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Potential and challenges for large-scale application of biodiesel in automotive sector

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ABSTRACT

Biodiesel is receiving serious attention globally as a potential alternative fuel for replacing mineral diesel, partially or fully. In this review paper, most prominent methods of biodiesel production commercially, life-cycle analysis and economic issues related to biodiesel, engine performance, combustion and emission characteristics including particulate, engine compatibility issues and effect of biodiesel usage on engine component wear and lubricating oil are comprehensively discussed. Majority of biodiesel produced globally is via base-catalyzed transesterification process since this is a low temperature and pressure process, having high conversion rates without intermediate steps, and it uses inexpensive materials of construction for the plant. Catalyst types (alkaline, acidic or enzymatic), catalyst concentration, molar ratio of alcohol/oil, reaction temperature, moisture content of reactants, and free fatty acid (FFA) content of oil are the main factors affecting biodiesel (ester) yield from the transesterification process. Substantial reduction in particulate matter (PM), total hydrocarbons (THC) and carbon monoxide (CO) emissions in comparison to mineral diesel, and increased brake specific fuel consumption (BSFC) and oxides of nitrogen (NO_X) emissions are reported by most researchers using unmodified compression ignition (CI) engines. This review covers several aspects, which are not covered by previous review articles, such as effect of biodiesel on unregulated emissions, effect of biodiesel on carbon deposits, wear of key engine components, and lubricating oil in long-term endurance studies. It emerges from literature review that even minor blends of biodiesel help control emissions and ease pressure on scarce petroleum resources without sacrificing engine power output, engine performance and fuel economy. This review underscores that future studies should focus on optimization of fuel injection equipment and hardware modifications to develop dedicated biodiesel engines, improve low temperature performance of biodiesel fuelled engines, develop new biodiesel compatible lubricating oil formulations and special materials for engine components before implementing large-scale substitution of mineral diesel by biodiesel globally.

Contents

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Acronyms

ADC	Athens driving cycle
BSFC	Brake specific fuel consumption
BMEP	Brake mean effective pressure
BTE	Brake thermal efficiency
BTX	Benzene, toluene and xylene
CO	Carbon monoxide
CI	Compression ignition
COME	Castor oil methyl ester
CR	Compression ratio
CRDI	Common rail direct injection
DGM	Diglyme (diglycol methyl ether)
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
DSC	Differential scanning calorimetry
EC	Elemental carbon
ECU	Electronic control unit
EGR	Exhaust gas recirculation
EU	European union
FCO	Fresh cooking oil
FFA	Free fatty acid
FID	Flame ionization detection
FIP	Fuel injection pressure
FT	Fischer–Tropsch
HD	Heavy-duty
HEBO	High erucic Brassica oil
HOSO	High oleic sunflower oil
HRR	Heat release rate
HRR_{max}	Maximum heat release rate
HSDI	High speed direct injection
IDI	Indirect-injection
LCA	Life cycle analysis
LCV	Light commercial vehicle
LEBO	Low erucic Brassica oil
LSD	Low Sulphur diesel
NEDC	New European driving cycle
NFT	Nitrogen fixing trees
NO_X	Oxides of nitrogen
OC	Organic carbon
PLN	Pump-line-nozzle
PM	Particulate matter
P_{max}	Maximum in-cylinder pressure
PN	Particulate number
RFD	Reformulated diesel
RME	Rapeseed methyl ester
$RoPR_{max}$	Maximum rate of pressure rise
SEM	Scanning electron microscopy
SMD	Sauter mean diameter
SME	Soybean methyl ester
SoC	Start of combustion
SoI	Start of injection
SUV	Sports utility vehicle
SVOs	Straight vegetable oils
THC	Total hydrocarbons
TSOME	Tobacco seed oil methyl ester
WCOB	Waste cooking oil biodiesel
WVO	Waste vegetable oil
WZA	Tungstan-zirconia-alumina

1. Introduction

Global population is predicted to exceed 9 billion by 2050 therefore significantly higher fuel quantity would be required to meet the energy requirements in future [1]. BP Statistical Review showed that total proven oil reserves in the world crossed 1700 billion barrels in 2014 (Fig. 1), which is enough to meet ~50 years of global energy demand only [2]. However one should note with caution that such estimates are not very reliable and have to be considered carefully in estimating the assured energy supply for the future. This shrinking energy supply needs to be augmented by newer energy resources, preferably with the ones that recycle atmospheric GHG emissions so that increase in earth's temperature can be kept under check. In past couple of decades, development and use of various alternative fuels, particularly biofuels has attracted global attention. Biofuels are very

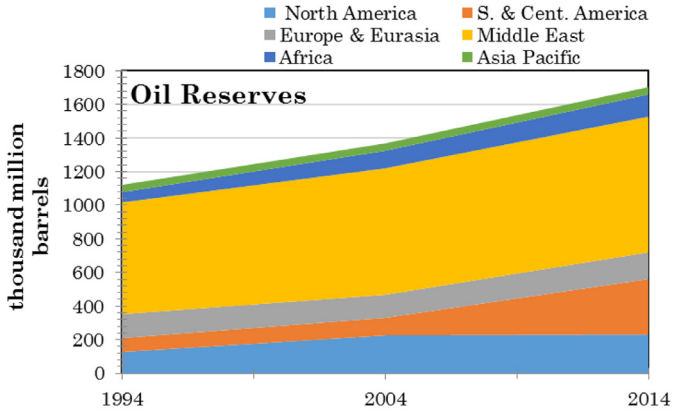


Fig. 1. Distribution of global oil reserves (Adapted from [2] with permission of The Editor, BP Statistical Review of World Energy).

attractive fuel option because they offer several promising benefits such as reduced dependence on fossil fuels and a potential to slow-down global climatic change, in addition to potential to grow on fallow lands and potential for rural job creation [3].

It emerges that the sustainable alternative fuels should be renewable, efficient, cost-effective and less polluting compared to conventional fossil fuels [4,5]. There are several biofuel candidates developed over past few decades however the main biofuels being considered seriously are biodiesel and ethanol. They are most acceptable biofuels because of minor or no modifications required in the engine hardware, easier fuel production technology, capability to use existing fuel delivery infrastructure and economic viability [4,6]. Though the thermal properties such as calorific value, cetane number, and volatility characteristics of biodiesel are very close to that of mineral diesel, there are considerable differences in some important physical properties of the two fuels, such as density, viscosity, pour point etc. Biodiesel has higher viscosity and density, 10–15% lower calorific value, higher bulk modulus, higher oxygen content, and lower stoichiometric air-fuel ratio compared to baseline mineral diesel [7–9]. Currently, engine control parameters can be tuned according to fuel properties, so that the engine can comply with prevailing emission norms. Biodiesel can be produced from various feedstocks and its properties depend on feedstock properties and the production process used to a great extent. Biodiesel properties influence engine performance and emission characteristics. For ensuring successful implementation of biodiesel in transport sector, several biodiesel production techniques were developed and tested on variety of feedstocks so that good quality biodiesel can be produced at economically feasible cost.

There are a large number of experimental studies published in open literature summarizing biofuel research e.g. Xue et al. [10] reviewed biodiesel research published between 2000–2011. This review article focused on finding the effect of biodiesel on engine power output, fuel economy, engine durability and emissions. Another review by Pinzi et al. [11] reviewed the literature and focused on biodiesel production from low-cost non-edible vegetable oils. Knothe and Razon [12] reviewed the experimental studies showing influence of varying FFA profiles and feedstocks on biodiesel production techniques, yield and properties. Cold flow behavior and oxidation stability of biodiesel and their effect on engine system were reviewed by Monirul et al. [13]. Imdadul et al. [14] reviewed combustion characteristics of diesel engines fuelled by biodiesel and biodiesel-diesel blends with and without additives. Moser [15] reviewed different biodiesel production processes and focused on reviewing the effect of FFAs, use of different monohydric alcohols, and different catalysts. In addition, influence of biodiesel composition, blending with other fuels, alternative usage for biodiesel and glycerol were also discussed in this review article. Sharma et al. [16] reviewed biodegradability, biodiesel production kinetics, and stability aspects of biodiesel. Basha et al. [17] reviewed biodiesel production processes, and engine combustion, performance and emission characteristics. Atabani et al. [18] critically reviewed biodiesel feedstocks, biodiesel production methods, properties and biodiesel quality, problems and potential solutions for using vegetable oil, advantages and disadvantages of biodiesel usage, economic viability and future prospects for biodiesel in their review article. Shameer et al. [19] reviewed the operating parameter discrepancies in engine emissions reported in different engines fuelled by biodiesel produced from different feedstocks by various researchers.

Most of these review articles focused on very limited canvass of biodiesel and didn't offer a comprehensive and updated picture. This review article is an attempt to fill this space in biodiesel domain since it covers most aspects related to biodiesel production, biodiesel utilization, engine performance, and combustion studies, emission characteristics, both gaseous and particulate emissions, long-term durability aspects, effect of biodiesel on fuel injection system, carbon deposits, material compatibility, wear and lubricating oil degradation in addition to economic analysis and provides an up-to-date and comprehensive picture. Fig. 2 shows the glimpse of the topics covered in this review article.

2. Biodiesel production potential: feedstock and availability

Biodiesel can be produced from straight vegetable oils (SVOs) such as Rapeseed, Soybean, Pongamia, Jatropha, Mustard, Jojoba, Flax, Sunflower, Palm, Coconut, Hemp, Waste vegetable oil (WVO) etc., animal fats including tallow, lard, yellow grease, chicken fat and by-products from the production of Omega-3 fatty acids from fish oil [20]. Algae, which can be grown using waste sewage water or in shallow ocean water without displacing land used for food

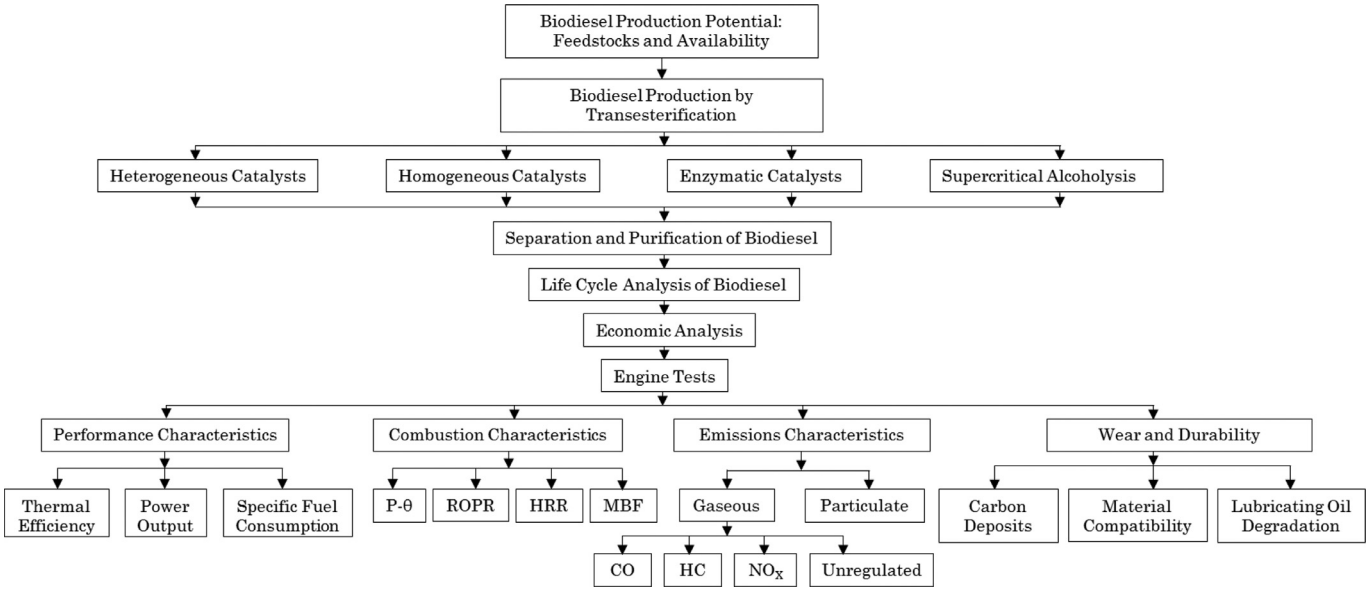


Fig. 2. Biodiesel landscape covered in this review article.

production, is also emerging as an important and promising feedstock for biodiesel production [21].

Different countries use variety of feedstocks for producing biodiesel, depending on local availability. Choice of feedstock for biodiesel production is therefore country-specific, depending on domestic production and is listed in Table 1 [22].

In European Union (EU), the most widely used biofuel is biodiesel and Rapeseed oil is the dominant feedstock, accounting for 49% of biodiesel production in EU in 2015. Share of Rapeseed in the biodiesel feedstock mix has considerably reduced from 72% in 2008, mostly due to higher use of recycled vegetable oil/used cooking oil (UCO) and palm oil [24]. UCO emerged as the second-most important feedstock in 2015 in EU. EU's biodiesel production capacity is expected to be 24.9 billion liters in 2016, which will increase to 25.5 billion liters in 2017 [24]. Germany, France, Netherlands, Spain, and Poland are the top five biodiesel producing countries in EU. Annual biodiesel production capacity in Germany increased from 3.2 billion liters in 2010 to 3.8 billion liters in 2014, which made Germany the largest biodiesel producer in EU [24]. Global distribution of biodiesel production during 2010–2014 (Table 2) shows that EU is the largest producer of biodiesel globally.

