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REVIEW OF REGULATED, UNREGULATED AND PARTICULATE EMISSIONS FROM BIODIESEL FUELLED COMPRESSION IGNITION ENGINES

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ABSTRACT–Compression-ignition (CI) engines have been utilised in transport and power generation sectors due to their excellent thermal efficiency, robustness and durability. However, the rapid depletion of crude oil reserves and environmental concerns have forced CI engines to be powered by alternative and environment-friendly renewable fuels. Biodiesel, which contains ~10 % (w/w) oxygen in its fuel molecules, has become a popular alternative fuel for CI engines. Biodiesel can be stored similar to mineral diesel. Hence it does not require a separate fuel distribution infrastructure. The fuel properties of biodiesel are very close to mineral diesel; hence conventional CI engines can be fueled with biodiesel/blends without major modifications in the engine hardware/software. It is also widely known that biodiesel in CI engines brings significant benefits of lower emissions such as unburned hydrocarbons, carbon monoxide, and particulate matter (PM). Since biodiesel is considered an attractive alternative fuel, there are many attempts to produce and utilise biodiesel in different applications from various feedstocks such as soybean, rapeseed, and waste cooking oil. Hence, it is necessary to understand the effects of biodiesel feedstocks and engine applications (operating conditions, engine type, etc.) on regulated and unregulated emissions. This paper reviews effects of biodiesel on regulated/unregulated/particulate matter (PM) emissions based on numerous experimental research studies in open literature conducted on a variety of engines using different biodiesels.

KEY WORDS : Compression ignition engine, Biodiesel, Regulated emissions, Unregulated emissions, Particulate matter

1. INTRODUCTION

Rapid depletion of petroleum sources is the main drive to explore the viability of alternative energy sources such as renewable biofuels and meet increasing energy demand to sustain the growing global economy. For example, biodiesel is a renewable, greener, cleaner, and less toxic biofuel, a partial or full replacement for mineral diesel. These fuels can be directly used in compression ignition (CI) engines since they do not require any significant hardware modification in the existing engines. They are easier and safer to store and handle because of their higher flashpoint. However, biodiesel has some drawbacks also. First, biodiesel can be produced from many plant-based or animal-based feedstocks, which makes their standardisation quite challenging. Second, biodiesel is still more viscous than baseline mineral diesel, making it unsuitable for use in cold weather conditions. Third, these fuels have short shelf life since they quickly become rancid. Fourth, these fuels are more expensive and have lower calorific value than baseline mineral diesel. Biodiesel properties are vital in forming gaseous emissions (regulated and unregulated) and particulates. Alptekin and Canakci (2009) characterised fuel properties of conventional diesel and methyl esters of Sunflower, Soybean, Canola, Corn, and Cottonseed oil. They indicated insignificant differences in biodiesel blend fuel properties of biodiesel blends vis-à-vis baseline diesel up to a 20 % blend level. However, beyond this biodiesel blending point, the density and viscosity of test blends increased with increasing methyl ester content. They also reported higher flashpoints for 50 % and 75 % methyl ester blends. Joshi and Pegg (2007) measured the fuel properties of fish oil ethyl esters and blends (20 %, 40 %, 60 %, and 80 %) with mineral diesel. Cloud point (or pour point) of biodiesel increased with increasing biodiesel concentration in the blend. Tate *et al*. (2006) measured Canola, Soy, and fish oil methyl esters' viscosities and reported a reduction in

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viscosity with increasing fuel temperature (Wang *et al.*, 2000). Demirbas (2008) reported a positive correlation between the viscosity and the density of vegetable oils. They reported that with an increase in density from 0.848 to 0.885 kg/l, the viscosity increased from 2.83 to 5.12 mm^2/s. Knothe (2005) measured biodiesel properties such as oxidation stability, viscosity, the heat of combustion, and cetane number and found that these properties were affected by biodiesel's fatty acid and ester contents. Ali *et al.* (2016) reported increased fuel density, kinematic viscosity, and heating value with increasing biodiesel content in diesel and increased specific fuel consumption. A similar trend was reported by Yoon *et al.* (2008) for different biodiesel blends as well.

In contrast, the test fuel viscosity was reduced with increased fuel temperature or reduced biodiesel blending ratio (Yoon *et al.*, 2008). Chattopadhyay and Sen (2013) measured the fuel properties for 10 % and 20 % (v/v) cottonseed biodiesel blended with mineral diesel and reported that increasing the biodiesel blending ratio led to a reduction in calorific value but an increase in the flashpoint, kinematic viscosity, and specific gravity. They also reported that higher biodiesel content reduced CO, CO_2, smoke, and unburned hydrocarbon emissions but increased NO_X emissions. Agarwal and Rajmanoharan (2009) measured the fuel properties of 10 %, 20 %, 50 %, 75 % Karanja biodiesel blends and Karanja biodiesel vis-à-vis baseline mineral diesel. They reported increased density, viscosity, flashpoint, and fire point with increasing biodiesel content in the test blend. The calorific value of the test blend was reduced with increasing biodiesel content. They also observed that HC emissions from unheated and preheated lower biodiesel blends (10 % and 20 %) were slightly lower than baseline mineral diesel. In this context, it is important to understand the effects of these biodiesel properties on the engine-out emission and their possible toxicity. With this objective in mind, a comprehensive literature review was done involving several experimental studies covering regulated emissions such as CO, HC and NO_X, unregulated emissions such as carbonyl emissions (formaldehyde, acetaldehyde), unsaturated hydrocarbons such as 1,3-butadiene, propene and ethene, aromatic compounds such as Benzene, Xylene and Toluene, and particulate emissions from compression ignition engines using different biodiesels and blends. These are discussed comprehensively in the following sections of this review paper.

2. REGULATED EMISSIONS

2.1. NO_X Emissions

There are severe health issues primarily attributed to NO_X emissions emitted by diesel engines, such as respiratory tract irritation, reduced functionality of the lungs, asthma, and permanent lung damage (Fernando *et al.*, 2006). To reduce the health effects of biodiesel fueled engines, the formation of NO_X in the compression ignition engines needs to be controlled. There are three main mechanisms responsible for NO_X formation in the engine combustion chamber: thermal NO_X, fuel NO_X, and prompt NO_X. Oxygen and nitrogen combine at higher peak in-cylinder temperatures when fuel is burned in the engine combustion chamber, and during this process, thermal NO_X is generated (Fernando *et al.*, 2006). The mechanism for the NO_X formation via this route is called the "Zeldovich mechanism", which follows the principal reactions shown below.

$$\mathrm{O} + N_2 = \mathrm{NO} + N \tag{1}$$

$$\mathrm{N} + O_2 = \mathrm{NO} + \mathrm{O} \tag{2}$$

$$\mathrm{N} + \mathrm{OH} = \mathrm{NO} + \mathrm{H} \tag{3}$$

As the in-cylinder temperature increases because of combustion reactions, the amount of diatomic nitrogen dissociated from the monatomic nitrogen increases, resulting in high NO_X emissions. Thermal NO_X is a dominant contributor to the total NO_X produced by diesel engines. Prompt NO_X is produced when hydrocarbons of the fuel combine with nitrogen to form NO_X. Diesel engine mainly operates in lean conditions; hence there is a small amount of prompt NO_X emissions from the diesel engines. Fuel NO_X is produced when nitrogen, chemically bound to the fuel molecules, combines with oxygen present in the ambient during combustion. Biodiesel does not contain nitrogen in its molecular structure; hence fuel NO_X is negligible from the biodiesel fuelled engines (Fernando *et al.*, 2006). Table 1 summarises numerous studies covering NO_X emission characteristics of biodiesel fulled engines/ vehicles compared to baseline mineral diesel in different engine/vehicle configurations and various biodiesel feedstocks.

Several experimental studies used a variety of engines and vehicles to assess NO_X emissions from various biodiesels and their blends with mineral diesel. Most studies (Table 1) revealed that the use of biodiesel/blends leads to higher NO_X emissions than baseline mineral diesel. This trend was generally explained by the fuel oxygen content of biodiesel, which is an important factor in higher NO_X formation. It provides a higher local peak temperature by forming closer to the stoichiometric fuel-air mixture than fuels that do not have oxygen in their fuel molecules. The formation of PM in the engine cylinder is characterised by the radiative heat transfer, which lowers the peak in-cylinder temperature due to heat loss by radiative heat transfer. Overall peak in-cylinder temperature in the engine combustion chamber using biodiesel can be higher due to lower particulate formation and higher fuel oxygen content.

Table 1. Summary of experimental studies showing the effect of using biodiesels/blends on NO_X emissions from different engines/vehicles.

