous phase, and a surfactant [64,65].

Patidar et al. [73] studied phase behavior and physicochemical properties of Karanja oil-ethanol microemulsion with span 80 (sorbitan monooleate) and span 85 (sorbitan trioleate) as surfactants. Karanja oil was a mixture with up to 15% ethanol. Variable amounts of the span were added when the concentration of ethanol reached above 15% under 500 rpm of continuous stirring condition. It can be seen from the phase diagram that span 80 made better solubilization of ethanol in the oil phase due to its higher content of OH group. The physicochemical analysis showed that the ethanol-oil ratios of 65:35, 70:30, 75:25, 80:20, 85:15, 90:10, and 95:5 with span 80 had kinematic viscosity which meet the ASTM standard of B100 biodiesel (1.9-6 mm^2s^{-1}) at 313.15 K. Therefore, Karanja oil-ethanol-span 80 microemulsion could be used as alternative diesel fuel and is comparable to that made by transesterification process.

Span 80 as a hydrophilic surfactant was mixed with Tween 80 as a hydrophobic surfactant in different mixing ratios to obtain higher solubility and better stability for bio-oil-in-diesel microemulsion (BDM). GC-MS and other analysis methods were performed to investigate properties of BDM resulted, then the prepared fuels were stored over 90 days at indoor temperature to determine their stability. The results showed that mixed surfactant of 7:3 of Span 80-Tween 80 with the help of 2% n-hexanol as cosurfactant is the optimum formula to get BDM with better properties. This BDM formula was tested in a single-cylinder, 4-stroke, DI diesel engine and found to have well performance characteristics (higher BSFC and BTE compared to diesel), while reduced CO, CO_2, and NO_x emissions by 21.4%-66.7%, 7.1%-27.3%, and 1.5%-14.7%, respectively [74].

A non-ionic sunflower oil-aqueous ethanol microemulsion with a composition of 53.3% sunflower oil, 13.3% 190-proof ethanol, and 33.4% 1-butanol by volume was tested in in 4-cylinder, turbocharged, DI diesel engine, and the effects were evaluated. Although the engine fueled by microemulsion completed the 200 hours of EMA screening test cycle and was observed to reduce BSFC by 4% and smoke emission significantly, the use of this microemulsion still has so many disadvantages and is not recommended for long-term use in DI diesel engine. The major problems found during the screening test were

incomplete combustion during engine start and low load conditions, premature injection nozzle deterioration, and excessive deposits on the internal parts of the fuel injection pump [75]. In another study, coconut oil-based hybrid fuel which was coconut oil-aqueous ethanol microemulsion with butan-1-ol as a surfactant in various compositions was prepared and performed on PowerTec 170FG, 4-stroke, single-cylinder, air-cooled, DI diesel engine. Positive results were recorded from the test as micro emulsification of coconut oil was successful to obtain diesel-like fuel with relatively low viscosity close to the viscosity value of diesel. The engine efficiency gained from the use of coconut oil-ethanol microemulsion is almost similar to diesel and the significantly lower NO, SO_2, and CO_2 emissions level were noted. However, the specific fuel consumption and CO emission level of hybrid fuel were higher compared to that of diesel due to lower gross calorific value and incomplete combustion respectively [76].

The experiment conducted by Charoensaeng et al. [77] used butanol, octanol, and decanol as cosurfactant in ethanol-in-palm oil-diesel microemulsion biofuel. The effect of that cosurfactant on fuel consumption and emission was compared as they vary in the carbon chain length. All microemulsion biofuel samples indicated better emission

characteristics for CO, NO_x, and CO_2 with an increase in BSFC. Moreover, it was found that the use of the longer carbon chain alcohol as cosurfactant resulted in lower fuel consumption and CO emission, but NO_x and CO_2 emissions were gradually increased.

Some vegetable oils have been used as blend materials for microemulsions. Engine test and physicochemical analysis of those microemulsions have been done in the past studies. Table 3 presents data collected from several studies related to physicochemical properties and engine performance and emission characteristics obtained from vegetable oil-based microemulsions.