Brazil is global leader in biofuel utilization, particularly ethanol. Brazil's advanced energy matrix shows that 47.3% of its primary energy is from renewable energy resources. Global average is still ~13%. In just 2 years, Brazil has reached its target of 5% biodiesel addition in mineral diesel [26]. EU policy goals for biodiesel usage were 2% by 2005, 5.75% by 2010, and 10% by 2020. To meet these policy goals, a concerted effort was necessary. Austria is doing exceedingly well on this count and has already achieved EU target of 10% biofuels in 2010, and expects to reach 20% biofuels usage goal by 2020. In the transport sector, Denmark achieved the EU target of 5.75% by 2010 and expects to attain target of 10% by 2020 [27–28]. For encouraging research and implementation of second and third generation biofuels, EU is considering substitution of first generation biodiesel usage targets by second and third generation biofuels. This trend is catching up in North America, Asia, South America and Australia, which also produce biodiesel commercially albeit on a smaller scale. This trend is also catching up in large economies such as India and China, which have huge dependence on imported petroleum. South Asia has a large number of non-edible vegetable oil species (300+), which are available in surplus quantities. Potential availability of such non-edible oils in India alone is roughly 1 million tons per year [29]. The surplus oil available in abundance are *Sal oil* (180,000 tons), *Mahua oil* (180,000 tons), *Neem oil* (100,000 tons) and *Karanja oil* (55,000 *tons*) annually. Biodiesel policy of Government of India recognizes non-edible *Pongamia Pinnata* (Karanja) and *Jatropha Curcas* (Jatropha) oils as the most promising feedstocks for biodiesel production in Indian context. However due to shorter gestation period, *Jatropha Curcas* has got prominence over *Pongamia pinnata* as major feedstock for India's biodiesel program [30–31]. The seed production potential of *Jatropha* reportedly ranges from ~0.4 tons/ha/year to >12 tons/ha/year [30]. Neglecting such a large variation in Jatropha production, poor planning in large-scale implenetation has resulted in discouraging results and has created doubts about the benefits of biofuels, their potential and financial viability [32]. Jatropha can be grown in areas with low rainfall (200 mm/year), on low fertility, marginal, degraded, fallow and waste lands but seed yield is lower under these conditions. On the other hand, *Pongamia Pinnata* is one of the few nitrogen fixing trees (NFT) which produces seeds with 30–40% (w/w) oil content. It is often planted as an ornamental and shade tree. Average seed yield of *Pongamia Pinnata* is reportedly ~4–9 tons/ha/year [33]. Rice-bran oil is also an underutilized non-edible vegetable oil, which is available in large quantities in rice cultivating countries including India and China, however very little research has been done to utilize this oil as a partial/full replacement of mineral diesel [34].

Some studies have suggested that biofuels derived from agricultural food crops have adverse social and economic impact on the global population and has created 'food versus fuel' conflict in the society whereas there are some studies refuting the possibility of such a conflict [35]. Biofuels generated from non-edible oilseeds such as *Pongamia Pinnata, Jatropha Curcas*, high erucic Mustard, green seed Canola, micro algae, etc. [36] bypass the 'food versus fuel' dilemma. In such a controversial situation, non-edible vegetable oils have emerged as the most suitable biodiesel feedstocks because the demand for edible oils exceeds domestic supply and many large developing economies are net importers of edible oils. Significant fraction of edible oils produced worldwide are converted to biodiesel. Approx. 95% of biodiesel in the world is produced using edible vegetable oils [37]. Using edible vegetable oil for producing biodiesel increases its cost as well as the cost of food due to reduced availability of vegetable oils. Therefore use of non-edible oil for biodiesel production can reduce the food price inflation. Non-edible crops can be planted in many parts of the world, which have huge swaths of waste land. This will reduce deforestation rate and avoid competition with the food crops. Moreover, non-edible vegetable oil crops and trees are more efficient and environment friendly [37]. Global agricultural land area has increased from 4.56 billion ha in 1970 to 4.89 billion ha in 2010, however per capita agricultural land availability has reduced from 1.24 ha/person to 0.72 ha/person during the same period due to

Table 1
List of major biodiesel feedstocks used in different countries [23].

Country	Feedstock
Canada	Canola, Animal fat
USA	Soybean, Waste cooking oil
Mexico	Animal fat, Waste cooking oil
UK	Rapeseed, Waste cooking oil
France	Rapeseed, Sunflower
Spain	Sunflower
Sweden	Rapeseed
Finland	Rapeseed, Animal fat
Germany	Rapeseed
Italy	Rapeseed
Russia	Rapeseed, Soybean, Sunflower
Brazil	Soybean, Palm, Castor, Cottonseed
India	Jatropha, Karanja
China	Jatropha, Waste cooking oil
Malaysia	Palm
Indonesia	Palm, Jatropha
Japan	Waste cooking oil
Korea	Waste cooking oil
Philippines	Coconut, Jatropha
Thailand	Palm, Coconut, Jatropha
Australia	Waste cooking oil, Animal Fat
New Zealand	Waste cooking oil, Animal Fat

Table 2
Biodiesel Production ('000 barrels per day) [25].

	2010	2011	2012	2013	2014
North America	23.2	66.3	66.1	91.9	88.5
Central & South America	44.6	76.8	103.8	100.5	120.4
EU	132.1	203.6	188.8	202.3	203.1
Eurasia	2.96	2.2	4.6	4.4	4.9
Middle East	0.1	0.1	0.1	0.0	0.0
Africa	0.14	0.14	0.04	0.0	0.0
Asia & Oceania	28.3	68.5	72.3	87.0	111.7
World	231.3	417.8	435.8	486.1	528.6

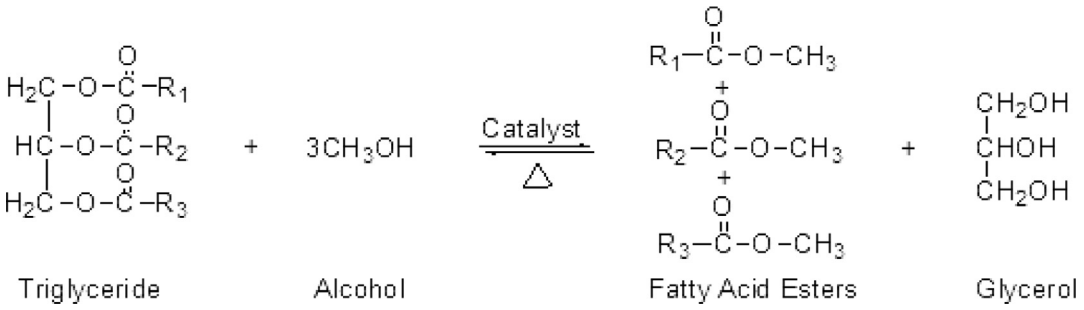
increase in global population [38–39]. Production of corn and oilseeds, which can be used for either food/ feed, or fuel/ energy, have sharply increased with their harvest areas expanding by 30.6 and 82.2 million hectares respectively, from 1990 to 2010 [40].

Vegetable oil prices in international market fluctuates just like any other commodity, depending on the feedstock, and its demand e.g. in August 2012, soybean oil was priced at US $ 1230/t, while palm oil was priced at US $ 931/t [41]. Feedstock cost is the most crucial factor affecting biodiesel production cost. Therefore use of less expensive feedstocks such as used cooking oil (priced at US $ 331/t) and non-edible vegetable oils like *Jatropha* (priced between US $ 350/t to US $ 500/t) is gaining momentum [41]. Biodiesel derived from edible oils is more expensive than that from non-edible oils, with negative global economic impact as feedstock prices escalate. With global targets of at least 10% biodiesel usage by 2020, it makes economic sense to carry out research and exploit biofuels derived from waste cooking oils, non-edible oils, and algal biomass to reduce production costs in comparison to mineral diesel.

Zhang et al. [42] reported that biodiesel cost was >1.5 times that of mineral diesel, while the cost of waste cooking oil was ~2.5 to 3 times cheaper than virgin vegetable oil [43]. In addition, the cost of virgin vegetable oil accounts for 75–80% of biodiesel production cost, whereas waste cooking oil accounts for only 50% of direct manufacturing cost of biodiesel, therefore biodiesel from WCO turns out to be significantly cheaper [44]. It is amply clear that the cost of biodiesel production is directly dictated by the feedstock cost. Biodiesel production from edible oils depends on the price dictated by the international market, whereas the prices of waste cooking oil and non-edible oils such as Jatropha and Karanja are not influenced by the international market therefore they do not fluctuate significantly and biodiesel can be produced from them at a significantly cheaper cost. The availability of such oils is however less than canola or soybean oils. Moreover, waste cooking oil requires additional processing for purification, whereas production of Jatropha and Karanja could be limited by its low market value, which makes their cultivation on arable lands less appealing, however it may be economically viable to cultivate them on marginal/ fallow lands [41]. In essence, global population increase has led to reduction in per capita land availability therefore a safer option available is to grow fuel crops (non-edible vegetable oils/ biomass) on fallow and non-fertile lands. This will help afforestation, and limit environment impact of fuel usage.

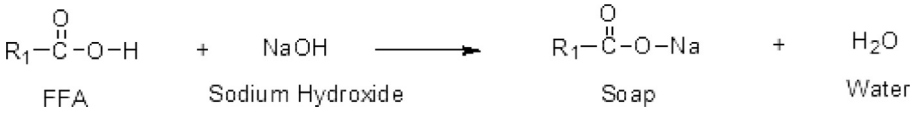
3. Biodiesel production using transesterification of oils

Biodiesel is produced by transesterification of triglycerides present in SVOs/ animal fats on an industrial scale. Transesterification is the reaction of triglycerides present in vegetable oils/ animal fats with primary alcohols in presence/ absence of a catalyst. Equation 1 depicts the most basic transesterification reaction, which produces primary esters, known as 'biodiesel' in addition to glycerol, which is the main by-product [7].



(1)

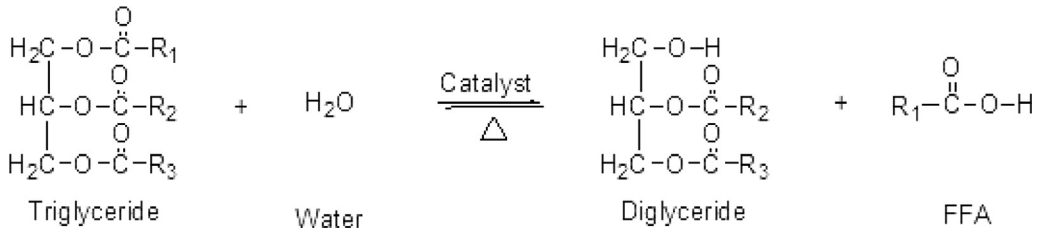
Transesterification is a reversible reaction. Higher than stoichiometric alcohol quantity is used to force the reaction equilibrium towards product side. Methanol and ethanol are the most frequently used primary alcohols in this process. Most of the experimental studies reviewed suggest that alcohol-to-oil molar ratio of 6:1 with catalyst concentration in the range of 0.2–1.5% (w/w_{oil}) at 65 °C reaction temperature is optimum for completion of transesterification reactions [7]. Methanol is preferred over ethanol for biodiesel production because of its relatively lower cost and favorable physical and chemical properties (polar compound and shortest carbon chain alcohol) [7], however, methanol is highly toxic and can be even absorbed by skin upon exposure. On the other hand, ethanol is more hygroscopic than methanol and it demonstrates higher affinity towards moisture. Ethanol can even absorb moisture from ambient air, if exposed directly, which is a negative aspect of considering ethanol for transesterification reaction's reactant. Methanol and ethanol are also completely miscible with water hence any accidental spill presents a serious ecological challenge [45]. In comparison to methanol, toxicity of ethanol is significantly lower. Current industrial production of ethanol is from agricultural products therefore utilization of ethanol for biodiesel production, makes it a completely renewable fuel however it runs the risk of "Food.versus Fuel" dichotomy [45–46]. Due to an extra carbon atom, ethyl esters have marginally higher calorific value and cetane number vis-à-vis methyl esters. Ethyl esters also offer superior cold flow properties compared to methyl esters [45–46]. Type of catalyst (alkaline, acidic or enzymatic), catalyst concentration, alcohol/ vegetable oil molar ratio, reaction temperature, moisture content, and FFA content of the vegetable oil affect ester yield from transesterification process [4,7,47,48]. In presence of an alkali catalyst, FFAs present in the vegetable oils undergo saponification reaction in preference to transesterification (Reaction 2).



(2)

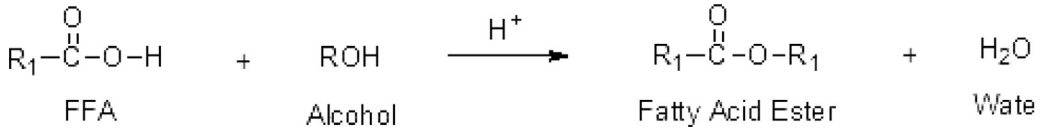
Saponification is an undesirable reaction because formation of soap lowers biodiesel yield significantly and inhibits separation of esters from glycerol [47,48]. Saponification reaction also consumes the catalyst hence lowers the ester yield, thus increasing catalyst

requirement. Higher moisture content of reactants either from (i) water formed during saponification reaction; or (ii) from the moisture content of the reactants starts hydrolysis reaction (Reaction 3). During hydrolysis, triglycerides are hydrolyzed into diglycerides and FFA formation takes place. Hydrolysis reaction retards transesterification reaction as well [48].