Researchers	Fuel	Effect on emissions	Engine/Vehicle
Salvi *et al*., 2012	Biodiesel	Increase in NO_X	Medium-duty diesel engine
Wang *et al*., 2000	B35	Increase in NO_X	Heavy-duty trucks (9 nos.)
Monyem and Van Gerpen, 2001	Biodiesel and 20 % blend	13 ~ 14 % higher NO_X	John Deere 4276 T turbocharged diesel engine
Usta, 2005	Tobacco-seed oil methyl ester blend (up to 25 %)	Increase in NO_X	Turbocharged IDI diesel engine
Lin *et al*., 2006	Palm biodiesel and blends	1.25 ~ 4.97 % reduction in NO_X	Heavy-duty diesel engine
Özener *et al*., 2014	10 %, 20 % and 50 % (v/v) soybean biodiesel blends	6.95 ~ 17.62 % increase in NO_X	Single cylinder DI diesel engine
How *et al*., 2014	Biodiesel blends	9.4 ~ 20.8 % Increase in NO_X	Medium-duty CRDI engine
Zhang *et al*., 2008	Soybean biodiesel blends	Higher NO_X	–
Raheman and Ghadge, 2007	20 %, 40 %, 60 % and 80 % (v/v) Mahua biodiesel blend	Higher NO_X	Single-cylinder Ricardo engine
Öztürk, 2015	5 %, 10 % (v/v) Biodiesel blend of canola oil-hazelnut soap-stock	Higher NO_X	–
Chauhan *et al*., 2013	Karanja biodiesel blends	Higher NO_X	–
Sayin *et al*., 2013	Biodiesel and 5 %, 20 %, 50 % blends with diesel	Highest NO_X for B100	–
Mosarof *et al*., 2016	10 %, 20 % and 30 % biodiesel blends of Palm and calophylluminophyllum	Higher NO_X	Single-cylinder DI diesel engine
Man *et al*., 2016	Waste cooking oil biodiesel (B100) and 10 %, 20 % and 30 % (v/v) blends with diesel	Higher NO_X emissions from biodiesel and biodiesel blends	4-cylinder natural aspirated direct-injection diesel engine
Ghadikolaei *et al*., 2019	0 %, 20 %, 50 %, 75 % and 100 % blends of biodiesel with Diesel	24.2 %, 27.2 %, 36.9 % and 52.4 % increase in NO_X emissions with 20 %, 50 %, 75 % and 100 % biodiesel blend	In line 4-cylinder DI engine
Geng *et al*., 2021	Soybean biodiesel	Higher NO_X compared to biodiesel	Turbocharged CRDI engine
Patel *et al*., 2021	20 % blends of Jatropha and Waste cooking oil biodiesel with diesel	Higher NO_X for 20 % blends of Waste cooking oil biodiesel compared to diesel	Turbocharged, aftercooled with EGR CRDI engine (BS-IV)
Ge and Choi, 2020	10 %, 20 %, 30 % and 100 % blends of biodiesel compared with diesel	Higher NO_X for all biodiesel blends compared to diesel	Turbocharged CRDI diesel engine
Puškár *et al*., 2019	10 %, 30 %, 50 % and 100 % biodiesel (kitchen waste oil biodiesel) compared with diesel	Higher NO_X for all biodiesel blends compared to diesel	CRDI engine

Therefore, the application of biodiesel could lead to an elevated peak in-cylinder temperature compared to baseline mineral diesel, which could be the main reason for higher thermal NO_X emissions.

Engine operating conditions and physiochemical properties of biodiesel play a dominant role in forming NO_X emissions. Contradictory results are also found in the literature, which shows the reduction of NO_X emission for biodiesel blended fuel compared to biodiesel. The main reason is that fuel characteristics and chemistry played an important role in NO_X emission due to the combustion of biodiesel fuels. Palm-based biodiesel showed a NO_X reduction mainly due to the higher cetane number, which resulted in a shorter ignition delay period and comparatively lower adiabatic flame temperature (Karavalakis *et al.*, 2009).

2.2. CO Emission

The presence of CO in the engine exhaust reflects the lost chemical energy of the fuel that is not fully utilised during combustion. The CO emission from combustion engines could be controlled primarily by the air/fuel ratio. Several experimental studies used a variety of engines and vehicles to evaluate CO emissions from biodiesel and blend fueled engine operations. Most studies shown in Table 2 reveal that the use of biodiesel/blends leads to lower CO emissions than baseline diesel.

Various factors affect the formation of CO in an engine, such as fuel density, viscosity, flash point, spray droplet diameter distribution, evaporation energy and spray droplet velocity. In addition, insufficient air availability and inferior air-fuel mixture formation also affect the formation of CO. The principal CO oxidation reaction and rate constant in the hydrocarbon-air flames are known to be determined by the following equation:

$$\mathrm{CO} + \mathrm{OH} = CO_2 + H \tag{4}$$

$$k_{co}^{+}[cm^3/gmol] = 6.76 \cdot 10^{10} \exp\left(\frac{T}{1102}\right) \tag{5}$$

As seen in these equations, the oxidation of CO emission would progress efficiently with reactive radicals and at higher combustion temperatures. The lower CO emission with biodiesels could be due to relatively higher in-cylinder temperature, which is consistent with the trends observed in the previous section's NO_X emissions because of higher in-cylinder temperatures. The fuel-bound oxygen of biodiesel was beneficial during the combustion process, resulting in higher in-cylinder temperature, which helps reduce CO emission for biodiesel and blends.

2.3. HC Emissions

HC emissions are a consequence of the incomplete combustion of hydrocarbon fuel. HC emissions are significant from diesel engines at low load conditions. The lean fuel-air mixture may survive the combustion and eventually escape into the exhaust because of non-uniform fuel distribution in the combustion chamber. Several experimental studies used a variety of engines and vehicles to evaluate HC emissions from biodiesels and blends, which are summarised in Table 3.

Most studies (Table 3) revealed that the use of biodiesel/blends gives lower HC emissions compared to baseline diesel. This was primarily due to biodiesel/blend's relatively higher oxygen content, which helped achieve a greater degree of combustion of fuel droplets in the mixing control combustion phase, resulting in lower HC emissions. This may be due to slightly lower HRR_{max} in the premixed combustion phase, shortened premixed combustion phase, lower heat release rate in the mixing controlled combustion phase, and reduced stoichiometric air requirement due to fuel bound oxygen.

3. UNREGULATED EMISSIONS

3.1. Carbonyl Compounds

Carbonyl compounds (formaldehyde and acetaldehyde) are absent in hydrocarbon fuels. Still, they are formed as intermediate combustion products during fuel oxidation, especially in low-temperature combustion of ultra-lean mixtures. They also get formed by reducing the temperature and oxygen content during combustion, which interrupts the oxidation of unburnt fuel. In addition, combustion and exhaust gas temperatures also play a vital role in forming carbonyl compounds (Wei *et al.*, 2017). Wei *et al.* (2017) investigated the formation of carbonyl compounds from B20, B50, B75, pure biodiesel (B100) and baseline diesel in DI diesel engines (Figure 1). They reported increasing formaldehyde and acetaldehyde emissions with increasing biodiesel content in the test fuels.

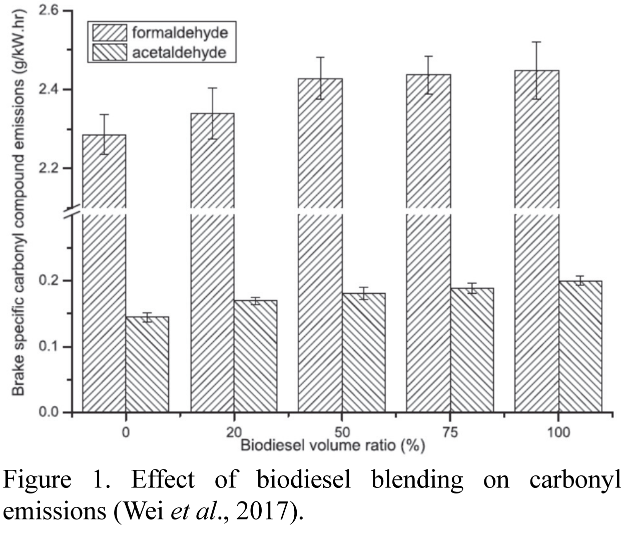


Figure 1. Effect of biodiesel blending on carbonyl emissions (Wei *et al.*, 2017).

Table 2. Summary of experimental studies showing the effect of using biodiesels/blends on CO emissions from different engines/vehicles.

Researchers	Fuel	Effect on emissions	Engine/Vehicle
Wang *et al*., 2000	B35	12 % lower CO	Heavy-duty trucks (9 Nos)
Monyem and Van Gerpen, 2001	Biodiesel and 20 % blend	28 % lower CO	John Deere 4276 T turbocharged diesel engine
Usta, 2005	Tobacco seed oil methyl ester blend (up to 25 %)	Reduction in CO	–
Lin *et al*., 2006	Palm biodiesel and blends	0.664 ~ 15.6 % lower CO	Heavy-duty diesel engine
How *et al*., 2014	Biodiesel blends	2.8 ~ 36.7 % lower CO	–
Al-Dawody and Bhatti, 2014	Soybean oil methyl ester and blends	Reduction in CO	–
Zhang *et al*., 2008	Soybean biodiesel blends	Reduction in CO	–
Rahman and Ghadge, 2007	20 %, 40 %, 60 % and 80 % (v/v) Mahua biodiesel blend	Reduction in CO	Single-cylinder Ricardo engine
Özener *et al*., 2014	10 %, 20 % and 50 % (v/v) soybean biodiesel blends and biodiesel	Reduction in CO	Single-cylinder DI diesel engine
Sayin *et al*., 2013	5 %, 20 %, and 50 % (v/v) biodiesel blends, and biodiesel	B100 emitted least CO	–
Mosarof *et al*., 2016	10 %, 20 % and 30 % (v/v) biodiesel blend of Palm and calophylluminophyllum	PB20 and PB30 emitted lower CO	Single cylinder diesel engine
Man *et al*., 2016	Waste cooking oil biodiesel (B100) and 10 %, 20 % and 30 % (v/v) blends with diesel	Lower CO from biodiesel and blends	4-cylinder natural aspirated DI diesel engine
Ghadikolaei *et al*., 2019	0 %, 20 %, 50 %, 75 % and 100 % blends of biodiesel with Diesel	8 %, 15.9 %, 22.9 % and 26.5 % decrease in CO emission with 20 %, 50 %, 75 % and 100 % biodiesel blend	In line 4-cylinder DI engine
Geng *et al*., 2021	Soybean biodiesel	Lower CO emission compared to diesel	Turbocharged CRDI engine
Patel *et al*., 2021	20 % blends of Jatropha and Waste cooking oil biodiesel with diesel	Higher CO emission at no load for 20 % blends of Jatropha and Waste cooking oil biodiesel compared to diesel. CO emission negligible at higher load.	Turbocharged, aftercooled with EGR CRDI engine (BS-IV)
Ge and Choi, 2020	10 %, 20 %, 30 % and 100 % blends of biodiesel compared with diesel	Reduction in CO emission for all biodiesel blends compared to diesel	Turbocharged CRDI diesel engine
Puškár *et al*., 2019	10 %, 30 %, 50 % and 100 % biodiesel (kitchen waste oil biodiesel) compared with diesel	Reduction in CO emission for all biodiesel blends compared to diesel	CRDI engine

Table 3. Summary of experimental studies showing the effect of using biodiesels/blends on HC emissions from different engines/vehicles.