Table 3. The physicochemical properties and engine test parameters of several biodiesel microemulsions

Emulsion	80% B30 tung oil-diesel - 20% Ethanol	80% soybean biodiesel - 20% ethanol	81% B20 soybean biodiesel - 15% NP5EO - 4% water	52% crude *Pongamia* oil (CPO) - 23% ethanol - 25% buthanol	95% B15 palm biodiesel - 5% ethanol
Reference	[78]	[79]	[80]	[81]	[82]
Density (g/ml)	0.843	0.8552	0.871	0.864	0.833
Kinematic viscosity (mm2/s)	4.8 (at 40°C)			13.51 (at 21°C)	3.23 (at 40°C)
Lower heating value (kJ/kg)	37,990	31,283			
Flash point (∘C)			46.2		84.5
Stoichiotric air-fuel ratio (kg/kg)	12.87	11.249			
Engine	6-cylinder, 4-stroke, turbocharged, inter-cooled, CRDI diesel engine	single cylinder, 4-stroke, WC, CR 16.5:1, DI diesel engine	single-cylinder, 4-stroke, AC, DI diesel engine	single-cylinder, 4-stroke, DI diesel engine	single cylinder, 4-stroke, DI diesel engine
Performance	BSFC ↑, BTE ↑ slightly	BSFC ↑ slightly		BSFC ↑, BTE ↓ 2.75%	BSFC ↑, BTE ↓

4.3. Pyrolysis

Vegetable oil is known to have a problem with high viscosity and density which affects the fuel atomization in the engine, so it could not be used directly as fuel in a diesel engine without modification. Pyrolysis or thermal cracking offers a solution to this problem since this process is able to convert the complex structure of hydrocarbons into its simplest structure by means of heat, with or without a catalyst. Pyrolysis will occur in high-temperature conditions ranging between 250°C and 350°C [83]. The flow of biodiesel production process using the pyrolysis method is shown in Figure 2.
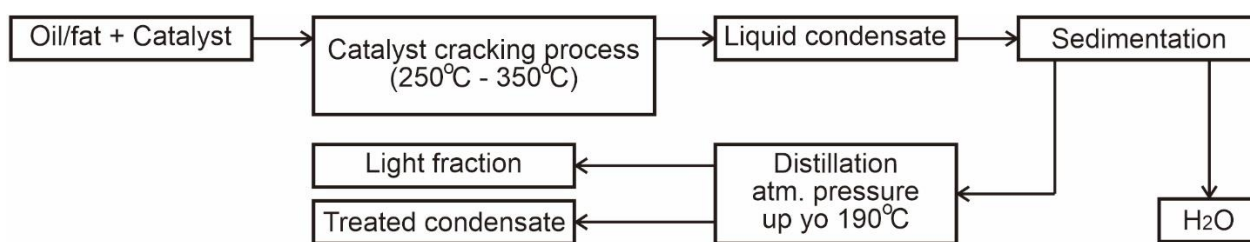
Figure 2. The flow of biodiesel production process using the pyrolysis method [83].

A study conducted by Du et al. [84] assessed biofuel production from microalgae biomass named *Chlorella sp.* using the microwave-assisted pyrolysis method. The pyrolysis was carried out in a microwave oven at a frequency of 2,450 MHz for 20 minutes of reaction time. The maximum bio-oil yield of 28.6% was produced under the microwave power of 750 W. The algae bio-oil produced in this experiment was characterized and found to have a density of 0.98 kg/L, a viscosity of 61.2 cSt, and a higher heating value (HHV) of 30.7 MJ/kg.