(3)

FFA content of vegetable oils can be converted into alkyl esters by acid catalyzed esterification (Reaction 4). This reaction is very useful for biodiesel production from high FFA feedstocks.



(4)

Conversion of triglycerides into fatty acid alkyl esters can be efficiently executed using different catalysts. Alkaline and acidic homogeneous catalysts are the most commonly used catalysts. For feedstocks with low FFA content, alkali catalyzed transesterification is an efficient and fast biodiesel production method. However for feedstocks with high FFA content, base-catalyzed transesterification gives very low yield of biodiesel [49,50]. For feedstocks with high FFA content, acid-catalyzed esterification should be used however this reaction is very slow compared to alkali catalyzed transesterification [51] and requires higher alcohol-to-oil molar ratio [50,52]. A two-step process involving reduction of FFA by acid catalyzed esterification, followed by alkali catalyzed transesterification is considered to be a superior process compared to one step esterification process for biodiesel production from high FFA feedstocks [49,53,54]. Utilization of homogeneous catalyst adds separation and purification steps to biodiesel production process for ensuring compliance with prevailing biodiesel specifications [48]. Contamination of glycerol produced in homogeneous catalyzed transesterification by the catalyst affects glycerol quality adversely, which reduces the value of glycerol produced. During industrial scale biodiesel production, large quantity of contaminated waste water is also generated because multiple water washing steps of biodiesel are necessary for removing the catalyst from it. Water washing steps also remove traces of glycerol, and methanol in addition to the catalyst from the biodiesel produced [55]. Catalyst contaminated water is an environmental hazard and needs safe disposal. It is very difficult to recover and reuse the homogeneous catalyst from it. The problems related to disposal of contaminated waste water, loss of catalyst, and reduction in process yield can be eliminated to a certain extent by using heterogeneous catalysts and enzymes. However these catalysts give lower biodiesel yield at significantly higher cost compared to homogeneous catalysts [52,56]. Catalytic activity of methoxides is superior to that of hydroxides [57] however hydroxides are more commonly used due to their easier availability and lower cost [58]. Transesterification can also be performed by supercritical alcohols at high temperatures and pressures without using any catalyst. In this super-critical alcohol transesterification process, yield is not affected by FFA and moisture content of the feedstock [56,59]. However requirement of higher temperatures (~400 °C) and pressure (~450–650 bar) makes industrial implementation of this process rather challenging and expensive [60,61].

3.1. Homogeneous catalysts

Homogeneous alkali catalyzed transesterification; homogeneous acid catalyzed transesterification and two-step transesterification process involving acid catalyzed esterification followed by base catalyzed transesterification are the three most popular methods of biodiesel production using homogeneous catalysts. Potassium hydroxide, sodium hydroxide, potassium methoxide and sodium methoxide are the most commonly used basic catalysts. Fig. 3 shows the effect of FFAs on the yield of methyl esters during alkali catalyzed transesterification process. There is significant drop in the ester conversion, when the FFA content increases beyond 2% (4 mg KOH/g) in the feedstock [62–64]. Keeping this in mind, Ma et al. [65] and Zhang et al. [66] recommended the upper limit of 1% FFA content for use of alkaline catalysts.

Alcohol-to-oil molar ratio, reaction temperature and catalyst concentration are the other most important factors affecting biodiesel yield from transesterification process, while using homogeneous catalysts. Table 3 summarizes a large number of experimental studies aimed to optimize the single step transesterification reaction conditions and yield of biodiesel using alkaline and acidic catalysts.

Alcohol-to-oil molar ratio of 6:1 with catalyst concentration in the range of 0.2–1.5% (w/w) at 65 °C reaction temperature was sufficient for the completion of transesterification reactions in most of

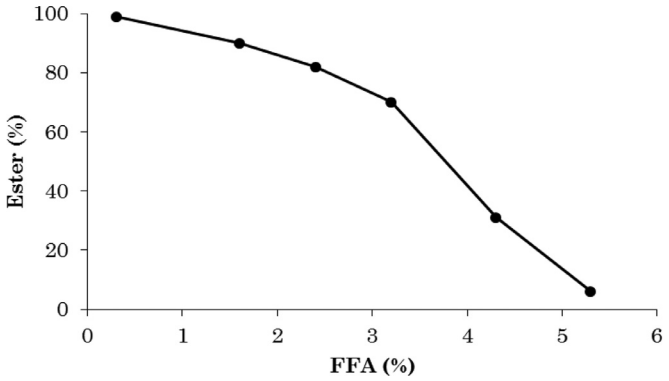


Fig. 3. Effect of FFA on biodiesel yield during alkali catalyzed transesterification (Reprinted from [64], with permission of Elsevier).

Table 3
Optimum reaction conditions for single step transesterification process for biodiesel production using homogeneous catalysts.

Feedstock	FFA $^{(mg\ KOH/\ g_{oil})}$	Catalyst (% w/w_{oil}), Alcohol (Alcohol-to-oil molar ratio), Reaction duration, Reaction Temperature	Yield (%)	Reference
Rapeseed oil	–	KOH (1.5%), CH_3OH (6:1), 1 h, Room temp.	97	Fröhlich et al. [67]
HOSO	0.45	KOH (1.5%), C_2H_5OH (6:1), 1 h, 32 °C	95	Bouaid et al. [46]
HEBO	0.83	KOH (1.5%), C_2H_5OH (6:1), 1 h, 32 °C	91	Bouaid et al. [46]
LEBO	1.16	KOH (1.5%), C_2H_5OH (6:1), 1 h, 32 °C	99	Bouaid et al. [46]
Brassica carinata oil	–	KOH (1.5%), CH_3OH (6:1), 1 h, 30–40 °C	98	Cardone et al. [68]
Camelina sativa oil	–	KOH (1.5%), CH_3OH (6:1), 1 h, Room temp.	97	Fröhlich et al. [67]
Karanja oil	–	KOH (1%), CH_3OH (10:1), 1.5 h, 60 °C	92	Meher et al. [69]
Karanja oil	0.6	KOH (1%), CH_3OH (6:1), 2 h, 65 °C	97	Karmee et al. [70]
Sunflower oil	0.45	KOH (1%), CH_3OH (6:1), 3 h, 65 °C	91.67	Vicente et al. [57]
Used frying oil	–	KOH (1%), CH_3OH (6:1), 0.5 h, 25 °C	95	Tomasevic et al. [71]
Sunflower oil	–	KOH (0.28%), CH_3OH (9:1), 1 h, 70 °C	96	Antolin et al. [72]
Sunflower oil	0.15	KOH (1.3%), CH_3OH (6:1), 1 h, 25 °C	98	Vicente et al. [73]
Sunflower oil	0.45	NaOH (1%), CH_3OH (6:1), 3 h, 65 °C	86.71	Vicente et al. [57]
Beef tallow	–	NaOH (0.5%), CH_3OH (6:1), 1.5 h, 60–70 °C	95	Muniyappa et al. [74]
Neem oil	–	NaOH (0.5%), CH_3OH (6:1), 1 h, 60 °C	92	Puhan et al. [75]
Jatropha curcas oil	30	NaOH (3.3%), CH_3OH (18:1), 2 h, 65 °C	55	Berchmans et al. [53]
Soybean oil	–	$NaOCH_3$ (1.5%), CH_3OH (6:1), 2 h, 60 °C	90	Alcantara et al. [76]
Used frying oil	–	$NaOCH_3$ (1.5%), CH_3OH (6:1), 2 h, 60 °C	90	Alcantara et al. [76]
Tallow	–	$NaOCH_3$ (1.5%), CH_3OH (6:1), 2 h, 60 °C	90	Alcantara et al. [76]
Sunflower oil	0.45	$NaOCH_3$ (1%), CH_3OH (6:1), 3 h, 65 °C	99.33	Vicente et al. [57]
Sunflower oil	0.45	$KOCH_3$ (1%), CH_3OH (6:1), 3 h, 65 °C	98.46	Vicente et al. [57]
Waste cooking oil	76	H_2SO_4 (4%), CH_3OH (20:1), 10 h, 95 °C	90	Wang et al. [77]
Waste animal fat	–	H_2SO_4 (22%), C_2H_5OH (9:1), 2 h, 50 °C	82	Tashtoush et al. [78]
Waste palm oil	–	H_2SO_4 (22%), C_2H_5OH (6:1), 3 h, 90 °C	>90	Al-Widyan et al. [79]
Waste palm oil	–	HCl (8%), C_2H_5OH (6:1), 3 h, 90 °C	> 90	Al-Widyan et al. [79]
Soybean oil		H_2SO_4 (1%), CH_3OH (30:1), 69 h, 65 °C	99	Freedman et al. [80]

the studies reviewed. Some studies [46,67,68,71,73] reported completion of base catalyzed transesterification within 1 h at temperature below 40 °C. For high FFA feedstocks, acid catalyzed transesterification was more effective than base catalyzed transesterification however it was sensitive to traces of moisture in the feedstock [50,59]. Higher cost of methoxides can be partially offset by savings in biodiesel purification step. Strong acids like Sulphuric acid (H_2SO_4) and Hydrochloric acid (HCl) are the most commonly used acid catalysts in acid catalyzed transesterification process [49,78,79]. However due to higher corrosiveness, HCl is not preferred for commercial production of biodiesel. For efficient conversion of triglycerides using acid catalysts, moisture content of the feedstock should be less than 0.5% (w/w) for achieving greater than 90% biodiesel yield [50]. Kusdiana et al. [59] reported 20% reduction in biodiesel yield for 1% (w/w) moisture content and zero yield for 5% (w/w) moisture content in the feedstock using acid catalyzed transesterification process. Higher molar ratio of alcohol-to-oil (> 20:1) and catalyst (< 5% w/w) is required for completing the reaction in 3 h. With higher acidic catalyst concentration, lower alcohol-to-oil ratio may be used [79,52]. For accelerating the reaction rate, higher temperature (90–95 °C) [77,79] can be employed in case of acidic catalysts. This suggests that more severe reaction conditions are required for acid catalyzed transesterification reactions compared to base catalyzed transesterification reactions. Requirement of higher quantities of alcohols and catalysts, longer reaction duration, and corrosion of equipment by strong acids coupled with difficulty in separating biodiesel from excess alcohol used in the process makes acid catalyzed transesterification process unsuitable for industrial scale biodiesel production [49,81].

In view of these limitations of acid catalyzed transesterification process, a two-step process involving reduction of FFA content of feedstock by acid catalyzed esterification in the first step, followed by transesterification of mixture of fatty acid esters, remaining FFA and triglycerides by base-catalyzed transesterification in the second step is used commercially. Table 4 summarizes a large number of experimental studies aimed to optimize two-step biodiesel production reaction conditions (in both steps) and biodiesel yield.

In two-step process, effectiveness of acid catalyzed esterification process in converting FFA into esters is utilized for reduction of FFA content of the feedstock. First step of esterification process can be completed using 6:1 molar ratio of alcohol-to-oil, with acidic catalyst (2% w/w_{oil}) in 1 h reaction duration as indicated in Table 4 by several studies. After this step, water and glycerol formed are separated and normal base catalyzed transesterification process is carried out, as discussed earlier (Table 3) [44,82,85]. However, two steps required for separating the glycerol remains the major limitation of this process.

Table 4
Optimum reaction conditions for two-step biodiesel production process using homogeneous catalysts.

Feedstock	FFA $^{(mg\ KOH/\ g_{oil})}$	First step catalyst (% w/w_{oil}), Alcohol (Alcohol-to-oil Molar ratio), Reaction duration, Reduced FFA	Second step catalyst (w/w_{oil}), Alcohol (Alcohol-to-oil Molar ratio), Reaction duration, Reaction temperature	Yield (%)	Reference
Polanga oil	22	H_2SO_4 (0.65%), CH_3OH (6:1), 4 h, 2%	KOH (1.5%), CH_3OH (9:1), 4 h, 65 °C	>85	Jacobson et al. [53]
Rubber oil	14	H_2SO_4 (0.5%), CH_3OH (6:1), 0.5 h, 2%	NaOH (0.5%), CH_3OH (9:1), 0.5 h, 45–50 °C	99	Ramadhas et al. [54]
Mahua oil	19	H_2SO_4 (0.5%), CH_3OH (7–9:1), 1 h, < 1%	KOH (0.7%), CH_3OH (6:1), 1 h, 60 °C	98	Ghadge et al. [82]
Tobacco oil	18	H_2SO_4 (2%), CH_3OH (13:1), 1 h, < 1%	KOH (1%), CH_3OH (6:1), 1 h, 60 °C	> 91	Veljković et al. [83]
Rice-bran oil	>20	H_2SO_4 (2%), CH_3OH (5:1), 2 h, < 2%	H_2SO_4 (2%), CH_3OH (27:1), 8 h, 100 °C	98	Zullaikah et al. [84]
Waste cooking oil	38	Ferric Sulphate (2%), CH_3OH (10:1), 4 h, < 1.5%	KOH (1%), CH_3OH (6:1), 1 h, 65 °C	93	Wang et al. [77]
Jatropha oil	15	H_2SO_4 (1%), CH_3OH (15:1), 1 h, 1%	KOH (1.4%), CH_3OH (6:1), 2 h, 65 °C	90	Berchmans et al. [44]
Neem oil	20	H_2SO_4 (4.5%), CH_3OH (6:1), 1.5 h, 3.5%	NaOH (1%), CH_3OH (6:1), 1 h, 60 °C	90	Dhar et al. [85]

Biodiesel yield and time required for completion of reactions are also dependent on the intensity of mixing during homogeneous transesterification process because alcohol and triglyceride are immiscible fluids, which form two separate layers due to different densities and incompatible mixing characteristics [50,56,86]. High mixing intensity increases the mass transfer rate by dispersing the alcohol in triglyceride phase as tiny droplets, thereby increasing the contact area between these two immiscible reactants [87].