Researchers	Fuel	Effect on emissions	Engine/Vehicle
Wang *et al*., 2000	B35	Reduction in THC	Heavy-duty trucks (9 Nos)
Monyem and Van Gerpen, 2001	Biodiesel and 20 % blend	51 % reduction in THC	John Deere 4276-T turbocharged diesel engine
Lin *et al*., 2006	Palm biodiesel and blends	10.7 ~ 44.2 % reduction in THC	Heavy-duty diesel engine
Özener *et al*., 2014	10 %, 20 % and 50 % (v/v) soybean biodiesel blends	20 ~ 44 % reduction in HC	Single cylinder DI diesel engine
Al-Dawody and Bhatti, 2014	Biodiesel and biodiesel blends made from Soybean oil and	Reduction in HC	–
Öztürk, 2015	5 %, 10 % Biodiesel blends of Canola oil-hazelnut soap-stock biodiesel	Reduction in THC	–
Sayin *et al*., 2013	5 %, 20 % and 50 % biodiesel blends, biodiesel and diesel	B100 emitted the least HC	–
Man *et al*., 2016	Biodiesel and blends (B20, B30, B100)	B100 emitted the least HC	4-cylinder natural aspirated DI diesel engine
Mosarof *et al*., 2016	10 %, 20 % and 30 % biodiesel blend of Palm and calophylluminophyllum	PB20 and PB30 emitted lower HC	Single cylinder diesel engine
Man *et al*., 2016	Waste cooking oil biodiesel (B100) and 10 %, 20 % and 30 % (v/v) blends with diesel	Reductions in HC emissions for biodiesel and blends	4-cylinder natural aspirated direct-injection diesel engine
Ghadikolaei *et al*., 2019	0 %, 20 %, 50 %, 75 % and 100 % blends of biodiesel with Diesel	18.3 %, 26.7 %, 40.6 % and 50.1 % decrease in THC emission with 20 %, 50 %, 75 % and 100 % biodiesel blend	In line 4-cylinder DI engine
Geng *et al*., 2021	Soybean biodiesel	Lower HC emission compared to diesel	Turbocharged CRDI engine
Patel *et al*., 2021	20 % blends of Jatropha and Waste cooking oil biodiesel with diesel	Higher HC emission at no load for 20 % blends of Jatropha and Waste cooking oil biodiesel compared to diesel. HC emissions were negligible for all fuels at higher loads.	Turbocharged, aftercooled with EGR CRDI engine (BS-IV)
Ge and Choi, 2020	10 %, 20 %, 30 % and 100 % blends of biodiesel compared with diesel	Reduction in HC emission for all biodiesel blends compared to diesel	Turbocharged CRDI diesel engine
Puškár *et al*., 2019	10 %, 30 %, 50 % and 100 % biodiesel (kitchen waste oil biodiesel) compared with diesel	Reduction in HC emission for all biodiesel blends compared to diesel	CRDI engine

Table 4. Summary of experimental studies showing the effect of using biodiesels/blends on carbonyl emissions from different engines/vehicles.

Researchers	Fuel	Effect on emissions	Engine/Vehicle
Yage Di *et al*., 2009	Waste cooking oil biodiesel (B100)	Formaldehyde emission decreased by 81.1 %	DI diesel engine (four-cylinder)
Peng *et al*., 2008	20 % waste cooking oil biodiesel	23 % reduction of formaldehyde emissions reduction in acetaldehyde emissions	DI diesel engine (four-cylinder) 2.84 L
Krahl *et al*., 2003	Rapeseed oil methyl ester	30 % reduction of Formaldehyde emission Reduction of acetaldehyde emission	DI diesel engine
Turrio-Baldssarri *et al*., 2004	20 % blend of biodiesel	Increase in formaldehyde emission 6.3 % increase in Acetaldehyde emission	DI diesel engine
Zervas *et al*., 2008	Biodiesel blended fuel	Decrease in Formaldehyde emission	DI diesel engine
Cheung *et al*., 2009	Biodiesel (B100)	1.3 to 6.4 % higher formaldehyde emission Acetaldehyde emission increased by 21%	DI diesel engine (four-cylinder)
Correa and Arbilla, 2008	2 %, 5 %, 10 % and 15 % biodiesel	2.6 %, 7.3 %, 17.6 % and 35.5 % increase in formaldehyde emissions 1.4 %, 2.5 %, 5.4 % and 15.8 % acetaldehyde emissions	DI diesel engine
Karavalakis *et al*., 2011	10 %, 20 % and 30 % biodiesel blend	Higher emission of carbonyl compound for biodiesel blends	Euro IV diesel passenger car
Jedynska *et al*., 2015	5 %, 10 %, 20 % and 100 % biodiesel	Reduction in emission of aldehydes for biodiesel	Euro III diesel truck
Karavalakis *et al*., 2009	5 %, 10 % and 20 % biodiesel blend	Carbonyl emissions reduced with biodiesel blends	IDI diesel engine Euro II car
Di *et al*., 2009	20 %, 40 %, 60 %, 80 %, 100 % waste cooking oil biodiesel and blends	Reduction in formaldehyde, increase in acetaldehyde	DI diesel engine (four-cylinder)
Man *et al*., 2016	Waste cooking oil biodiesel (B100) and 10 %, 20 % and 30 % (v/v) blends with diesel	Formaldehyde and acetaldehyde emissions increased with biodiesel and its blends	DI diesel engine (four-cylinder) natural aspirated
Agarwal *et al*., 2016	5 % and 20 % Karanja biodiesel blends	Formaldehyde and acetaldehyde emissions were higher with Karanja biodiesel blends	DI diesel engine (four-cylinder) transportation
Ghadikolaei *et al*., 2019	0 %, 20 %, 50 %, 75 % and 100 % blends of biodiesel with Diesel	5.4 %, 9.8 %, 10.4 %, 12.5 % increase in formaldehyde emission with 20 %, 50 %, 75 % and 100 % biodiesel blend 9.6 %, 18.4 %, 19.4 %, 26.5 % increase in Acetaldehyde emission	In line 4-cylinder DI engine
Patel *et al*., 2021	20 % blends of Jatropha and Waste cooking oil biodiesel with diesel	Higher formaldehyde emission for 20 % blends of waste cooking oil biodiesel than diesel.	Turbocharged, aftercooled with EGR CRDI engine (BS-IV)
Puškár *et al*., 2019	10 %, 30 %, 50 % and 100 % biodiesel (kitchen waste oil biodiesel) compared with diesel	Formaldehyde and Acetaldehyde emissions increase with an increase in biodiesel content in the fuel	CRDI engine

Several researchers conducted emission studies involving the measurement of carbonyl emissions under different engine operating conditions on different types of engines and reported a general trend of increase in the emissions of these species with the use of biodiesel and blends. Formaldehyde and acetaldehyde emissions mostly increased in the engine exhaust using oxygenated fuels and blends. Higher acetaldehyde emissions resulted from greater synergistic effects of fuel oxygen content and higher cetane number of biodiesel. Methyl ester of biodiesel fuel is a short-chain hydrocarbon that helps form short-chain carbonyl compounds such as formaldehyde and acetaldehyde. Biodiesel derived from waste cooking oil already contains some carbonyl compounds in the oil during the cooking process. These help form carbonyl compounds during combustion, resulting in carbonyl emissions from the engines. Some investigators also reported that biodiesels help reduce carbonyl emissions or insignificant differences between test fuels. These conflicting results were due to variations in the chemical composition of biodiesels, the test engines used, the experimental methods used, and engine operating conditions, as shown in Table 4. These results suggest that carbonyl emissions are affected not only by the type of fuel and engine used in the tests but also by the chemical characteristics of the biodiesel, such as chain length and purity level. In addition, an increase or decrease in the H/C ratio of the fuel also plays a dominant role in reducing or increasing carbonyl emissions, especially formaldehyde (Zervas *et al*., 2001). However, he also points out that formaldehyde has several sources and should not always link with the fuel composition. Higher engine speeds resulted in lower carbonyl emissions due to higher peak in-cylinder and exhaust temperature.

3.2. Olefins (Unsaturated Hydrocarbons)

Olefins or unsaturated hydrocarbons such as 1,3-butadiene, propene, and ethene are intermediate products during combustion. In the high-temperature combustion environment, thermal cracking affects the long-chain olefins present in the fuel and produces 1,3-butadiene, propene, and ethene (Wei *et al*., 2017).