Pyrolysis of soybean oil and high oleic safflower oil was carried out in air and nitrogen sparge by Schwab et al. [85] The distillation method and equipment used were based on the ASTM standard. Gas chromatography-mass spectrometry (GC-MS) analysis was conducted to determine the composition of pyrolyzed materials. Biofuels with properties of two-third lower viscosity and higher cetane number were successfully obtained by distillation. The main compositions of the products observed were alkanes, alkenes, aromatics, and carboxylic acids with carbon numbers ranging from four to more than 20 by percentages as shown in Table 4.

Table 4. Data of pyrolyzed oil compositions [85].

	Percent by Weight			
	High oleic safflower		Soy	
	N2 sparge	Air	N2 sparge	Air
Alkanes	37.5	40.9	31.3	29.9
Alkenes	22.2	22.0	28.3	24.9
Alkadienes	8.1	13.0	9.4	10.9
Aromatics	2.3	2.2	2.3	1.9
Unresolved unsaturates	9.7	10.1	5.5	5.1
Carboxylic acids	11.5	16.1	12.2	9.6
Unidentified	8.7	12.7	10.9	12.6

A study by Lima et al. [86] investigated pyrolysis reactions and products of soybean, palm tree, and castor oils. The pyrolysis oil distillates were separated into four fractions based on the distillation temperature (<80°C, 80°C-140°C, 140°C-200°C, and >200°C) and the fraction gained from distillation temperature >200°C which contains 60-75% of pyrolyzed products was observed by GC, FTIR, and ASTM analysis methods. Some compounds such as hydrocarbons alkanes, alkenes, alkadienes, and carboxylic acids were

identified from this fraction. However, different from the results of the previous study, there was no sign of aromatic product detected. Physicochemical properties of pyrolysis products from soybean and palm tree oils were found comparable with standard diesel fuel used in Brazil. Furthermore, the preliminary test of catalytic deoxygenating of soybean pyrolyzed product using HZSM-5 zeolite at 400°C was successful to obtain an enriched hydrocarbon diesel-like fuel.

Wood pyrolysis oil (WPO) obtained from the vacuum pyrolysis process of pine wood was mixed with diesel fuel by volume ratio of 1:9 and some percentages of diethyl ether (DEE). An experiment was carried out using a single-cylinder, four-stroke, air-cooled, DI diesel engine fueled by WPO emulsion in order to investigate its combustion, performance, and emission parameters. The WPO emulsion was found exhibiting longer ignition delay and combustion duration due to the poor ignition quality of the WPO. The BTE of WPO emulsion increased by 6.35%, but the exhaust gas temperature was observed to be lower than that of diesel. In terms of emission, the WPO emulsion emitted 19.21% lower NO, 14.28% higher HC, and slightly higher CO. Addition of DEE on WPO emulsion by percentages of 2% and 4% has been proven to cause improvement in all parameters observed [87]. In another study by the same author, the WPO of 5%, 10%, and 15% by volume was emulsified with *Jatropha* methyl ester (JME) and tested using the same diesel engine. Based on the experimental results, JME and its emulsion with WPO indicated better combustion at high load, higher BTE, and lower smoke emissions compared to diesel [88].

Table 5. Physicochemical properties of the cracked samples of rice bran oil compared to diesel [89].

		Catalyst load (kg/100 kg oil)			
	Diesel	**0.5**	**1.0**	**2.0**	**3.0**
API gravity	31-41	32.08	35.75	33.80	33.99
Specific gravity	0.82-0.87	0.865	0.846	0.856	0.855
Pour point (°C)	+ 4.5-15	+ 12	+ 6	0.0	+ 6
Kinematic viscosity ($m^2S^{-1} \times 10^6$)	≤ 7	8.61	7.19	9.42	9.39
Calorific Value (MJ/kg)	44.3	40.437	38.199	39.675	35.860
Heating value compared to diesel	1	0.91	0.86	0.89	0.81
Flash point (°C)	≥ 55	54	51	56	51
Cetane number	≥ 55	59.69	52.24	52.26	59.68
Cetane index	-	51	54	52	54