Effect of mixing also has profound effect on biodiesel yield and has been an area of interest for several studies, with an objective to increase biodiesel yield and enhance the effectiveness of biodiesel production process. Meher et al. [69] reported that 180 rpm stirring speed was not enough for methanolysis reaction however with increased stirring speed of 360 and 600 rpm for 3 h, 97% biodiesel yield was obtained. Stavarache et al. [88] and Thanh et al. [89] used ultrasonic irradiation assisted mixing for increasing the mass transfer between alcohol and triglyceride phases for biodiesel production. Ultrasonic irradiations causes cavitation of bubbles near the phase boundary between immiscible liquid phases. The asymmetric collapse of cavitation bubbles disrupts the phase boundary and starts emulsification instantly. Santos et al. [90] reported 98–99% biodiesel yield (without heating) using ultrasonic energy with 2–3 times lower concentration of base catalyst in relatively shorter duration (10–40 min). In summary, stirring speed and method of mixing the two separable phases of alcohol and triglycerides also need to be optimized for a given feedstock for optimum biodiesel yield.

3.2. Heterogeneous catalysts

Production of biodiesel using homogeneous catalysts is kinetically the fastest method of biodiesel production with moderate energy requirement during the process therefore it is economically very attractive method for commercial production [91]. However requirement of phase separation and issues related to disposal of contaminated waste water, are the main motivation for exploring application of heterogeneous catalysts for biodiesel production. An ideal biodiesel production method should be based on a continuous flow reaction that does not deactivate or consume the catalyst, and minimizes/ eliminates the need for downstream separation of products as well as purification steps. With the aim of developing a continuous production process with reusable heterogeneous catalysts, zeolites, hydrotalcites, oxides, γ-alumina, resins etc. have been investigated for biodiesel production [50]. Performance of some of these important heterogeneous catalysts used in various experimental studies is summarized in Table 5.

Table 5 suggests that more severe reaction conditions and higher quantities of alcohols are required for heterogeneous catalyzed transesterification reactions. Requirement of higher quantities of alcohols and exotic catalysts, and longer reaction duration makes heterogeneous catalyzed transesterification process less preferred for industrial scale biodiesel production as of now however this process holds great potential for improvements in yield and may possibly emerge as the cheapest process for biodiesel production on a commercial scale in future.

3.3. Enzymatic catalysts

Many researchers have investigated using enzymes as catalysts for transesterification of triglycerides for biodiesel production. Extracellular lipases and intracellular lipases are the two classes of enzymatic catalysts normally considered for biodiesel production. In case of extracellular lipases, the enzymes are recovered from live micro-organisms broth and then purified, while intracellular lipases remain either inside the cell or in the cell producing walls [102–104]. Both extracellular and intracellular lipases are immobilized when used as catalysts, which eliminates downstream process steps such as separation of glycerol and recycling of lipases [103,104]. Immobilized enzymes are defined as “enzymes physically confined or localized in a certain defined region of space with retention of their catalytic activities, and can be used repeatedly and continuously” [105]. Extracellular lipases give higher biodiesel yield in comparison to intracellular lipases however they have relatively higher cost due to complex separation and purification procedure involved in their production [102]. Catalytic activity of different lipases is dependent on different structural features of acyl- chains such as nature of acyl- source (free acid, alkyl ester, glycerol ester etc.), chain length, position of double bonds, configuration of double bonds, and presence of branched groups [102]. In transesterification process of biodiesel production, methanol and ethanol are the most commonly used acyl- receptors due to their excess availability and low cost [102]. However inactivation of lipases in presence of higher concentrations of alcohols reduces biodiesel yield [106]. Inactivation of lipases can be overcome by step-wise addition of methanol and ethanol to the reaction mixture [55,107], using organic solvents and using other acyl-acceptors such as methyl acetate [108], ethyl acetate [109], 1-butanol [110], diesel [111] etc. Hexane, acetone, petroleum ether [112] and t-butanol [113] are commonly used solvents. Difficulties associated with solvent recovery discourages use of solvents for prevention of lipase inactivation at an industrial scale [103]. Use of diesel as solvent simplifies this process because there is no need to separate organic solvents from the final product and can be used in engines without any issues [111].

In lipase catalyzed biodiesel production, water plays multiple roles since it strongly influences catalytic activity as well as the stability of lipases [114]. Trace of water is essential in order to keep the enzymes active in the organic solvent [102]. Lipase activation by

Table 5
Optimum reaction conditions for biodiesel production process using heterogeneous catalysts.

Feedstock	Heterogeneous Catalyst (% w/w_{oil}), Alcohol (Alcohol-to-oil Molar ratio), Reaction duration, Reaction temperature	Yield (%)	Reference
Soybean	Alumina-supported potassium iodide (2.5), CH_3OH (15:1), 8 h, 60–65 °C	96	Xie et al. [92]
Soybean	Amorphous zirconia catalysts (TiO_2/ ZrO_2, Al_2O_3/ ZrO_2), CH_3OH (40:1), Continuous process, 250 °C	80	Furuta et al. [93]
Soybean	Tungstan-zirconia-alumina (WZA),CH_3OH (40:1), Continuous process, 250 °C	85	Furuta et al. [94]
Soybean	Anion-exchange resin (Diaion PA306s) (40%), C_2H_5OH (10:1), 1 h, 50 °C	80	Shibasaki-Kitakawa et al. [95]
Soybean	SnO (5%), CH_3OH (4:1), 3 h, 60 °C	93	Abreu et al. [96]
Jatropha	Calcium oxide/ Ammonium carbonate (1.5%), CH_3OH (9:1), 2.5 h, 70 °C	93	Huaping et al. [97]
Triolein	K_2CO_3/ Al_2O_3 (2.6 mmol/g-Al_2O_3) 0.3 g catalyst for 1 mmol of triolin), CH_3OH (24.8:1), 1 h, 60 °C	94	Ebiura et al. [98]
Palm	ZnO and SO_4^{2-}/ZrO_2 (1%), CH_3OH (6:1), 1 h, 200 °C	90	Jitputti et al. [99]
Coconut	ZnO and SO_4^{2-}/ZrO_2 (1%), CH_3OH (6:1), 1 h, 200 °C	86	Jitputti et al. [99]
*Soybean (2.6% FFA content)	ETS-10 ($Na_{21.9}K_{7.5}Ti1_{6.5}Si_{77.5}O_{208}$) and Sodium azide occluded NaX ($Na_{82.8}K_{1.8}Al_{85.8}Si_{106.2}O_{384}$), C_2H_5OH (6:1), 24 h, 120 °C	90	Suppes et al. [100]
Soybean (5:1 soybean oil to n-hexane molar ratio)	Na/NaOH/γ-Al_2O_3 (2%), CH_3OH (9:1), 60 °C	94	Kim et al. [101]

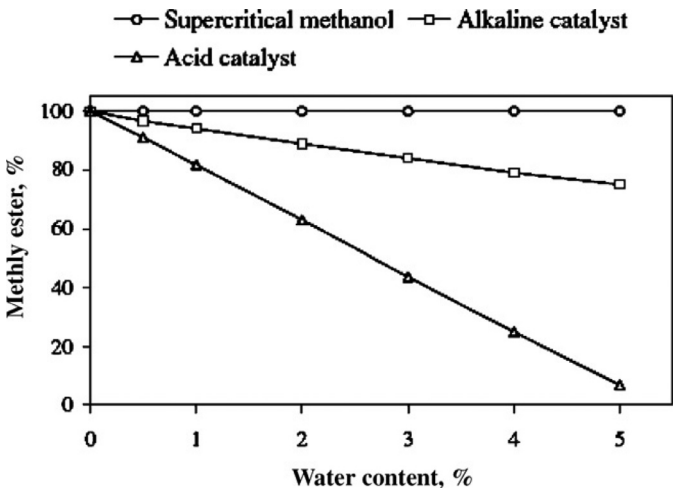


Fig. 4. Methyl esters yield vs. water content in various transesterification processes (Reprinted from [119], with permission of Sila Science Publications).

water involves conformational changes in the enzyme, which is dependent on the availability of an oil-water interface [115]. Therefore transesterification product yield depends on the size of oil-water interfacial area, which can be increased by addition of water. Higher quantity of water however starts encouraging hydrolysis reactions, which reduces transesterification process yield [102]. Optimal water content is therefore a compromise between maximizing enzymatic activity by increasing the interfacial area and minimizing hydrolysis reactions, and must be evaluated for each given lipase [102,103].

As of now, use of enzymatic catalysts for transesterification of triglycerides for biodiesel production is still in research phase and the technology has not matured enough to be deployed for production of biodiesel at a commercial scale economically. The future of this route of biodiesel production is essentially dependent on reducing the production cost of enzymatic catalysts, which could deliver higher biodiesel yield.

3.4. Supercritical alcoholysis

Biodiesel production using transesterification of triglycerides requires purification steps for catalyst removal, which increases the production cycle time, reduces biodiesel yield and generates large quantity of contaminated waste water. All these factors increase the cost of final product i.e. biodiesel [60,116,117]. Supercritical alcoholysis is a method, which can potentially overcome some of these issues. In supercritical alcoholysis, mixture of vegetable oil and alcohol is heated to a high temperature (350–400 °C) in a pressurized reactor (450–650 bar) without any catalyst [60,61]. The critical temperature and critical pressure of methanol are 512.4 K and 8.0 MPa respectively [60,118]. Increasing the reaction temperature and methanol-to-oil molar ratio has favorable effect on the ester yield [118]. Biodiesel yield is not adversely affected by presence of moisture (Fig. 4) and FFAs in the feedstock, since FFAs are also converted simultaneously into esters in supercritical alcoholysis process [64,117–121].

Kusdiana et al. [59] investigated the effect of moisture on methyl ester yield in supercritical alcoholysis at 42:1 molar ratio of methanol-to-oil, and 350 °C and 43 MPa reaction temperature and pressure respectively. Biodiesel yield was ~100% for 5% moisture content in the reactants. In comparison, 5% moisture content in the reactants led to biodiesel yield dropping to ~70% and < 5% in case of alkali-catalyzed and acid-catalyzed transesterification processes respectively. They also reported 95% biodiesel yield from waste palm oil with 61% water content and 21% FFA content. There are several studies conducted on supercritical alcoholysis of vegetable oils for biodiesel production, which are summarized in Table 6.

Madras et al. [124] investigated the yield of biodiesel in supercritical alcoholysis process using methanol and ethanol, at different reaction temperatures (Fig. 5). At 400 °C, 96% conversion (Fig. 5) of oil to biodiesel was reported using methanol-to-oil ratio of 40:1. For ethanol under the same reaction conditions, biodiesel yield was found to be slightly higher because the solubility of ethanol in vegetable oil was higher than methanol [124]. Absence of pretreatment steps, soap removal step and catalyst removal step significantly reduce the cost of biodiesel plant however the operating cost of the plant increases because of use of higher temperature and pressure requirement of the process, which are also the main drawbacks of using supercritical alcoholysis for commercial biodiesel production [60]. However there is by and large agreement in the scientific community that supercritical alcoholysis has great potential for production of high quality biodiesel at cheaper cost and more research is required to bring down the process temperature and pressure, thereby energy input for biodiesel production at a commercial scale.

3.5. Separation and purification of biodiesel

Products of transesterification include a mixture of fatty acid alkyl esters (biodiesel) and glycerol, excess alcohol traces, moisture and catalyst. Glycerol is denser than esters therefore it can be easily separated by gravity separation and is collected at the bottom of the separating vessel [48,125,126]. In a commercial biodiesel production plant, centrifuge is used sometimes for increasing the separation speed [126,127]. Crude biodiesel obtained after glycerol removal contains residual catalyst, moisture, unreacted alcohol, free glycerol, and soaps, which may have generated during transesterification process [48]. In presence of acids, soaps are converted into water soluble salts and FFA [128]. Therefore acid is added to crude biodiesel for

Table 6
Reaction conditions and biodiesel yield from supercritical alcoholysis process.