Figure 2 shows the emissions of 1,3-butadiene, propene, and ethene in the engine exhaust from an engine fuelled by

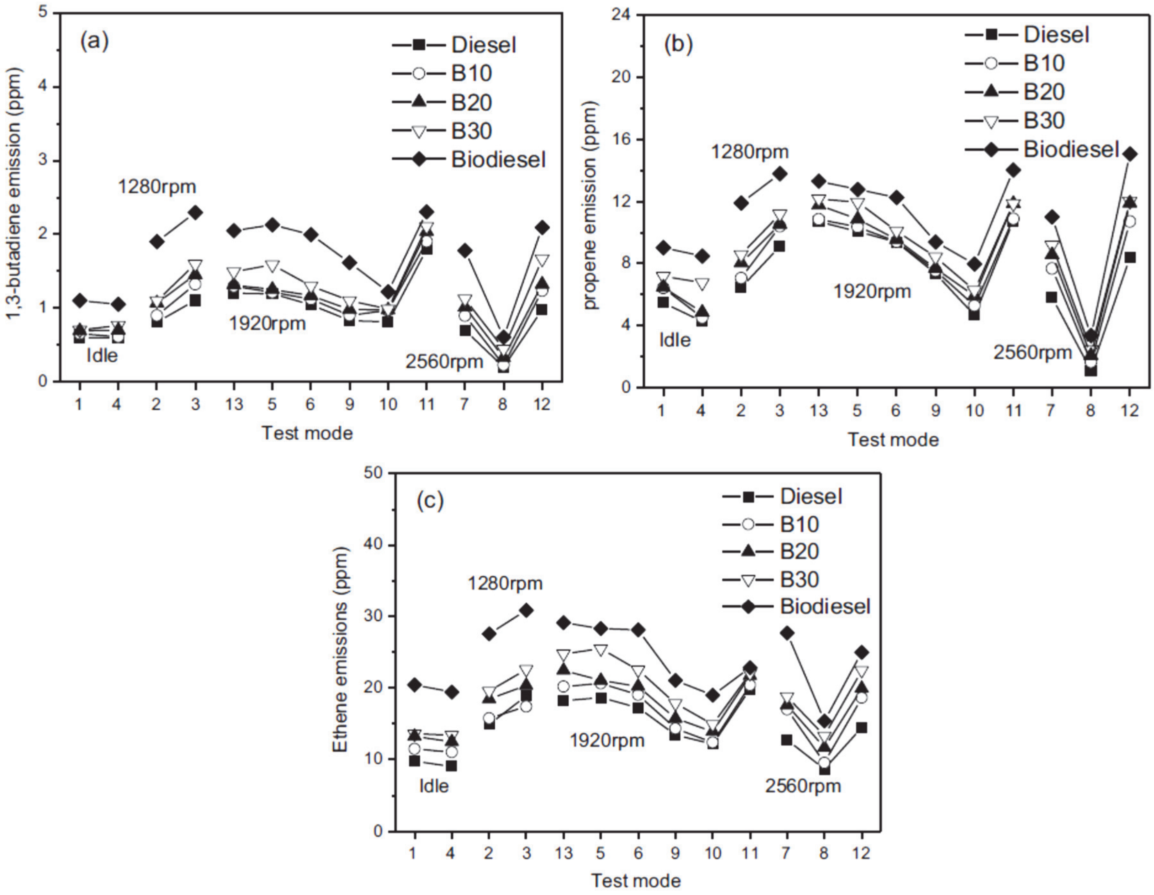


Figure 2. Effect of biodiesel blends on the emissions of 1,3-butadiene, propene and ethene from the engine (Wei *et al*., 2017).

waste cooking oil biodiesel and blends. It was observed that these emissions were higher than baseline mineral diesel under most engine operating conditions. Several other researchers also investigated the emission of unsaturated hydrocarbons from biodiesel/blends fuelled engines/vehicles in various experiments. The majority of the researchers reported an increase in 1,3-butadiene, propene, and ethene emissions, as seen in Table 5.

Higher emissions of 1,3-butadiene, propene, and ethene from biodiesel are mainly attributed to higher in-cylinder temperature, which helped in the pyrolysis of long-chain olefins and increased the production of unsaturated hydrocarbons during combustion (Wei *et al*., 2017). In addition, the combustion duration of biodiesel is generally shorter, which reduces the further oxidation reaction of the combustion products before they are emitted through the tailpipe. The formation of 1,3 butadiene in biodiesel fuelled engines mainly occurs in the oxygen-rich zone of the combustion chamber (Takada *et al*., 2003).

3.3. Aromatic Hydrocarbons (Benzene, Toluene and Xylene)

Aromatic hydrocarbons such as benzene, toluene, and xylene (BTX) are intermediate combustion products generated during thermal cracking and recombination of long-chain olefins and paraffins present in the fuels. They are also produced due to fuel pyrolysis. Aromatic hydrocarbons generally form at higher temperature conditions in the engine combustion chamber because of the removal of hydrogen from the hydrocarbon's fuel molecules and ring structure formation reactions. Table 6 summarises several experimental studies covering BTX

Table 5. Summary of experimental studies showing the effect of using biodiesels/blends on unsaturated hydrocarbon emissions from different engines/vehicles.

Researchers	Fuel	Effect on emissions	Engine/Vehicle
Wei *et al*., 2017	20 %, 50 %, 75 % and 100 % Waste cooking oil biodiesel blends	Increase in 1,3-butadiene (9 ~ 72 %), propene (7 ~ 48 %), ethene (20 ~ 84 %) emissions	DI diesel engine (four cylinder) natural aspirated
Borillo *et al*., 2015	Waste cooking oil biodiesel	Increase in emissions of Ethene, Propene and 1,3-butadiene	DI diesel engine
Bermúdez *et al*., 2011	20 % soybean biodiesel blend	Increase in emissions of Ethene, Propene and 1,3-butadiene	DI diesel engine
Di *et al*., 2009	20 %, 40 %, 60 %, 80 %, and 100 % waste cooking oil biodiesel blends	Reduction in 1,3-butadiene	4-cylinder DI diesel engine
Man *et al*., 2016	Waste cooking oil biodiesel (B100) and 10 %, 20 % and 30% (v/v) blends with diesel	Increase in emissions of Ethene, Propene and 1,3-butadiene	DI diesel engine (four-cylinder) natural aspirated
Cheung *et al*., 2009	Waste cooking oil biodiesel (B100)	Reduction in emission of 1,3-butadiene	DI diesel engine (four-cylinder)
Gupta and Agarwal, 2015	20 % Karanja biodiesel blend	Ethene, propene and 1,3-butadiene emissions decreased	DI diesel engine (four-cylinders) transportation
Ghadikolaei *et al*., 2019	0 %, 20 %, 50 %, 75 % and 100 % blends of biodiesel with Diesel	7.4 %, 18.3 %, 44.4 % and 67.6 % increase in 1,3-butadiene emission with 20 %, 50 %, 75 % and 100 % biodiesel blend. 11.5 % and 8.6 %, 33.3 % and 36.1 %, 45 % and 64.3 %, 67.4 % and 70.9 % increase in ethene and propene with 20 %, 50 %, 75 % and 100 % biodiesel blend	In line 4-cylinder DI engine
Puškár *et al*., 2019	10 %, 30 %, 50 % and 100 % biodiesel (kitchen waste oil biodiesel) compared with diesel	1,3-butadiene, ethene and propene emissions increase with an increase in biodiesel content in the fuel	CRDI engine

emissions from biodiesel/blends fuelled engines/vehicles.

Most research studies reported an increase in benzene emissions from biodiesel/blends at lower load conditions. Under these conditions, the exhaust gas temperature was lower, resulting in higher benzene emissions (Turrio-Baldassarri *et al*., 2004; Takada *et al*., 2003). Biodiesel blending with diesel resulted in lower exhaust gas temperature, which promoted benzene formation. However, Some researchers (Cheung *et al*., 2009; Machado Corrêa and Arbilla, 2008) also reported relatively lower benzene emissions from biodiesel/blends. They argued that oxygen enrichment due to biodiesel's fuel oxygen improved the oxidation/combustion process, resulting in lower benzene emissions. Most researchers found reductions in toluene and xylene emissions with biodiesel/blends. This was also due to oxygen enrichment by biodiesel's fuel oxygen, which helped improve the oxidation of toluene and xylene, leading to reductions of these species in the tailpipe.

4. PARTICULATE FORMATION

The formation of soot particles is generally a result of six distinct processes that take place quickly inside the engine combustion chamber and in the tailpipe, starting from the

Table 6. Summary of experimental studies showing the effect of biodiesels/blends on aromatic emissions from different engines/vehicles.

Researchers	Fuel	Effect on emissions	Engine/Vehicle
Turrio-Baldassari *et al*., 2004	20 % biodiesel	Increase in Benzene Reduction in Toluene and Xylene by 77.1 % and 63.4 % Overall, BTX emissions decreased by 51.3 %	DI diesel engine
Correa and Arbilla, 2006	20 % biodiesel blend	23 %, 25 % and 20 % reductions in Benzene, Toluene and Xylene	DI diesel engine (Six-cylinders)
Di *et al*., 2009	20 %, 40 %, 60 %, 80 %, 100 % Waste cooking oil biodiesel blends	Benzene emissions increased, and toluene and xylene emissions decreased	DI diesel engine (four-cylinders)
Man *et al*., 2016	Waste cooking oil biodiesel (B100) and 10 %, 20 % and 30 % (v/v) blends with diesel	Benzene emissions increased, and toluene and xylene emissions decreased for biodiesel/blends	DI diesel engine (four-cylinder) natural aspirated
Cheung *et al*., 2009	Waste cooking oil Biodiesel	Reductions in benzene, toluene, xylene emissions	DI diesel engine (four-cylinder)
Wei *et al*., 2017	20 %, 50 %, 75 %, 100 % waste cooking oil biodiesel blends	Benzene emissions increased, and toluene and xylene emissions decreased for biodiesel/blends	DI diesel engine (four-cylinder) natural aspirated
Ghadikolaei *et al*., 2019	0 %, 20 %, 50 %, 75 % and 100 % blends of biodiesel with Diesel	3.7 %, 15.4 %, 30.9 % and 39.2 % increase in benzene emission with 20 %, 50 %, 75 % and 100 % biodiesel blend. 21.8 % and 27.4 %, 30.5 % and 37.8 %, 43.2 % and 63.1 %, 47.6 % and 71.1 % decrease in toluene and xylene emissions with 20 %, 50 %, 75 % and 100 % biodiesel blend	In line 4-cylinder DI engine
Ge and Choi, 2020	10 %, 20 %, 30 % and 100 % blends of biodiesel compared with diesel	Reduction in BTX emission with an increase in biodiesel concentration in diesel	Turbocharged CRDI diesel engine
Puškár *et al*., 2019	10 %, 30 %, 50 % and 100 % biodiesel (kitchen waste oil biodiesel) compared with diesel	Benzene increases and toluene and xylene decrease for biodiesel blends compared to diesel	CRDI engine

fuel injection. These include fuel pyrolysis, nucleation, surface growth, coalescence, agglomeration of primary particles, and oxidation. The oxidation can occur at any stage in the soot formation process, and it converts hydrocarbons in the soot into CO, CO_2, and H_2O. It competes with the soot formation process; therefore, the net soot emissions can be estimated by soot formation rate minus the soot oxidation rate. From fuel pyrolysis to agglomeration, the first five processes are depicted in a schematic shown in Figure 3 (Tree and Svensson, 2007).