Thermal catalytic cracking or pyrolysis with catalyst process was used in past studies to produce diesel-like fuel from rice bran and palm oils [89,90]. The thermal cracking

process of rice bran oil was carried out at 450°C using calcium oxide (CaO) in a load ranging between 0.5% and 3% to the weight of oil. The process using a catalyst with more CaO content was observed to produce more product up to 71.5% with a faster process. Meanwhile, crude palm oil was thermally cracked at 450°C using sodium carbonate (Na2CO3) of 20% proportion to the weight of oil. The rice bran and palm oils gained from the thermal cracking process were then distilled and physical-chemical characterized using standard ASTM and other analysis methods. The properties of diesel-like fuels produced from rice bran and palm oils can be seen in Table 5 and Table 6, respectively.

Table 6. Physicochemical properties of the cracked samples of palm oil (green diesel) compared to diesel [90].

Properties	Unit	Green diesel	Diesel
Density	kg/m3	790	820–880
Kinematic viscosity	mm2/s	1.48	2–5
Flash point, min	◦C	10	38
Copper strip corrosion, 3 h 50 ◦C, max	-	1a	1a
Carbon residue, max	wt.%	0.02	0.25
Acid value	mg KOH/g	1.68	0.5
Saponification value	mg KOH/g	7.93	-
Refraction index	-	1.44	-
Ester value	mg KOH/g	6.25	-

4.4. Transesterification

Transesterification is the reaction of fat or oil with an alcohol to form esters (biodiesel) as the main product and glycerol as a by-product. This displacement of an alcohol from an ester by another alcohol occurred in transesterification is similar to hydrolysis process, except that the hydrolysis process employs water instead of alcohol. Thus, transesterification is also known as alcoholysis. The process of transesterification is basically a sequence of three step reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol. One methyl ester molecule is yielded from each glyceride at each step [64,65,91–93]. The reaction is shown in Figure 3. Where the basic scheme of biodiesel production with transesterification is shown in Figure 4.

Moisture or water content strongly affected the efficiency of transesterification, especially for a method called in situ transesterification where the process is carried out on very raw biomass rather than oil. A study by Sathish et al. [94] about the effect of moisture on in situ transesterification of microalgae clearly supported this statement. They reported a significant reduction in biodiesel yield occurred when the moisture content exceeded around 15 to 20 wt% of algae dry mass. They also reported that an increase in the amount of sulfuric acid as a catalyst could overcome this problem and improve the biodiesel yield to greater than 80% even when using algae biomass with 84% moisture content. However, this addition resulted in a higher cost of production which is not economically sustainable. A study by Haas et al. [95] also concluded a similar result about the comparison of the biodiesel production cost when using low-moisture soy

flakes and full-moisture soy flakes. They found that the use of low-moisture soy flakes with 2.6 wt% of moisture content could substantially reduce the reagent requirements for high-efficiency transesterification. It required 40% less methanol and 33% less NaOH compared to that required by transesterification of full-moisture flakes, making the biodiesel production significantly cheaper.
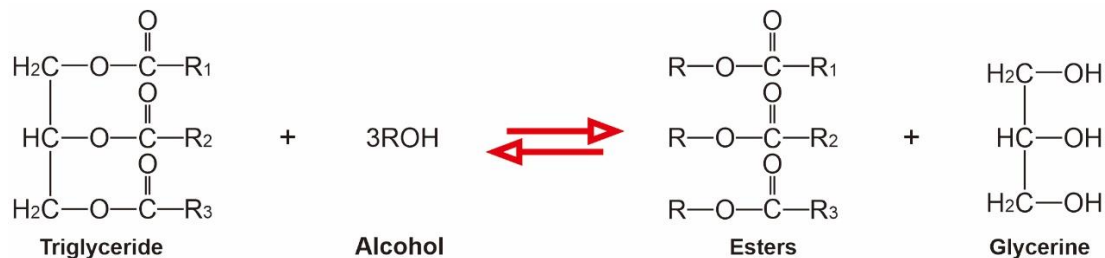