Feedstock	Co-solvent (Co-solvent-to-alcohol molar ratio), Alcohol (Alcohol-to-oil Molar ratio), Reaction duration, Reaction temperature and Pressure	Moisture	FFA	Yield (%)	Reference
Soybean oil	Propane (0.05), Methanol (24:1), 10 min, 280 °C and 12.8 MPa	–	–	98%	Cao et al. [61]
Soybean oil	CO_2 (0.1), Methanol (24:1), 10 min, 280 °C and 14.3 MPa	–	–	98%	Han et al. [120]
Palm oil	Heptane (0.2 molar ratio of heptane-to-methanol), methanol (30:1), 20 min, 280 °C and 15 MPa	–	–	66%	Tan et al. [122]
Palm oil	None, methanol (30:1), 20 min, 360 °C and 22 MPa	< 20% (w/w)	< 30% (w/w)	80%	Tan et al. [122]
Rapeseed oil	None, methanol (20 MPa, 15 min), ethanol (15 MPa, 45 min), 1-propanol (10 MPa, 45 min), 1-butanol (9 MPa, 45 min) and 1-octanol (6 MPa, 45 min) Molar ratio (1: 42 for all alcohols), 300 °C	0%	0%	~100% (for methanol, ethanol and 1-propanol), 85% (for 1-butanol) 62% (for 1-octanol)	Warabi et al. [123]
Sunflower oil	None, methanol (40:1), 40 min, 200–400 °C, and 200 bar	–	–	80–100%	Madras et al. [124]

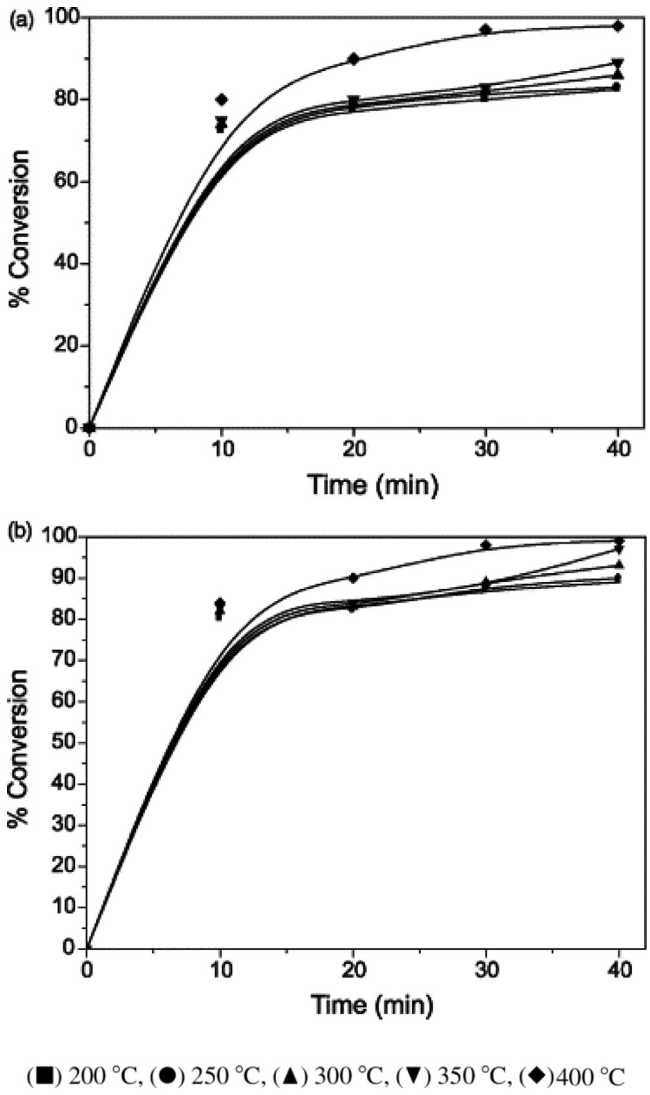


Fig. 5. Supercritical alcoholysis using (a) methanol (b) ethanol at different reaction temperatures (Reprinted from [124], with permission of Elsevier).

neutralizing the residual basic catalyst and for converting soaps into water soluble salts. Remnants of the catalyst, soap, salts, alcohol, and free glycerol are removed from crude biodiesel by water washing step [126]. Alcohol present in crude biodiesel may be recovered by distillation before the washing step. Performing the neutralization and alcohol removal steps before water washing step reduces the quantity of water required for washing step and minimizes the potential for emulsion formation during washing step [128–130]. Purified biodiesel after the water washing step is heated to remove the moisture traces [126,131]. Due to problems of contaminated waste water disposal, energy and time involved in the process and loss of ester due to emulsion formation, dry washing and membrane purification methods are also used sometimes for biodiesel purification. Berrios et al. [129] evaluated the effectiveness of Magnasol (magnesium silicate) for purification of crude biodiesel and the purity of biodiesel was compared with biodiesel purified by water washing step. Magnasol concentration higher than 0.75% (w/w) and contact time more than 10 min was required for effective adsorption of impurities however its effectiveness was not sufficient to achieve the soap and glycerol limits prescribed by European biodiesel specifications (EN 14214). In the same study, water washing purified the biodiesel to meet the limits prescribed by EN 14214 [129]. He et al. [131] purified biodiesel by injecting crude biodiesel in polysulfone fiber membrane placed in a distilled water beaker at 20 °C. The refined biodiesel was heated with Na_2SO_4 (10% $w/w_{biodiesel}$) for 12 h and then filtered. In the refining process using polysulfone, the refining losses of the ester reduced to 8.1%, in comparison to 15.2% when water washing step was used at 20 °C [131].

Process economics and biodiesel yield from different processes are ultimately influenced by the reactants including type and quantity of catalyst (alkaline/ acidic/ combination of the two/ enzymatic/ super-critical alcoholysis/ heterogeneous), alcohol/ oil molar ratio, reaction temperature and pressure, reaction duration etc. in addition to complexity of unit operations for purification and handling waste streams. While efforts are being made to improve existing processes, from review of the studies given above, it is amply clear that heterogeneous catalysis for transesterification and supercritical alcoholysis appear to have great potential for continuous biodiesel production due to availability of wide variety of regeneratable basic and acidic solid catalysts, low sensitivity to both FFA and moisture content in the reactants, reduced unit operation costs with simple product separation and purification steps, and no need for neutralization process. Biodiesel yield in excess of 90% can be obtained from these two processes after suitable parameteric optimization.

3.6. Life cycle analysis of biodiesel

Life cycle analysis (LCA) and economics of biodiesel is very critical for taking decisions about economic feasibility of a feedstock and the production process combination in a specific geographical location. LCA evaluates the impact of biodiesel production and utilization cycle on global warming and other possible harmful effects on human health, depletion of non-renewable resources and net energy ratio (NER) [132–135]. The largest producers and users of biodiesel, EU and US have setup a list of sustainability requirements for biofuel production specified by LCA analysis. EU targets require 35% energy input and emission reduction during fuel production stage by 2009, which would be 50% in 2017, and 60% from 2018 onward for all new biofuel plants setup on their soil [134,136]. Setting of life cycle emission reduction targets with respect to mineral diesel at the place of end use partially helps in providing common basis for comparing the life cycle efficiency of energy sources irrespective of the effect of local variations. Interpretation of LCA data for various biodiesel resources indicates that use of biodiesel helps in reducing GHG emissions and it generally has NER > 1.3.

Rocha et al. [132] assessed the health and environmental impacts of biodiesel production from soybean and palm oils as well as ethanol. Biofuel production with higher agricultural yields and extensive use of co-products in its life cycle offers best environmental results. Comparison of large biodiesel production plants (0.12 million liters/ day) from palm and soybean oil revealed higher NER for palm biodiesel due to higher production of palm oil per hectare and use of lower fertilizer quantity. Average NER of biodiesels was 1.31 and 3.25 for soybean and palm biodiesels respectively for various plants. These NERs improved to 2.88 and 3.89 for soybean and palm biodiesels respectively, when energy content of by-products was also taken into consideration. Despite availability of a multitude of LCA studies, though not fully updated, it remains difficult to evaluate, which feedstock leads to real time favorable NER along with less environmental impact (GHG, resource input and depletion, impact on human health). One approach for consistent common systematic quantitative LCA could be to draw meaningful conclusions from comparison of different biofuels with corresponding fossil fuels at global level by involving all stakeholders rather than relying on individual LCA studies. This would entail elaboration of methodologies for harmonization and updating database in order to enable global measurement of biofuel's sustainability and evaluate environmental impact over the entire life cycle, starting from raw materials, through to biodiesel production and its (as well as by-products) use,

up to reuse and disposal at the end of the useful life. At the same time, in order to achieve higher sustainability of biodiesel production, new plantation technologies with lower usage of fertilizers and pesticides along with increased crop yield and improved methods to produce biodiesel are equally important.

3.7. Economic analysis

In 2014, prices of natural gas, gasoline, diesel and biodiesel (B100) were US$ 2.09, US$ 3.34, US$ 3.49, and US$ 4.22 per gallon energy equivalent respectively [137]. In Germany, price for biodiesel was ~75.60 euro cents per liter (US$ 3.066 per gallon) in October 2015, excluding energy tax. This exceeded the price for agricultural diesel (i.e., off-road diesel) by nearly 10 euro cents per liter (US$ 0.416 per gallon) [138]. The realistic situation is that biodiesel production cost without taxes currently is higher than the selling price of mineral diesel, which makes it an unviable fuel in the open market place, without subsidy. Literature shows that cost of feedstock oil comprises of ~80–85% of the total biodiesel production cost [139]. Productivity of the base catalyzed transesterification process was comparatively higher (1.010 kg biodiesel/ kg vegetable oil), than that of acid catalyzed transesterification process (0.85 - 0.95 kg biodiesel/ kg vegetable oil) [140]. Typical processing cost for base catalyzed Jatropha biodiesel was reported to be US$ 0.15/L, and for acid catalyzed waste cooking oil was US$ 0.23/L, which excluded feedstock cost [140]. Shirazi et al. [141] estimated biodiesel production cost to be US$ 1.2/L using base catalyzed transesterification of waste cooking oil. Cost of waste cooking oil was ~55% of the total cost of biodiesel, making it economically viable fuel. On the other hand, biodiesel production cost using enzymatic catalysts was US$ 1.8/L, which makes it economically unviable compared to conventional fuels [142]. Fig. 6 shows that even in supercritical alcoholysis process for biodiesel production, ~90% cost is accounted for feedstock procurement, ~5% production cost is accounted for procurement of alcohol and ~5% production cost is attributed towards the energy used in the process [143].

In 2014, total installed capacity for biodiesel production in EU was ~23 million tons/ year [144]. In a sharp contract, total installed capacity for biodiesel production in Canada and USA was 0.56 million tons /year and 9.2 million tons /year respectively in 2015 [138]. Most of these biodiesel production capacities were underutilized due to scarcity of feedstock at competitive price. The price of biodiesel can compete with fossil fuels only when crude oil price is higher and biodiesel feedstock prices are lower. With increase in global biodiesel production, the price of major feedstock oils have considerably increased over the years and this trend will continue, affecting the biodiesel economics adversely [145]. Currently biodiesel is economical in USA only with US$ 1.0/gallon subsidy, which is provided by the government due to its contributions towards job creation and carbon emission reduction.

Biodiesel as an alternative fuel has been and is the key for many government policies, research initiatives and investments with implications on agriculture and developmental economics worldwide. Production cost of biodiesel from vegetable oils remains the main barrier to its large-scale replacement of mineral diesel. Hence, the focus is on process improvements and innovations; and making the feedstocks available in larger quantities economically for long-term energy sustainability. In the interim period, animal fat and waste cooking oils offer an opportunity to reduce biodiesel production cost, however their production volumes are far below the demand for biodiesel. Therefore with limited land resources, it is important to consider deployment of more productive crops, which can accrue higher oil yield and can be grown on nutrient deprived, fallow and marginal lands.

4. Engine performance and biodiesel compatibility

Interest of researchers in biodiesel as an alternative to mineral diesel to operate CI engines is reflected by the large number of papers published in last couple of decades [146,147]. These studies reported successful operation of CI engines with biodiesel derived from a host of feedstocks. However engine performance and emission characteristics with respect to mineral diesel vary considerably, depending on biodiesel properties, biodiesel blend concentration and engine technology used. Effect of biodiesel on engine performance, emissions and combustion characteristics of CI engines, and their effect on particulate, engine wear and lubricating oil degradation are reviewed comprehensively in this section.

4.1. Engine performance

Engine performance is measured in terms of maximum power/ torque generated by the engine at a given speed, BSFC and brake thermal efficiency (BTE). Maximum torque produced by any fuel at a given engine speed determines the acceleration characteristics of the vehicle, which makes a qualitative difference in the driving experience. BSFC and BTE are the other engine performance parameters, which represent fuel economy and efficiency of conversion of fuel into useful work/ power output respectively.

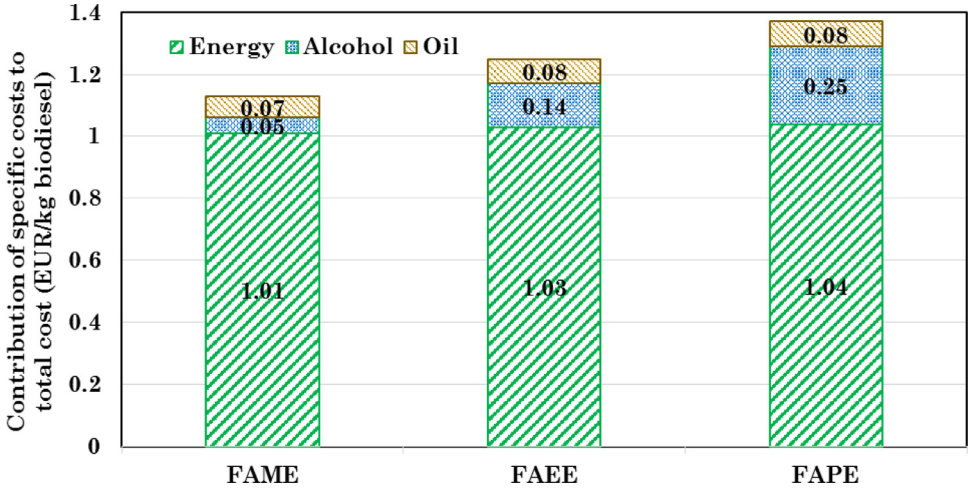


Fig. 6. Contribution of specific costs to the total costs in supercritical alcoholysis process of biodiesel production, depending on type of alcohol in the equilibrium state (Reprinted from [143], with permission of Elsevier).