In the pyrolysis process, the fuel molecules are broken down into simpler molecules under high-temperature and pressure ambient conditions without interaction with oxygen. The pyrolysis usually does not involve visible flames but leads to direct soot formation. This endothermic reaction changes the molecular structure of organic components. This leads to the formation of less saturated, lighter weight hydrocarbons than the parent species (Smith, 1981). The reaction rate is determined by ambient temperature and fuel concentration (Tree and Svensson, 2007). It is known to have a higher rate under fuel-rich high-temperature conditions. The pyrolysis produces basic building blocks for the formation of soot particles, e.g., unsaturated hydrocarbons, poly-acetylenes, polycyclic aromatic hydrocarbons (PAHs), and acetylene (C_2H_2). Combustion of premixed charge leads to low soot emissions, while diffusion flames produce much higher soot precursors. As mentioned above, oxidation can occur instantaneously during any step of the soot formation process; therefore, pyrolysis also competes against oxidation. It is well established that both rates of both reactions, pyrolysis and oxidation, increase with increasing ambient temperature. However, the oxidation rate overwhelms the pyrolysis rate under extremely high-temperature conditions.

Nucleation is a basic process that converts gaseous reactants into multi-composition particles. It forms a particle's core region where the nuclei exist. The particle inception begins from the nuclei with a 1.5 ~ 2 nm diameter. Meanwhile, mass is added to the soot nuclei by surface growth. It is reported that both processes occur under ambient temperatures ranging from 1300 ~ 1600 K, and there is no clear differentiation between the termination of the nucleation process and the start of surface growth processes (Tree and Svensson, 2007). A previous study by Calcote *et al.* (1988) proposed a mechanism for nucleation, as shown by the schematic in Figure 4.

In this mechanism, the $C_3H_3^+$ ion was considered a primary soot precursor. This ion then undergoes surface growth by reacting with C_2H_2 molecules. During this

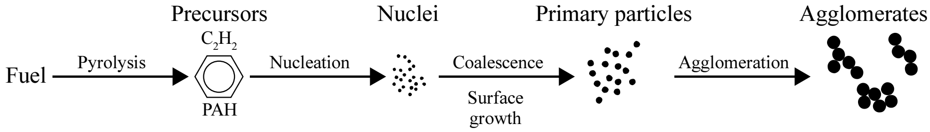


Figure 3. Schematic of distinct processes during the soot formation (Tree and Svensson, 2007).

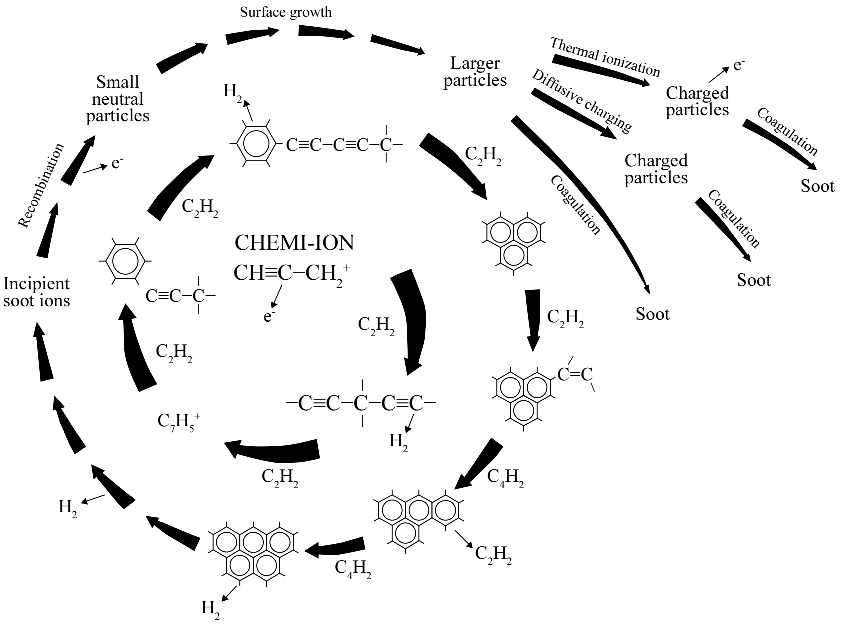


Figure 4. Ionic reaction mechanism for nuclei to soot formation processes (Calcote *et al.*, 1988).

growth period, the reactive surfaces of the soot particles accept hydrocarbons from the gas phase. The number of particles remains constant; however, this procedure increases the total mass of particles. It is known that smaller particles have more reactive sites on the soot surface; hence they have a higher surface growth rate than larger particles (Tree and Svensson, 2007). At the end of the growth period, the reaction with negative ions and free electrons increases, producing small neutralised soot particles. They became thermally ionised under high ambient temperature conditions, leading to further coalescence and agglomeration of soot particles (Calcote *et al*., 1988). In a previous study by Bryce *et al*. (1999) the soot generation in this process was characterised by two different paths. Under low ambient temperature, aromatic rings dehydrogenate and form poly-cyclic components.

On the other hand, break-up and recyclisation of rings occur at high ambient temperatures. After surface growth, soot particles undergo coalescence and agglomeration. Coalescence means the recombination of primary particles. For example, two small primary particles are combined into one large primary particle. Agglomeration indicates the formation of a chain-like structure by connecting many primary particles. The difference between coalescence and agglomeration is shown by the schematic given in Figure 5.

The process of agglomeration forms typical soot particles in the exhaust stream of the engines. Engine variables such as engine speed, load, fuel injection pressure, fuel injection timing, and EGR rate affect the shape and size of the soot agglomerates (Burtscher, 2005). Different combinations of each engine variable can lead to a completely different soot morphology. For example, Rohani (2017) showed significant contradiction from the previous studies.

Finally, oxidation occurs during each soot formation stage. If hydrocarbons undergo oxidation to form CO or CO_2, they never return to soot, even in the high-temperature regions (Tree and Svensson, 2007). It is reported that the oxidation process takes place above an ambient temperature of 800 K (Glassman *et al*., 2014). Under fuel-lean conditions, O_2 and OH radicals are responsible for soot oxidation. On the other hand, OH radicals act as dominant soot oxidisers under fuel-rich conditions (Glassman *et al*., 2014). Apart from individual soot formation steps, a conceptual model was proposed by Kosaka *et al*. (2005). This conceptual model was developed based on an optical engine's OH and soot imaging. The development of soot particles in an engine is conceptually captured in Figure 6.

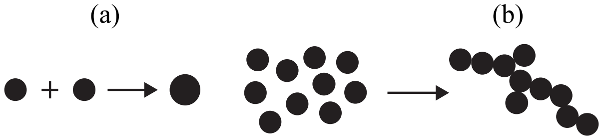


Figure 5. Schematic showing (a) Coalescence; (b) Agglomeration processes.

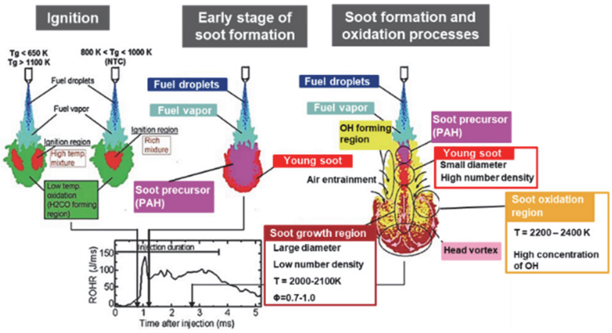


Figure 6. Conceptual model of soot process in a compression ignition engine (Kosaka *et al*., 2005).

First of all, in a very early ignition stage, low-temperature oxidation of fuel occurs before the main ignition in a fuel spray. The mixture composition has a dominant effect on the peak combustion temperature. For example, high-temperature combustion occurs in the core of the spray, where the fuel-air mixture is rich. On the other hand, low-temperature combustion occurs at the spray periphery, where the fuel-air mixture is lean. Thus, most soot precursors such as PAHs are produced in the spray core region, and it gives birth to young soot nuclei as the spray evolves. The young soot formed in the central fuel-rich region of the spray becomes larger by surface growth and coalescence processes during convection to the leading edge of the spray. In this stage, the number density of soot particles decreases due to agglomeration. However, the size of the individual soot agglomerates increases. The soot particles travel along with the vortical motion of the ambient air, and they get re-entrained into the leaner side of the flames, where the OH radical concentration is rather high. This process facilitates the oxidation of soot particles. Since the in-cylinder pressure decreases after the peak, the oxidation of soot freezes and soot particles are eventually emitted into the exhaust tailpipe.