Figure 3. Transesterification of triglycerides with alcohol   [52]
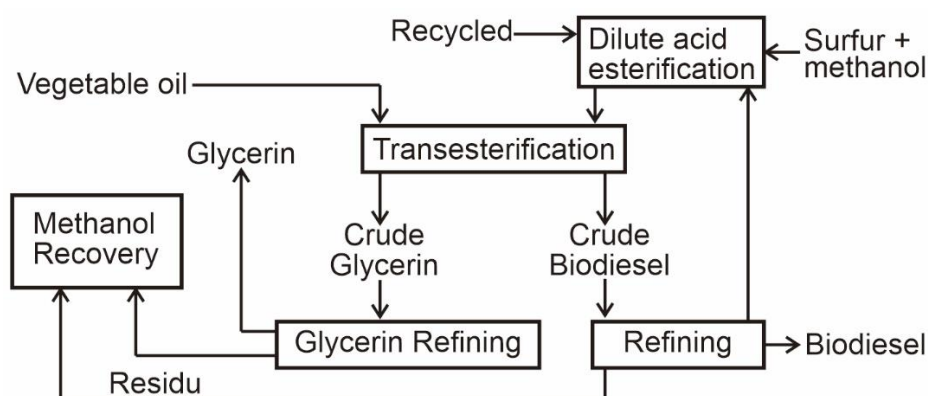

Figure 4. The basic scheme of biodiesel production with transesterification [92]

Many researchers have studied the kinetics of the transesterification process to reveal how parameters such as the molar ratio of alcohol to oil, reaction temperature, and reaction time affect the production of biodiesel. Kusdiana et al. [96] studied the kinetics of free catalyst transesterification of rapeseed oil made in subcritical and supercritical methanol. They found the optimum condition for the free-catalyst process of biodiesel fuel production from rapeseed oil was at a temperature of 350°C with a 42:1 of the molar ratio of methanol and oil. Another study by Kapilakarn et al. [97] used simulation software to find the optimum operating condition of transesterification of triglycerides based on the percentage of purity of the products and predicted cost. The molar ratio of methanol and oil at 6:1, reaction temperature of 70°C, and 20-minute reaction time were the optimum conditions of transesterification proposed from the simulation analysis.

The effect of various catalysts on the transesterification process has been studied by many researchers in the past. The efficiency of two-dimensional zeolites as a basic catalyst of the transesterification process was studied by Pang et al. [98] The prepared Na-zeolite samples were used as catalysts in the base transesterification reaction of triolein (soybean oil) with methanol at a mass ratio of methanol:triolein:catalyst = 100:10:1 and 60°C reaction temperature. Na/zeolite catalysts were able to increase the yield of biodiesel up to 80% and 2D Na/ITQ-2 was found to be the best catalyst compared to other samples. 2D Na/ITQ-2 zeolites possess large external surface areas, hierarchical characteristics, stable active sites, and a high concentration of strong basic sites that contribute to enhancing the mass transfer of bulky molecules and providing more accessible and stable active sites in

the transesterification of bio-derived oil to produce biodiesel. A similar investigation conducted by Mansir et al. [99] using bimetallic tungsten-zirconia (W-Zr) samples to catalyze simultaneous esterification and transesterification of unrefined palm-derived waste oil (PDWO) to biodiesel. The catalyst with a 7 wt% concentration of W-Zr loaded on CaO support (7WZC) was able to achieve a maximum biodiesel yield of 94% in one-hour reaction time under the optimum reaction condition (methanol and oil molar ratio of 15:1, 2 wt% catalyst loading, 80∘C reaction temperature). The high catalytic activity of 7WZC was attributed to its moderate basicity and acidity composition that could easily convert both FFA and triglycerides present in PDWO to biodiesel.