4.1.1. Power output

Maximum power produced by a diesel engine is dependent on fuel quantity injected, which can be burned efficiently in the combustion chamber. Due to lower calorific value of biodiesel compared to mineral diesel, maximum power produced in an unmodified CI engine operating on biodiesel is slightly lower compared to mineral diesel. Xiaoming et al. [148] reported that torque output of B50 fueled engine reduced by ~2.6% in the speed range of 1000–2400 rpm at full load. Kawano et al. [149] used Rapeseed methyl ester (RME) to fuel a modern diesel engine equipped with common rail direct injection (CRDI) system and exhaust gas recirculation (EGR). They reported that both, the torque and power outputs of RME were inferior to mineral diesel at all engine speeds. Volumetric heating value of RME calculated using fuel density and calorific value was ~8% lower than mineral diesel. Injection of fixed fuel volume at maximum torque resulted in lower torque and power outputs from biodiesel fueled engine [149]. On the other hand, Sinha and Agarwal [150] reported that maximum torque output of the transport engine was either equal or slightly higher than mineral diesel, when rice-bran biodiesel blends in lower concentrations (B05, B10, and B20) were used. However the torque output decreased slightly for higher biodiesel blends vis-à-vis mineral diesel at lower engine speeds in a DICI engine. At higher speeds, torque was almost identical for all test fuels. In a EURO-5 compliant vehicle tested using new European driving cycle (NEDC), lower biodiesel blends (B7 and B20) delivered lower power and torque output compared to baseline mineral diesel at lower engine speeds (Fig. 7). Biodiesel in this study was produced from Soybean oil (84%) and Palm oil (16%). For remaining test conditions, B7 exhibited increased engine power and torque output (by $< 1.6\%$) at the highest engine speed. This tendency was also exhibited by B20, however on a lower magnitude [151]. Fuel distillation characteristics, fuel viscosity and oxygen content of biodiesel affected the combustion and heat release rate (HRR), which improved the power and torque characteristics of the test engine, particularly at high engine speeds as seen in Fig. 7 [151].

Dhar and Agarwal [152] also reported approximately 0%, 0.7% and 0.3% higher torque for lower Karanja biodiesel blends (B05, B10 and B20) compared to mineral diesel (Fig. 8) however torque reduced by 1.4% and 2.1% for higher biodiesel blend (B50) and B100 respectively. There are numerous studies in the literature (Table 7), which suggest slight increase/ equal/ slight decrease in power output however for all practical purposes, the variations are small enough to be neglected and can be easily adjusted by engine tuning.

Brake power output/ torque generated by engines fuelled by biodiesel produced from different feedstocks is reportedly lower than

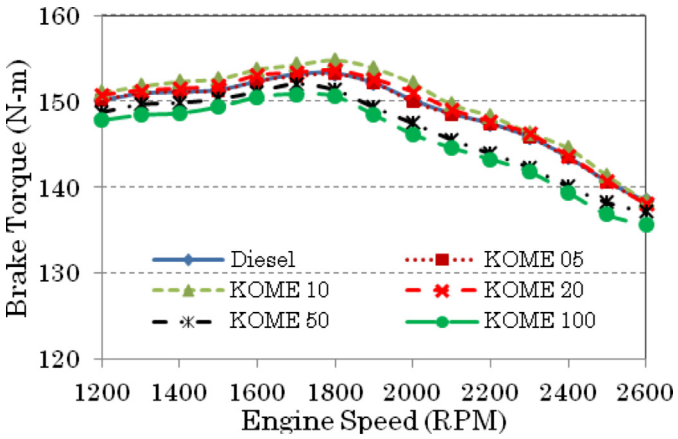


Fig. 8. Speed–torque characteristics for Karanja biodiesel blends (Reprinted from [152], with permission of Elsevier).

baseline mineral diesel, barring few exceptions. This is mainly attributed to relatively lower calorific value of biodiesel despite its higher density. Inspite of mixed results of brake power/torque output from various studies, overall engine performance differences were negligible, when lower blends of biodiesel and mineral diesel were used. These differences increased with increasing biodiesel blending ratio. This emphasized the need to optimize biodiesel blending ratio in order to achieve either comparable or slightly enhanced engine performance, in comparison to baseline mineral diesel, which could be achieved easily by tuning/recalibration of the fuel injection equipment of the engine. Therefore, it is not a serious issue to be considered in large-scale implementation of biodiesel in transportation sector.

4.1.2. Brake specific fuel consumption

BSFC is the ratio of mass of the fuel consumed to the brake power produced by the engine. Higher BTE results in lower BSFC and lower calorific value of fuel increases the BSFC. Most studies in open literature reported increased BSFC in case of biodiesel fuelled engines vis-à-vis mineral diesel fuelled engines. Alam et al. [162], Qi et al. [159], Usta et al. [160], and Canakci and Van Gerpen [163] reported that higher biodiesel quantity was required to release an equivalent amount of heat in the combustion chamber due to higher density but lower calorific value of biodiesel in comparison to baseline mineral diesel. No significant difference between BSFC of the engine operating with B20 and mineral diesel was observed [163]. Lin et al. [164] compared the BSFC of Soybean biodiesel produced using and

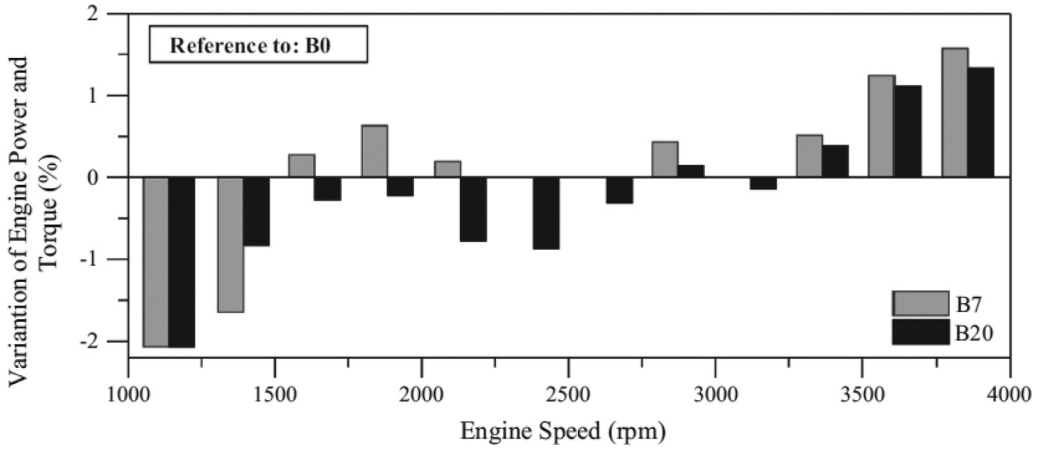


Fig. 7. Effect of biodiesel blending on the engine power and torque output (Reprinted from [151], with permission of Elsevier).

Table 7
Effect of biodiesel blends on engine power output.

Test fuel	Change in Power output (%)	Reference
B10, B20, B30 (Palm biodiesel)	−0.5, −1.6, −2.7	Ali et al. [153]
B20, B100 (Palm biodiesel)	−4.49, −11.34	Rashedul et al. [154]
B100 (Mixture of Rapeseed and Waste cooking oil methyl ester)	−10	Grimaldi et al. [155]
B100 (Waste cooking oil biodiesel)	−3 to −5	Çetinkaya et al. [156]
B70 (Mixture of 40% rapeseed biodiesel, 30% soybean biodiesel and 30% waste cooking oil biodiesel)	-ve	Tziourtzioumis and Stamatelos [157]
B25 (Tobacco seed oil methyl ester)	-ve	Utsa [158]
B100 (Soybean biodiesel)	Almost same	Qi et al. [159]
B7, B20 (Biodiesel produced from soybean (84%) and palm (16%) oils)	+1.6, +1.5	Serrano et al. [151]
B17.5 (Mixture of 50% Hazelnut soap stock and 50% waste sunflower oil biodiesel)	+ 1.3	Usta et al. [160]
B40 (Karanja biodiesel)	+≈6	Raheman and Phadatare [161]

without using peroxidation process vis-à-vis mineral diesel. Biodiesel produced using peroxidation process was found to have higher oxygen content and higher number of saturated carbon-to-carbon bonds. Peroxidation process however reduced the calorific value and cetane number of biodiesel. BSFC of both biodiesels produced with and without peroxidation process were higher than mineral diesel in the reverse order of calorific value [164]. Corgard and Reitz [165] reported similar BSFC for biodiesel and mineral diesel. Zhu et al. [166] reported higher BSFC for methanol and ethanol blended biodiesel compared to waste cooking oil biodiesel (WCOB) alone, while BSFC of biodiesel-methanol blends was higher than corresponding biodiesel-ethanol blends. Raheman and Ghadge [167] found that BSFC and exhaust gas temperature increased with increasing proportion of Mahua oil biodiesel in the blends in an indirect-injection (IDI) engine with compression ratio (CR) ranging from 18:1 to 20:1. Increasing the CR led to reduction in BSFC for both test fuels, however increasing CR showed greater benefits for biodiesel compared to baseline mineral diesel [167]. Biodiesel's performance was relatively superior at higher CR due to its relatively lower volatility and higher viscosity [167].

While these studies discussed earlier conclusive proved higher BSFC in case of biodiesel fueled engines, however there was another set of studies also, which reported lower BSFC in case of biodiesel fueled engines vis-à-vis mineral diesel fueled engines. Utsa [158] reported that BSFC of biodiesel (TSOME) blends were slightly lower than mineral diesel at full load, while they were slightly higher than mineral diesel at part loads. Comparison of fuel consumption for diesel, pure plant rapeseed oil (PPO) and 5% blend of rapeseed biodiesel in a CRDI engine showed (Fig. 9) that lower biodiesel blend resulted in reduction in BSFC, inspite of lower calorific value of biodiesel [168].

There are numerous experimental studies using different biodiesels, some of which are summarized in Table 8. Most of the engines fuelled with biodiesel showed increased BSFC however there are some exceptions, wherein lower BSFC of biodiesel in comparison to mineral diesel is also reported.

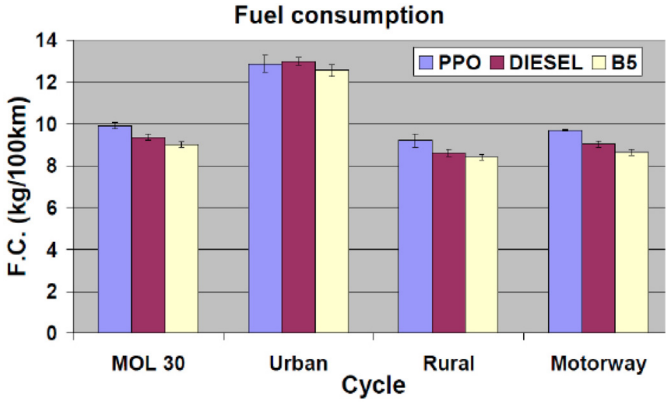


Fig. 9. Effect of 5% biodiesel blending on the brake specific fuel consumption (Reprinted from [168], with permission of SAE).

This trend in BSFC is primarily a result of lower calorific value, higher viscosity and density of biodiesels (feedstock and production process influenced), fuel injection pressure (FIP) and fuel injection technology used. Lower biodiesel blends improved BSFC in some studies, which was attributed to the molecular oxygen of biodiesels, which improved in-cylinder combustion. This improved the thermal efficiency hence dominated the lower calorific value contribution from biodiesel in lower biodiesel blends. It can be summarized from these studies that BSFC of biodiesels and blends is generally slightly higher than mineral diesel in most experimental studies and it depends on the FIP, injection strategy and fuel injection technology employed in the engine to a great extent.

4.1.3. Brake thermal efficiency

BTE is the ratio of useful work produced by an engine to the energy input by the fuel. BTE provides a rational basis for comparing the performance of test fuels having different calorific values. Most publications reported higher BTE for biodiesel compared to mineral diesel. Mahanta et al. [173] reported higher BTE for B20 compared to mineral diesel. Researchers suggested that the oxygen content of biodiesel was more effective in improving fuel rich combustion [159]. Agarwal and Das [178] tested all blends of biodiesel (Diesel, B5, B10, B15, B20, B25, B30, B40, B50, B75 and B100) (Fig. 10) and reported that 20% biodiesel (Linseed oil methyl ester) blend was the optimum biodiesel blend, which improved peak thermal efficiency of the engine by 2.5% compared to baseline mineral diesel in a single cylinder CI engine (Fig. 11).

Suryawanshi and Deshpande [179] reported slightly higher BTE for Pongamia oil biodiesel blends compared to mineral diesel and reported that retarding injection timing by 4° crank angle resulted

Table 8
Effect of biodiesel on Brake Specific Fuel Consumption.