4.1. Particulate Composition

It is essential to understand the combustion process to evaluate PM composition in diesel engines. As reviewed in the previous section, in modern DI compression ignition engines, fuel is injected when the piston reaches close to the top dead centre in the compression stroke. The combustion of the heterogenous air-fuel mixture takes place (Agarwal *et al*., 2015). In other words, spray atomisation and combustion occur concurrently. Depending on the mixture quality (equivalence ratio) in the spray plume, it tends to undergo complete combustion (low PM formation) or incomplete combustion (higher PM formation) (Dec, 1997). Since soot evolves from the nuclei mainly made of carbon, the young soot is more carbonaceous than the soot particles in the later combustion stages. During combustion, not only

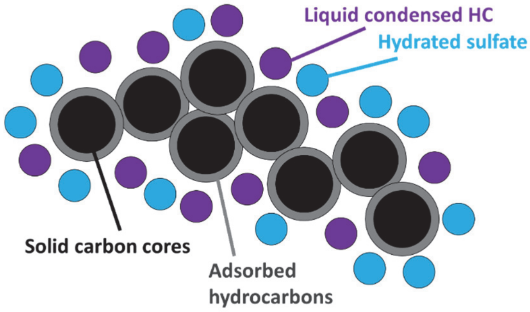


Figure 7. Schematic of soot agglomerates from compression ignition engine.

carbon but also unburned hydrocarbons and sulfates are also produced. Therefore, these species get adsorbed on the surface of soot agglomerates. In a study by Twigg and Phillips (2009), the composition of soot agglomerates was described as shown in Figure 7 (adapted from the original figure). The soot particle comprises of numerous primary particles, which are spherical. The core region of these primary particles is made of carbon mainly. This carbon core is surrounded by unburned hydrocarbons/soluble organic fraction (SOF). The adsorbed hydrocarbon layer can also be of vapour or liquid phase. If these particles are observed under a transmission electron microscope (TEM), blurry boundaries in the soot particle are observed because of SOF (Hirner *et al*., 2019a).

The composition of soot particles varies with engine operating conditions. Typically, the soot particle composition can be divided into four distinct categories: elemental carbon (EC), organic carbon (OC), ash, and sulfates (Abdul-Khalek *et al*., 1999). The sulfates/sulfuric acid are considered to have a proportional relationship with the sulfur content of the fuel. The fraction attributed to unburned fuel and lubricant oil (SOF) can range from < 10 % to > 90 % (w/w) (Eastwood, 2008). It is well established that lower exhaust gas temperature typically observed at low engine loads leads to higher SOF content in the particulates.

4.2. Effect of Biodiesel on Particulates

Biodiesel contains oxygen in the fuel molecules, affecting PM emissions and soot particle characteristics. This section first discusses a macroscopic view of particulate emissions, namely particulate mass and number emissions. After that, soot reactivity and EC/OC of particulates are discussed.

4.2.1. PM and PN emissions

Recent publications show a general trend of lower particulate mass and number emissions but higher NO_X emissions from biodiesel/blend vis-à-vis conventional diesel (Agarwal and Dhar, 2013; Singh *et al*., 2014). It is known as the 'NO_X-Soot trade-off' in modern diesel engines. In a previous study by Musculus (2005), they concluded that the cooling via radiation by soot particles reduced the flame temperature by 25 ~ 50 °C, leading to a corresponding NO_X reduction of ~12 ~ 25 %. Therefore, the in-cylinder temperature during biodiesel combustion can be maintained at elevated temperatures because of lower PM emissions, albeit with higher thermal NO_X emissions. The physics behind lower soot emissions with biodiesel is controlled by a lower equivalence ratio in the fuel-air mixture in the spray. Since biodiesel has ~10% oxygen (w/w) in the fuel molecules, it leads to a leaner mixture, promoting the oxidation of soot particles. The calculated equivalence ratio indicates that biodiesel has a lower equivalence ratio (fuel-lean) in the fuel spray, even though they have inferior spray atomisation characteristics (Hwang *et al*., 2016a). This trend was reported by many previous studies, which are summarised below.

Bhuiya *et al*. (2017) studied the influence of various biodiesels made from waste cooking oil (WCO) and Poppyseed oil blended with diesel. An increased biodiesel fraction in the test fuel decreased CO, HC, and PM emissions but increased the NO_X emissions. Other research groups also reported similar emission trends for different biodiesels and blends (Buyukkaya, 2010; Cheung *et al*., 2015; Kathirvelu *et al*., 2017). In a study by Buyukkaya (2010), rapeseed biodiesel blends were evaluated, whereas Cheung *et al*. (2015) evaluated 100 % WCO biodiesel and blends. Kathirvelu *et al*. (2017) evaluated Jatropha and WCO derived biodiesels and blends, and their results were compared with conventional diesel. In these studies, the main reason for lower soot emissions from biodiesels/ blends was the inherent oxygen present in biodiesel, which promoted soot oxidation. The absence of aromatics, considered a soot precursor, was another reason for lower soot emissions (Lapuerta *et al*., 2008). In addition, a higher cetane number of biodiesels was an important reason for lower soot emissions because it reduced the combustion delay, leading to lesser fuel-air mixture enrichment (Qi *et al*., 2009). Even though there is an underlying fact of variable raw materials for WCO biodiesel, the influence is not substantial since the quality of WCO biodiesel is also controlled by ASTM standards.

Meanwhile, in an experimental study by Agarwal and Agarwal (2007), a trend of CO, HC, and PM emissions at variance with previous studies was reported. They investigated Jatropha oil blends of different compositions and preheated conditions. Jatropha blends exhibited higher CO_2, CO, HC, and PM emissions with an increasing Jatropha blending ratio. Preheating the Jatropha oil to 90 ~ 100 °C or blends with diesel up to 30 % (v/v) exhibited fuel viscosity similar to mineral diesel. Emissions from preheated Jatropha oil were closer to baseline diesel, though. The emission characteristics in this study are reasoned to be because of inferior spray atomisation and poor fuel-air mixing of Jatropha oil.

Most previous studies have reported that PN reduces with biodiesel/blends. In a study by Dhar and Agarwal (2015), Karanja biodiesel exhibited a reduction in PN emissions up to a blending ratio of 50%, as shown in Figure 8. Karanja biodiesel (KB100) showed the highest PN emissions amongst all test fuels regardless of engine operating conditions. On the other hand, the 10 % Karanja biodiesel blend showed the lowest PN emissions compared to baseline diesel. While optimising emissions, the researchers suggested 20 % Karanja biodiesel blends to emit overall lower emissions than baseline diesel.

Similarly, in another study by Agarwal *et al.* (2014), the total PN emissions were lower for Karanja biodiesel blends than baseline diesel, especially when the start of injection timing was retarded. The level of PN emissions also reduced when the fuel injection pressure was increased from 300 to 500 bar because of the improvement in fuel spray atomisation and fuel-air mixing of biodiesel blends. Higher in-cylinder pressure and temperature supported this hypothesis of biodiesel combustion. This study also underscored that a lower biodiesel blending ratio reduces emission significantly from baseline diesel.

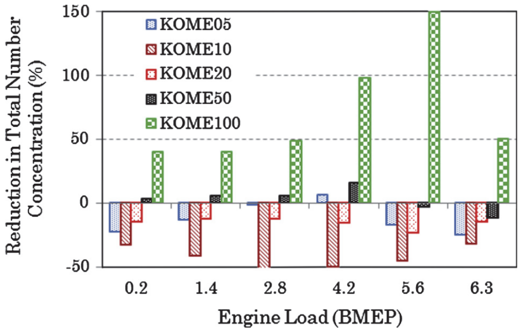


Figure 8. Reduction in PN emissions for Karanja biodiesel blends at varying engine loads (Dhar and Agarwal, 2015).

Table 7. Overview of emission trends upon using biodiesel/blends.

Test fuel/s	Engine Displ./Cyl [cc]	Trends	Ref.
10 %/20 %/30 %/40 %/50 %/ 75 %/100 % Jatropha + preheating	948	CO$_2$, CO, HC, FSN are higher than diesel If fuel preheated, emissions closer to diesel CO$_2$, CO, HC, FSN increased with Jatropha oil content	Agarwal and Agarwal, 2007
5 %/10 %/20 % blend of [WCO + Poppy (20 %/80 %)] biodiesel	830	CO, HC, PM decreased, and NO$_X$ increased with biodiesel	Bhuiya *et al.*, 2017
5 %/20 %/70 %/100 % Rapeseed biodiesel blend	2.138	Higher exhaust gas temperature with biodiesel CO, HC, FSN decreased, and NO$_X$ increased with biodiesel	Buyukkaya, 2010
10 %/20 %/30 %/100 % WCO blend,	1.084	CO, HC, PM decreased, and NO$_X$ increased with biodiesel	Cheung *et al.*, 2015
10 %/20 %/30 %/40 % Canola biodiesel blend + 0 %/5 %/10 %/15% water	498	CO, HC, FSN decreased, and NO$_X$ increased with biodiesel content	Elsanusi *et al.*, 2017
WCO biodiesel	980	CO, HC, PM decreased, and NO$_X$ increased with biodiesel	Hwang *et al.*, 2015
WCO biodiesel	980	In LTC mode, CO, HC, NO$_X$ are higher and FSN lower for biodiesel	Jung *et al.*, 2016
20 %/100 % Jatropha blend, 20 %/100 % WCO (fish-based) blend	661	CO, Smoke lower and NO$_X$ higher for biodiesel	Kathirvelu *et al.*, 2017
20 % Soybean biodiesel blend, 20 % Animal fat-based biodiesel blend	975	No significant difference in NO$_X$ HC emissions Lower PM for biodiesel at high loads Higher PM for biodiesel at medium loads	Ketterer *et al.*, 2014
20 %/50 %/75 % WCO biodiesel blend	1.083	PM decreased with biodiesel	Wei *et al.*, 2017
5 %/20 % Coconut biodiesel blend, 5 %/20 % Soybean biodiesel blend	422	NO$_X$ and PM emissions were similar for all fuels except Soybean B20. Here PM decreased, and NO$_X$ increased	Han *et al.*, 2008