Recently, some studies also have been conducted related to the utilization of biodiesel production waste from the transesterification process. Production of 100 kg of biodiesel via the transesterification process generates 10 kg of crude glycerol as a by-product. This crude glycerol derived from the biodiesel transesterification process can be used as a material to produce useful chemicals such as 1.3-propanediol and 2.3-butanediol. The production of those chemicals by a co-fermentation process with help from isolated strain *Enterobacter sp.* MU-01 bacteria has been proven efficient [100].

Compared to other biodiesel production methods available, transesterification of natural oils and fat is currently the best method due to its high efficiency and superior characteristics indicated by its products. Transesterification is affected by several factors such as the molar ratio of glycerides and alcohol, the catalyst, reaction temperature and time, and the content of moisture [64,65].

5. Future trends

Based on findings from all papers reviewed in this study, there are two main challenges in the development of biodiesel as renewable alternative energy that would possibly become a trend in future studies related to biodiesel. First, mass production of biodiesel still considered expensive compared to that of petrodiesel which causes less biodiesel use on daily basis. Researchers are encouraged to conduct studies and observations on various potential biomasses until one feasible feedstock is found. Second, it can be seen from Table 2 that using biodiesel as fuel results in an increase in NO_x emissions for almost all types of biodiesel. There should be some efforts to reduce NOx emissions from biodiesel fuel combustion in the future. Formation of NO in the combustion of biodiesel and petrodiesel fuels in a non-pressurized, water-cooled combustion chamber were observed by Bazooyar et al. [101]. The results showed that while the amount of thermal NO formed in biodiesel and petrodiesel was comparable, biodiesel produced significantly higher prompt NO than petrodiesel, making biodiesel emitting more NO in total than diesel. This higher formation of prompt NO in biodiesel fuel combustion is attributed to its higher number of bis-allylic sites. Sun et al. [102] found that the use of exhaust gas recirculation (EGR) system in diesel engines could effectively suppress NOx formation on biodiesel combustion, proven by a decrement of NOx emissions as the EGR rate increased. However, it has the opposite effects on CO and HC emissions and some disadvantages on engine combustion and performance characteristics. As of today, there has not been found a beneficial solution to reduce NOx emission in biodiesel combustion without raising any other problems. Thus, solving these

issues should be the main focus for future researchers or other people interested in this topic. Moreover, the metals and chemical coumpounds contaminants in biodiesel became the concern of researchers since in the real time operation, the time and long term operational have affect to the emissions and the engine performance [103,104].

6. Conclusions

In this review, various types of biodiesel and its production methods were comprehensively discussed. It is expected to assist the researchers, biodiesel producers, and other people who might be interested in this topic. This paper can ensure the information regarding natural sources of biodiesel, biodiesel production methods, and properties of biodiesel yielded from each source and method observed. Finally, the engine performance and exhaust emission characteristics of different types of biodiesel as well as their blends on the compression ignition engines have been evaluated in detail. Overall, the following critical findings could be drawn from the present study according to the published literature.

1. With increasing concerns about global warming partly caused by greenhouse gas (GHG) emissions from fossil-fuel combustion and the limited availability of fossil-fuels, sustainable, environmentally friendly, and renewable fuels such as biodiesel are important to be developed and applied immediately on a daily basis.

2. The cost of raw material takes up most of the biodiesel production cost. Economic, agricultural, and technical evaluations are needed to choose the most feasible natural sources in biodiesel production without having to sacrifice the quality.

3. The use of biodiesel is very beneficial from the environmental perspective since they generally reduce the amount of HC, CO, and smoke emissions. However, running biodiesel fuel in diesel engines usually cause an increase in NOx emission compared to straight diesel.

4. Biodiesel has some poor properties such as higher viscosity, higher density, and lower calorific value which cause a reduction in engine performance parameters when they are used as fuel on a diesel engine.

5. Performance and emission characteristics of biodiesel fuel and blends vary, depending on their natural sources, physicochemical properties, and engine operating conditions.

7. Of the various biodiesel production methods available, transesterification is currently the most superior method since it can efficiently yield biodiesel products that have superior characteristics compared to other biodiesel produced with other methods.

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