Test fuel	Change in Brake Specific Fuel Consumption (%)	Reference
B25, B50 and B75 (Lard methyl ester biodiesel)	3.2, 8.5 and 13.8	Mikulski et al. [169]
B10, B20, B30 and B100 (Waste cooking oil biodiesel)	slightly higher	Man et al. [170]
B100 (Waste cooking oil biodiesel)	slightly lower	Cheikh et al. [171]
B10, B20, B30 (Palm biodiesel)	1, 2.1 and 3	Ali et al. [153]
B25, B50, B75, B100 (Rapeseed oil biodiesel)	slightly higher	Lešnik and Biluš [172]
B50	+ 8.3	Xiaoming et al. [148]
B20 (Karanja biodiesel)	slightly higher	Mahanta et al. [173]
B100 (Soybean biodiesel)	+13.8	Canakci [174]
B100 (Karanja biodiesel)	+ ve	Prabhakar et al. [175]
B100 (Soybean biodiesel)	+ 12	Yehliu et al. [176]
B25 (Tobacco seed oil methyl ester)	- ve	Utsa [158]
Lower biodiesel blends, B100 (UVOME biodiesel)	- 5, + 4	Verhaeven et al. [177]

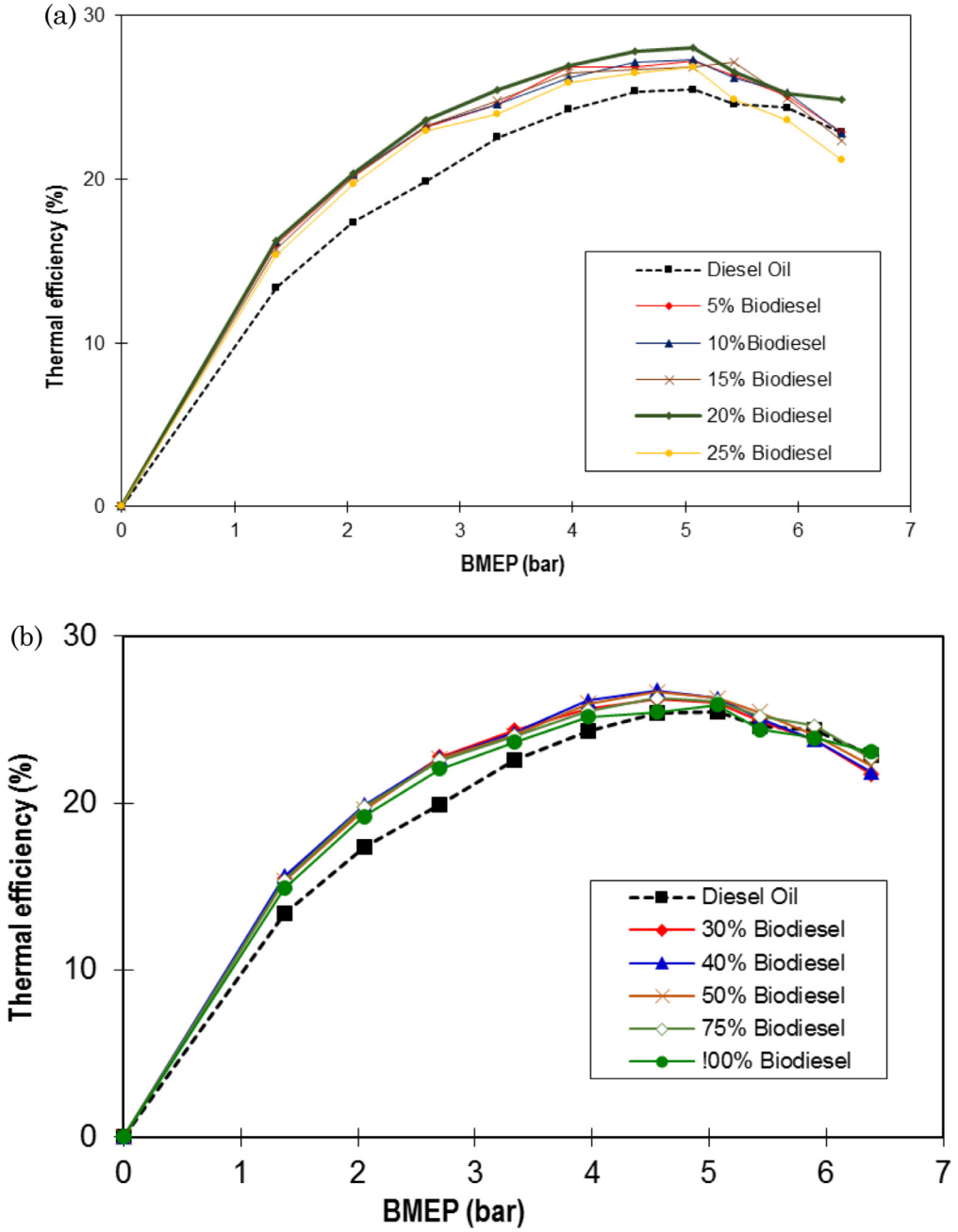


Fig. 10. Thermal efficiency vs. BMEP for (a) lower and (b) higher biodiesel blends (Reprinted from [178], with permission of ASME).

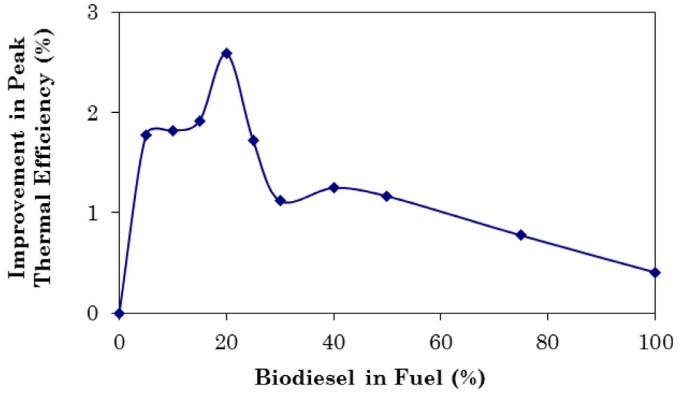


Fig. 11. Improvement in peak thermal efficiency vs. biodiesel blend concentration (Reprinted from [178], with permission of ASME).

in minor improvement in BTE at part loads however no change was observed at full load. Grimaldi et al. [155] also reported slightly higher BTE in case of biodiesel, particularly at high load compared to mineral diesel. At lower speeds and loads, biodiesel's BTE was reportedly lower than mineral diesel in this study and this was attributed to relatively inferior vaporization characteristics of biodiesel at lower in-cylinder temperatures [155]. Zhu et al. [166] reported that oxygenated test fuels, namely biodiesel, biodiesel-ethanol blends and biodiesel-methanol blends gave superior BTE at all operating conditions vis-à-vis mineral diesel. Researchers concluded that small amount of alcohol in the blend was favorable for reducing the viscosity and density of the test fuel, which improved spray atomization, leading to improved combustion. While in case of blended fuels containing higher percentage of alcohol, cooling effect due to higher latent heat of vaporization of alcohols was a dominant factor, which lowered the BTE [166].

Table 9
Effect of biodiesel on Brake Thermal Efficiency.

Test fuel	Change in BTE (%)	Reference
B100 (Waste cooking oil biodiesel)	slightly higher	Cheikh et al. [171]
B10, B20, B30 (Palm biodiesel)	+0.3, +0.1 and +0.4	Ali et al. [153]
B10, B20, B30 and B100 (waste cooking oil biodiesel)	slightly higher	Man et al. [170]
B25 (Cotton seed biodiesel)	+ 0.63	Subbarayan et al. [180]
B25, B50, B75, and B100 (waste fish oil biodiesel)	+0.74, +1.77, +2.75, +3.73	Gharehghani et al. [181]
B20 and B40 (Karanja biodiesel)	+ 2.17 and + 1.57	Raheman et al. [161]
B20 (linseed oil methyl ester)	+2.5	Agarwal and Das [178]
B100	+ 9	Gumus et al. [182]
Rice-bran biodiesel blends	+1.5- 3	Sinha and Agarwal [150]
B20 (Used fry oil biodiesel)	−2.95	Yilmaz et al. [183]
B17.5 (Hazelnut soap stock and waste sunflower equal oil mixture biodiesel)	slightly higher	Usta et al. [160]

In addition to these studies, there are a smaller number of researchers, who have reported almost similar or lower BTE for biodiesel compared to mineral diesel. Thermal efficiency of TSOME blends was reportedly lower than mineral diesel at part loads however it was higher than mineral diesel at full load [158]. Qi et al. [159] and Canakci [163,174] reported almost similar BTE for soybean biodiesel and mineral diesel. Prabhahar et al. [175] also reported lower BTE for Karanja biodiesel and blends compared to mineral diesel. Raheman and Ghadge [167] reported that BTE decreased with increasing proportion of biodiesel in the test blends for all investigated CRs (18:1–20:1) in the IDI engine. There are numerous experimental studies, whose results are summarized in Table 9.

Higher BTE of biodiesel blends with mineral diesel is a function of blending ratio, fuel oxygen content, fuel viscosity and density. Fuel oxygen content can be further improved by adding a small fraction of alcohol. BTE of biodiesels and blends can also be improved by employing higher FIP, which improves the spray atomization and vaporization of biodiesel droplets, thus offsetting its higher viscosity and density effects. In general, 20% (v/v) biodiesel blended with mineral diesel seem to deliver optimal BTE. From these studies, it can be summarized that biodiesel derived from different feedstocks and their blends with mineral diesel and/ or alcohols can deliver slightly higher BTE than baseline mineral diesel, except very few studies, which showed lower BTE of biodiesel. Nevertheless, engine performance of biodiesels is conclusively comparable to mineral diesel.

4.2. Emissions

Major pollutants of concern emanating from CI engine are NOx and PM due to their trade-off and ever shrinking limits being adopted for these pollutants in newer emission legislations. This section reviews the effect of biodiesel on CO, HC, NOx and PM emissions including particulate number (PN) from biodiesel fuelled engines. Emission legislations for the engines are becoming more and more stringent worldwide. For heavy-duty vehicles, NOx limits have been tightened from 5.0 g/kWh to 3.5 g/kWh from Euro-III to Euro-IV emission legislations. Similarly, for passenger cars and light commercial vehicles (LCV), NOx limit has been reduced from 0.5 g/km to 0.25 g/km from Euro-III to Euro-IV emission legislations [184]. In EURO-V legislations, these limits for NOx and PM are further reduced to 0.18 and 0.005 g/km respectively [185]. With implementation of EURO-V and EURO-VI emission legislations, limits on PN concentration (6.0×10^{11} #/km) in addition to particulate mass would come into force [185].

Famous historical EPA review study [186] of 2002 showed that emissions of HC, CO and PM reduced but NOx slightly increased, when biodiesel blend concentration was increased. Results for these

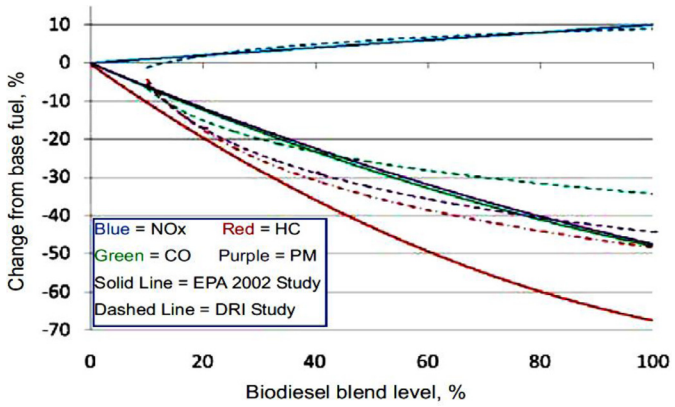


Fig. 12. Comparison of biodiesel engine emissions with EPA study (2002) (Reprinted from [187], with permission of SAE).

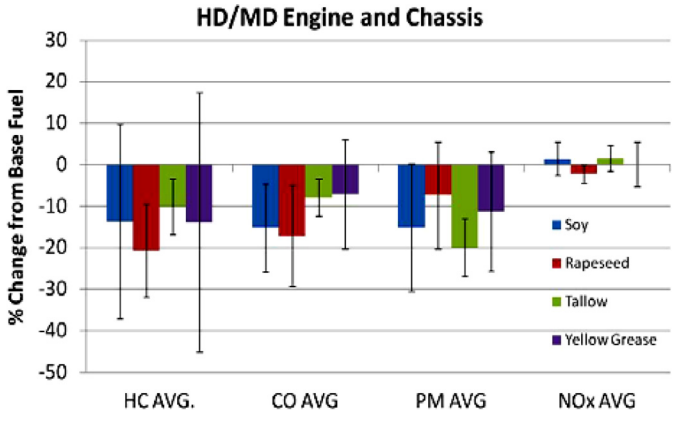


Fig. 13. Effects of biodiesel (B20) feedstocks on emissions (Reprinted from [187], with permission of SAE).

specific regulated pollutants (HC, CO, PM, NO_X) from heavy-duty (HD) 4-stroke CI engines using biodiesel blends were compared with the results from this 2002 EPA study. EPA study results are shown by solid lines and the acquired results are presented by dashed lines in Fig. 12 [187]. NOx emissions were nearly identical to the EPA study. THC and CO emissions were similar to the EPA study for B20. However, it showed relatively lower benefits for B100. Results showed slightly higher PM reduction than EPA study for B20, and slightly lower reduction for B100 (Fig. 12) [187].

Results from HD/ MD engine and chassis dynamometer tests were compared for B20 derived from different feedstocks (Fig. 13), and it was found that biodiesel from all feedstocks gave substantial reduction in HC, CO, and PM emissions, while in case of NOx emissions, these reductions were negligible and uncertain [187]. Emission characteristics of biodiesel fueled engine varied with feedstock due to differences in chemical and physical properties of biodiesels, especially the carbon chain lengths of the alkyl esters.