4.2.2. Soot reactivity

Several groups investigated diesel soot reactivity and reported higher reactivity of soot produced by biodiesels than conventional diesel (Ma *et al*., 2015; Man *et al*., 2015; Yehliu *et al*., 2012; Burtscher, 2005). One possible reason is that soot particles from biodiesels have a more amorphous nanostructure than diesel as,reflected by greater graphene layer tortuosity and a less ordered structure of the carbon fringes (Jung *et al*., 2016; Savik *et al*., 2016; Yehliu *et al*., 2012). Vander Wal and Tomasek (2003) studied the effects of nanostructure on the soot oxidation process. They indicated a relationship between higher tortuosity and shorter fringe length with the higher soot reactivity. They indicated that tortuosity is a dominating parameter since the soot reactivity is dependent on the accessibility of carbon layer edge sites. Higher curvature may cause the fringes to break into smaller ones, affecting the soot reactivity. In general, soot reactivity increases with a higher number of accessible edge sites in the graphene layers (Vander Wal and Tomasek, 2003; Yehliu *et al*., 2012; Hwang *et al*., 2019). This indicates that higher disordered nano-graphene layers lead to greater soot reactivity since a higher amorphous structure leads to a larger number of accessible carbon atoms on the edge sites. Also, the oxygen bonded to the edge sites can induce more microporous structures during an attack by oxygen in the air, resulting in enhanced biodiesel soot oxidation (Man *et al*., 2015). It was demonstrated that the soot macrostructure, the agglomerate size of palm-oil biodiesel soot, was slightly smaller than the one from baseline diesel (Karin *et al*., 2013).

Figure 9 summarises various parameters and their influence on the reactivity of soot particles.

Hwang *et al*. (2019) and Savic *et al*. (2016) also reported smaller primary particle sizes for WCO, microalgae, cottonseed biodiesel and blends compared to baseline diesel. However, it was noted that not every researcher reported similar trends as discussed above. For example, Ma *et al*. (2015) reported a higher-ordered soot structure for biodiesel than baseline diesel. Table 8 summarises the findings of various studies investigating morphological characteristics of biodiesel soot w.r.t. baseline diesel soot.

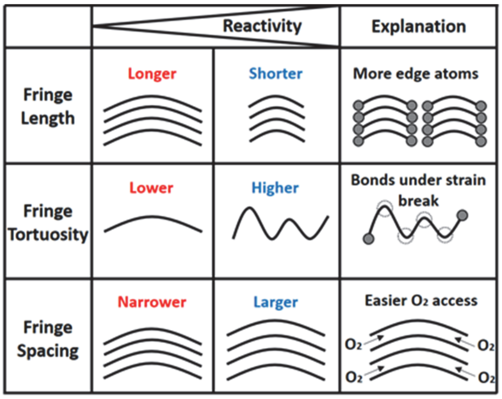


Figure 9. Effects of nano-graphene layer structure on soot reactivity (Hwang *et al*., 2019).

4.2.3. Elemental carbon (EC) and organic carbon (OC)

As described in the earlier section on soot formation, soot particles are mainly composed of a carbonaceous core and adsorbed hydrocarbons around the primary particles. The carbonaceous core is produced in a fuel-rich region in a spray through high-temperature pyrolysis. The carbon crystalises such that it seems stacked in nano-graphene layers. The adsorbed hydrocarbons are called volatile organic fraction (VOF) and SOF, usually including condensed materials from unburned hydrocarbon or sulfates. These have extremely harmful effects on human health. Hence many researchers investigated elemental carbon (EC) and organic carbon (OC) emissions from a variety of engines/vehicles fuelled by various biodiesels/blends (Shukla *et al*., 2015, Kweon *et al*., 2003).

Song *et al*. (2011) measured EC/OC emissions from cottonseed-oil biodiesel fuelled 4.5L multi-cylinder diesel engine in a 13-mode European stationary cycle (ESC) test. Nine different modes were tested, with three engine speeds, corresponding to 25 %, 50 % and 75 % loads. The test fuels included commercial diesel sold in Beijing, China and cottonseed oil (CSO) biodiesel. The experimental results shown in Figure 10 indicated that the EC and OC from neat CSO biodiesel emissions were lower than baseline mineral diesel regardless of operating conditions. EC and OC were reduced by 16 % and 15 % by switching to neat CSO biodiesel. The main reason was given as fuel bound oxygen in biodiesel. CSO biodiesel contained 11.91 % (w/w) oxygen versus nil for baseline diesel. A similar result was reported in a recent study by Shibata *et al*. (2019). They investigated the EC/OC emissions using a 10 % rapeseed methyl ester (RME) blend in a 3 L multi-cylinder diesel engine under three different engine operating conditions (Sibata *et al*., 2019). The emissions were analysed using a thermo-optical carbon analyser. The experimental results indicated that the EC was the most abundant carbonaceous component in the diesel exhaust particles in the engine-out emissions. Carbonaceous components were significantly lower for 10 % RME biodiesel than baseline diesel.

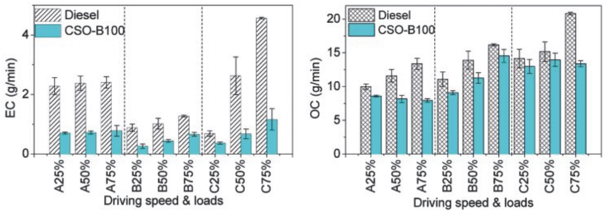


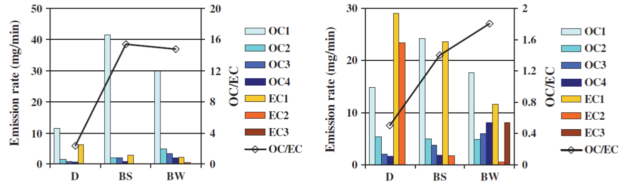
Figure 10. Comparison of EC/OC emissions for different engine operating conditions (A, B, and C correspond to low, middle, and high engine speeds) (Song *et al*., 2011).

Table 8. Summary of studies in the literature investigating biodiesel/blend fuelled engine's soot morphology and nanostructure.

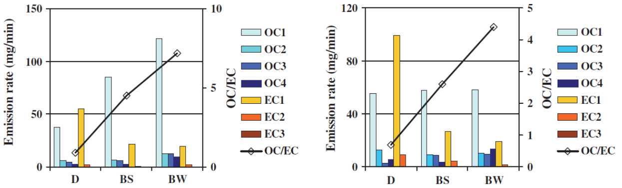
Test fuel/s	Engine Displ./Cyl [cc]	Trends of soot morphology and nanostructure	Ref.
Palm Biodiesel	683	Biodiesel agglomerate size is slightly smaller	Karin *et al*., 2013
10 %/20 %/30 %/100 % WCO Biodiesel blend	1.084	Volatile fraction increases with biodiesel content Lower load leads to easier burn-off	Cheung *et al*., 2015
WCO	980	WCO has a smaller primary particle diameter Volatile fraction increases with WCO WCO soot has lower carbon content, but more hydrogen, oxygen, and nitrogen	Hwang *et al*., 2015
WCO	980	Volatile fraction higher for WCO WCO has an amorphous structure	Jung *et al*., 2016
20 % Soy-Biodiesel blend 20 % Animal fat Biodiesel blend	975	Increase in soot organic fraction with biodiesel No significant difference in nanostructure (qualitatively assessment)	Ketterer *et al*., 2014
Soy biodiesel Rapeseed biodiesel Animal tallow biodiesel + combustion catalyst	211	Primary soot particles and agglomerates are smaller for biodiesel + catalyst Nano-structure and fractal dimension unchanged Reactivity increased with catalyst Biodiesel soot higher-ordered structure	Ma *et al*., 2015
WCO	1.075	More particles with a larger size at lower engine speed Lower load leads to a more amorphous structure with higher reactivity	Man *et al*., 2015
5 %/20 %/50 % Microalgae, 20 % WCO, 20 % Cottonseed biodiesel blends	-	Structural disorder increased with biodiesel content Higher load leads to smaller particles Smaller primary particle size for biodiesel	Savik *et al*., 2016
Soy-biodiesel	625	Higher soot reactivity for biodiesel Reactivity is connected to soot nanostructure	Yehliu *et al*., 2012
20 %/50 %/100 % WCO	441	Higher reactivity with increased WCO content The number of primary particles increases with WCO The diameter of primary particles decreases with WCO	Qu *et al*., 2016

On the other hand, tailpipe emissions did not show significant differences in reducing EC and OC from biodiesels. DPF was used as an after-treatment system, and its EC and OC reduction levels were ~99.7 % and 91.8 % for diesel and ~99.5 % and 87.8 % for 10 % RME biodiesel blend. This indicated that the performance of DPF was adequate to eliminate soot emissions from the engine exhaust. The reason for lower EC emissions from biodiesel was that fuel oxygen in biodiesel inhibited EC production in the engine cylinder. The fuel oxygen of biodiesel and higher air/fuel ratio prepared a more oxygen-rich environment.

Zhang *et al*. (2011) investigated particulate emissions from various test fuels, namely WCO, soybean biodiesels, and diesel, in a 4.75L four-cylinder direct injection diesel engine. $PM_{2.5}$, EC, and OC mass and particle size distributions were evaluated under two engine speeds and four-engine load conditions. Application of both soybean and WCO biodiesels reduced $PM_{2.5}$ emissions up to 20 % and 35 % with respect to baseline diesel at full load at 1400 rpm and 75 % load at 2300 rpm, respectively. This is consistent with the previous study by Haas *et al*. (2001), which obtained 53 % lower PM emissions with soybean biodiesel compared to baseline diesel.



(a) 1400 rpm, 50% load (b) 1400 rpm, 100% load



(c) 2300 rpm, 25% load (d) 2300 rpm, 75% load

Figure 11. Comparison of EC/OC emissions with varying engine loads and speeds (Haas *et al.*, 2001).

Biodiesels showed a higher portion of OC than baseline diesel. The EC/OC measurement trends according to engine load and speed are shown in Figure 11. At 50 % load, 1400 rpm, soybean and WSO biodiesels showed a 260 % and 160 % increase in OC compared to baseline diesel. On the other hand, EC emissions decreased by 53 % and 58 % for soybean and WCO biodiesels compared to baseline diesel. Under high engine loads, the ratio of OC to EC decreased significantly, showing a maximum level of 5. This indicated that biodiesel soot particles became carbonaceous under high-temperature and pressure conditions.

5. TRACE METALS

Other than unregulated/regulated emissions from CI engines, trace metal emissions from lubrication oil and friction wear origin are major concerns affecting human health and the environment. The trace metals can be Fe, Ca, Mg, and Na. Trace metals play a major role in clogging vehicle fuel lines and leave undesirable metal oxides residues on the engine parts (Agarwal *et al.*, 2015). In addition, transition metal- containing particulates have deep penetration into the human body. Therefore many researchers are trying to understand the effects of biodiesels on trace metal emissions and their relative impact. Pillay *et al.* (2012) investigated trace metals in Neem biodiesel and commercial biodiesels. They concluded that Neem biodiesel has a relatively lower trace metal content than the others. However, some trace metals emissions such as Mn, Cu, and Pb were higher in the engine exhaust from Neem biodiesel. Therefore, it was suggested that further biodiesel refinement for de-metallisation is essential for sustainable biodiesel usage from Neem oil. Dwivedi *et al.* (2006) reported that Cr increased while other trace elements such as Cd and Ni reduced with B20. Similar results were reported by Betha and Balasubramanian (2011), who investigated ultra-low sulfur diesel (ULSD), waste cooking oil biodiesel (B100) and a blend (B50) in a 0.3L single-cylinder diesel engine. They concluded that particulate emissions were reduced with biodiesel.

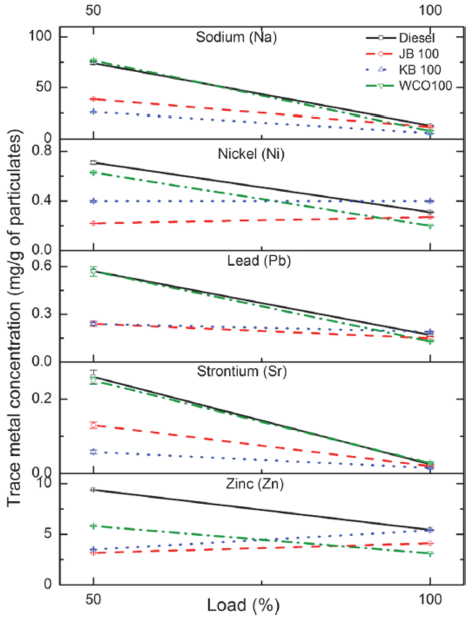


Figure 12. Comparison of trace metal emissions from different biodiesels and baseline diesel with varying engine loads (Patel *et al.*, 2019).

However, most trace metal elements are known to be toxic. For instance, Zn, Cr, and Ni traces were extremely high in biodiesel exhaust compared to ULSD fuelled engine exhaust. Trace elements such as Co, Al, and Mn were at higher levels in the ULSD. Patel *et al.* (2019) investigated trace metal emissions from various biodiesels from Jatropha, Karanja, and WCO in a 1L single-cylinder diesel engine. Comprehensive analysis of the emission of trace metals (Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Zn and Al) was done by using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The experimental results showed a consistent trend with existing literature, showing lower trace metal emissions from biodiesels. Figure 12 shows trace concentrations of Na, Ni, Pb, Sr and Zn in particulates from all test fuels.

Amongst the trace metals emitted, Na concentration was observed to be the highest. This implied that the engine oil or coolant played a major role in the emissions of these trace metals. Baseline diesel and WCO showed 74.1 mg/g and 76.62 mg/g of Na emissions, at double and triple levels compared to Jatropha and Karanja biodiesels. WCO biodiesel showed similar trace levels of Pb and Sr as baseline diesel. The trace metal emissions were reduced significantly at full load regardless of the test fuel.

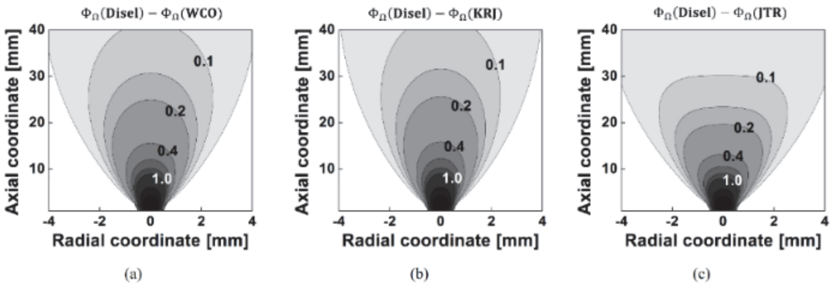


Figure 13. Differences in equivalence ratios between baseline diesel and (a) WCO; (b) Karanja; (c) Jatropha biodiesels (Hwang *et al*., 2017).

6. EMISSION REDUCTION

Research studies have reported lower harmful emissions from biodiesel combustion, such as CO, HC, and PM. There are two main reasons. The first is lower fuel sulfur and aromatic hydrocarbon (benzene, toluene, etc.) content than baseline diesel. They play a vital role in forming pollutants, especially PM emissions, since they are important soot precursors. The unsaturated hydrocarbons and polycyclic aromatic hydrocarbons are the basic building blocks for the formation of nuclei for the soot particles. The carbon layers gather around those species. Therefore biodiesel exhibits lower soot emissions. The second reason is that biodiesels contain ~10 % oxygen in their fuel molecule. This means that biodiesels exhibit a hydrocarbon-lean fuel-air mixture in their spray. In a previous study by Hwang *et al*. (2017), the equivalence ratios of various biodiesels (namely WCO, Jatropha, and Karanja) were calculated using a spray model derived from non-reacting conditions, proposed by Sievers and Naber (Siebers, 1999; Naber and Sibers, 1996). The calculated results are given in Figure 13, showing the differences in equivalence ratios between the biodiesels and baseline diesel.

It is shown that the equivalence ratio decreased in the axial and radial directions as fuel-air mixing occurred. It can be noted that the differences in equivalence ratios between baseline diesel and biodiesels are greater than 0, which indicates the equivalence ratio with baseline diesel is higher than biodiesels. This is attributed to the fuel oxygen in biodiesel. This is the main reason for lower CO, HC, and PM emissions with biodiesels, even though biodiesel's fuel properties are inferior to baseline diesel. Another supporting hypothesis of this result is that emission reduction benefits were maximized with higher fuel injection pressure, enabling biodiesels to compensate for inferior fuel properties.

On the other hand, few researchers reported increased CO, HC, and PM emissions from biodiesels. Hirner *et al*. (2019b) reported higher CO, HC, and PM emissions than baseline diesel used in a small-bore diesel engine. Interestingly, the CO and HC emission levels showed an exact match with trends of fuel viscosity. Thus a plausible explanation for the results was biodiesel's higher viscosity, which deteriorated the spray atomisation, leading to a more heterogeneous mixture formation (Patel *et al*., 2016). Especially the reasons given for higher HC emissions included flame quenching at the cylinder walls because of lower wall temperatures and incomplete combustion of liquid fuel droplets impinging on the cylinder walls (Fang *et al*., 2009). A previous study by Hwang *et al*. (2016b) supported this hypothesis for HC formation as they confirmed a longer liquid spray jet penetration length for Karanja and Jatropha biodiesels.

7. CONCLUSION

A comprehensive review of the literature was done for studies using different biodiesels from various feedstock used in different types of engines under different operating conditions. The effects of biodiesel and blends on regulated, unregulated, particulate, and trace metal emissions were optimized in this paper. Towards the end, emission reduction technologies were also discussed briefly. The following main conclusions could be drawn from the literature review. CO and HC emissions were reduced with the use of biodiesel and blends. It is due to a greater degree of combustion completion in favourable conditions. Higher NO_X emissions were observed for biodiesel and blends primarily due to higher temperature in the combustion chamber due to inherent fuel oxygen. It encouraged superior combustion and produced higher thermal NO_X. Carbonyl emissions such as formaldehyde and acetaldehyde increased with increasing biodiesel fraction in the test blends. Waste cooking-based biodiesel already contains carbonyl products generated during the cooking process. However, some biodiesel blends show a reduction in NO_X and carbonyl emissions. It suggests that engine operating conditions and physicochemical properties of the fuel play an important role in forming those emissions. In other biodiesels, the combustion of oxygenated fuels produces carbonyl emissions. Thermal cracking of long-chain olefins produces several unsaturated (1,3-butadiene, propene, and ethene) and saturated (Benzene, Toluene, and Xylene) hydrocarbons; hence biodiesels show higher emissions of 1,3-butadiene, propene, and ethene due to higher peak in-cylinder temperature, which provides superior conditions for pyrolysis for long-chain olefins into these products. In most studies, a shorter combustion duration reduces toluene and xylene emissions for biodiesels/blends; however, benzene emissions increased. Most researchers reported PM and PN emissions reductions and comparatively smaller primary particle diameters with biodiesels/blends. It was due to inherent fuel oxygen that improved the combustion. Most studies also reported reductions in EC/OC emissions. Several trace metal emissions such as Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Zn and Al are also found in the exhaust gas, and the origin of these trace metals was the lubrication oil and wear of the engine components.

For upcoming stringent emission regulations and RDE, biodiesel is believed to have more synergetic effects with advanced combustion strategies such as HCCI, PCCI, and RCCI to have optimised engine performance and emission characteristics. For example, a moderate level of EGR can improve NO_X issues with biodiesel while maintaining lower PM emission levels than diesel.

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