4.2.1. CO emissions

Review study by EPA (2002) covered 39 experimental studies, which have used heavy-duty engines without EGR and after-treatment systems and it reported average biodiesel emissions compared to baseline mineral diesel (Fig. 14). CO emission reduction of 50% for biodiesel (B100) and 11% for B20 vis-à-vis baseline mineral diesel was a general trend revealed by this study [186].

Table 10 summarizes the effect of different biodiesels on CO emissions in comparison to mineral diesel as reported by several engine studies. Though the CO emission from CI engines was not significant, there was a general trend towards lower CO emission from

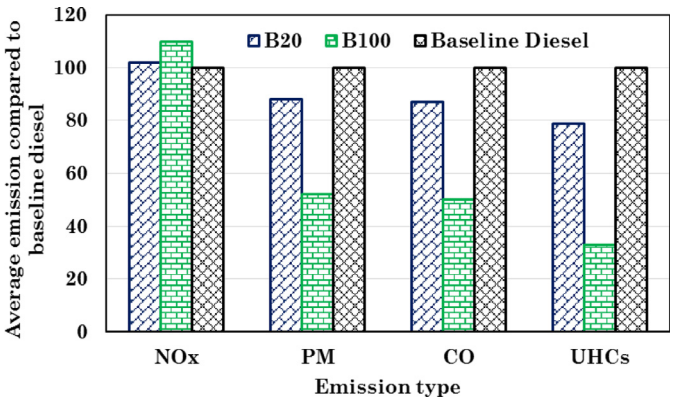


Fig. 14. Average emissions from biodiesel fuelled heavy-duty engines (Adapted from [186], with permission of EPA).

biodiesel fuelled engines. Reduction in equivalence ratio of fuel-air mixture using oxygenated fuel (biodiesel in this case) generally leads to lower CO emission [148].

Grimaldi et al. [155] reported comparable brake specific CO (BSCO) emission from biodiesel at 2500 rpm, but a noticeable reduction in BSCO emission at 4000 rpm. This behavior was due to higher localized oxygen availability, which was dominant at higher engine speeds. Fuel oxygen in biodiesel encouraged its more complete combustion and this was the primary reason for reduction in CO emission [163,164,198]. Some researchers also reported similar or increased levels of CO emission from biodiesel fueled engines, depending on operating condition. Lin et al. [199] reported lowest CO emission from 20% WCOB at all speeds however at lower engine speeds, higher biodiesel blends produced higher CO emission than mineral diesel in a pre-chamber engine IDI engine. Usta et al. [160] reported higher CO emission from biodiesel blends compared to mineral diesel in 1500 - 2200 rpm engine speeds at 75% and 100% loads, but reverse trend of relatively lower CO emission was seen at higher engine speeds. Authors suggested that fuel-air mixing was affected by difficulty in atomization of test fuels due to higher viscosity of biodiesel, which resulted in formation of fuel-rich regions that caused increased CO emission at low engine speeds [160]. Spessert et al. [200] reported that CO emission was quite similar in case of RME and mineral diesel. CO emission from RME was slightly higher at low loads however they decreased with increasing engine load.

Effect of mixing alcohol in biodiesel blends on CO emission depends on engine operating conditions. Zhu et al. [166] reported that biodiesel-alcohol blends with 10% or 15% alcohol content produced higher BSCO emission at light and medium loads but similar BSCO emission at high loads compared to baseline mineral diesel. For 5% alcohol blends, BSCO emissions were lower than biodiesel at all engine operating conditions [166]. Mixing of alcohols in biodiesel increased the oxygen content of the test fuel, since alcohols have higher oxygen content (w/w) than biodiesel, which resulted in reduction in CO emission. Shi et al. [201] reported that changes in CO emission from ethanol: methyl soyate: diesel (5:20:75) blend in comparison to baseline mineral diesel were not conclusive and they were dependent on engine operating conditions. Gumus et al. [182] observed decreasing CO emission with increasing biodiesel concentration in the blends. For all biodiesel blends, CO emission decreased with increasing FIP in a single cylinder, air-cooled, DI engine. Kousoulidou et al. [202] reported that biodiesel didn't have any significant effect on CO emission vis-à-vis mineral diesel in an engine equipped with CRDI system. In European test cycle, overall CO emission of B5 was 2.9% higher for one vehicle and slightly higher for another vehicle equipped with CRDI system in comparison to mineral diesel [168]. A noticeable increase in CO emission at low load was noticed for B30 and B100 of different feedstocks in comparison to baseline mineral diesel [203]. Engines fitted with CRDI fuel injection system didn't show any significant change in CO emission in most experimental studies. However engines fitted with other types of fuel injection equipment having relatively lower FIP generally showed lower CO emission from biodiesel blends compared to baseline mineral diesel.

Overall, CO emission were generally lower for biodiesel and blends compared to baseline mineral diesel. The extent of reduction remained a function of biodiesel feedstock, C/H ratio of the test fuel (compared to mineral diesel), fuel viscosity, oxygen content, cetane number, fuel injection equipment type, FIP, fuel injection strategy and engine operating parameters.

Table 10
Effect of biodiesel on CO emission.

Test fuel	Change in CO emissions (%)	Reference
B8.9 (Soy biodiesel); B17.7(Soy biodiesel)	−6.92; −14.44	McCormick et al. [188]
B100 (Rapeseed biodiesel)	−7.35	Bouch et al. [189]
B100 (Soy biodiesel)	−30.80	Graboski et al. [190]
B100 (Rapeseed biodiesel)	−50	Krahl et al. [191]
B20 (Soy methyl ester)	−9.09	Alam et al. [162]
B20 to B100 (Karanja methyl ester)	−73 to −94	Raheman and Phadatare [161]
B100 (Mahua methyl ester)	−30	Puhan *et al.* [75]
B20 Soy, B20 Tallow (1999 Cummins engine)	−16 to −18	Nuszkowski et al. [192]
B20 Soy, B20 Tallow (2004 Cummins engine)	−12 to −14	Nuszkowski et al. [192]
B20 (Soybean biodiesel)	+3	Nagaraju et al. [193]
B100 (JOME, SOME and HOME)	+37.78; +6.67; +28.89	Banapurmatha et al. [194]
B100(WPOME); B100 (COME)	−86.89; −72.68	Ozsezen et al. [195]
B50, B100 (Soy oil biodiesel)	+54, +95	Fontares et al. [196]
B100 (Soy oil biodiesel); B20 (Soy oil biodiesel)	+83.33; +33.33	Poitras et al. [197]
B100 (Tallow biodiesel)	−60	Poitras et al. [197]

4.2.2. THC emissions

THC comprise of all types of hydrocarbon species being emitted by the engine, which cannot be measured individually therefore they are clubbed together and presented as THC emissions equivalent to C_1, C_3 or C_6. There may be several hydrocarbon species emitted by diesel and biodiesel engines. When all such hydrocarbon emissions are measured and presented together, they are regulated emissions. If we are interested in studying the emission of individual hydrocarbon species, which are a part of THC emission, they are unregulated emissions, and are discussed separately in this article. The review study by EPA (2002) dealing with impact of biodiesel on pollutants from heavy-duty CI engines without EGR and after-treatment system indicated 65% and 21% reduction in THC emissions by B100 and B20 respectively as a general trend [186]. Qi et al. [159] and Canakci [174] reported an average 42.5% reduction in THC emissions from B100 (Soybean biodiesel) fueled engine compared to baseline mineral diesel. Table 11 summarizes the effect of different biodiesels on THC emissions compared to mineral diesel.

The Table 11 conclusively shows that THC emissions from biodiesel/ blend fueled engines are lower than baseline mineral diesel. There are few other interesting studies related to THC emissions, which are discussed individually. Suryawanshi et al. [179] reported significant reduction in THC emissions from Pongamia methyl ester blends compared to mineral diesel at part loads as well as full load. THC emissions further reduced by 31.8% at lower loads for B100 at retarded injection timings compared to B100 at standard injection timing [179]. Grimaldi et al. [155] observed substantial reduction in

Table 11
Effect of different biodiesels on THC emissions.

Test fuel	Changes in THC emissions (%)	Reference
B20 (Soy biodiesel)	−2.13	Grabowski et al. [204]
B100 (Soy biodiesel)	−43.97	Grabowski et al. [204]
B20 (Soy biodiesel)	−12.8	Graboski et al. [205]
B100 (Soy biodiesel)	−43.90	Graboski et al. [205]
B 8.9 (Soy biodiesel)	+0.66	McCormick et al. [188]
B 17.7 (Soy biodiesel)	−10.21	McCormick et al. [188]
B100 (Rapeseed biodiesel and #2 diesel)	−38.46	Bouche et al. [189]
B100 (Soy biodiesel)	−26.67	Graboski et al. [190]
B20 (Soy biodiesel and #2 diesel)	−17.65	Alam et al. [162]
B20 (Soybean biodiesel); B20 (Tallow biodiesel)	−16 to −18	Nuszkowski et al. [192]
B20 (Soy biodiesel)	−9	Nagaraju et al. [193]
B20 (Rapeseed biodiesel)	00	Krahl et al. [206]
B-20 (Soy biodiesel)	−33.5	Dahodwala et al. [207]
B20 (Fish oil biodiesel)	−58%	Manish et al. [208]
B100 (Waste cooking oil biodiesel and corn oil biodiesel)	−30%	Tesfa et al. [209]
B10, B20, B30 and B100 (waste cooking oil biodiesel)	-ve	Man et al. [170]

THC emissions for biodiesel. At medium loads ($\lambda = 2-3$), B100 reduced THC emissions by ~50%. However, they indicated towards condensation of THC in the flame ionization detector (FID) analyzer, which was maintained at 191 °C because the boiling range of unburned biodiesel was ~300–350 °C. This condensation resulted in recording of lower than actual THC emissions by the FID analyzer [155].

Zhu et al. [166] observed 30- 59% reduction in THC emissions from biodiesel vis-à-vis mineral diesel, depending on the engine load. Addition of 5% alcohol (methanol/ ethanol) to biodiesel further reduced THC emissions by ~9%. THC formation is attributed to air-fuel mixtures that are too lean to auto-ignite or to support a propagating flame or air-fuel mixtures that are too rich to auto-ignite [198,210]. Higher oxygen content and cetane number of biodiesel promoted more complete combustion, which resulted in lower THC emissions [198]. Gumus et al. [182] reported that THC emissions decreased with increasing biodiesel concentration in the test fuel as well as with increasing FIP (Fig. 15).

Sinha et al. [150] reported that THC emissions were higher for lower rice-bran oil biodiesel blends (B5, B10, and B20) compared to mineral diesel, and were highest for B10, although the absolute values were close to being negligible. For higher biodiesel blends, THC emissions were in the same range as mineral diesel (Fig. 16).

Kousoulidou et al. [202] compared THC emissions from palm biodiesel and RME with mineral diesel in an engine equipped with CRDI

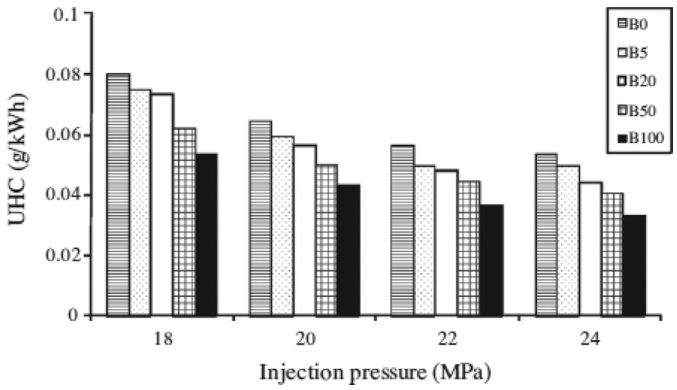


Fig. 15. Total hydrocarbon emissions vs. fuel injection pressure (Reprinted from [182], with permission of Elsevier).

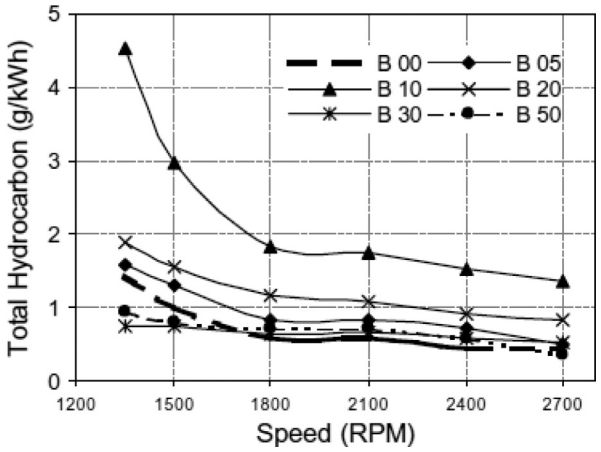


Fig. 16. THC emissions from biodiesel blends (Reprinted from [150], with permission of SAE).

fuel injection system. For palm biodiesel and RME, THC emissions increased by 40% and 15% respectively in comparison to mineral diesel [202]. In European test cycle, overall THC emissions from B5 were slightly higher for one vehicle but slightly lower at higher speeds for other vehicle equipped with CRDI system compared to baseline mineral diesel [204]. A noticeable increase in THC emissions at low load was seen from B30 and B100 of different feedstocks compared to baseline mineral diesel [205]. In another study using CRDI engine, THC and CO emissions from B100 were slightly lower than mineral diesel under most operating conditions. EGR increased THC and CO emissions however effectively reduced NOx emissions. Increasing the FIP also reduced the THC and CO emissions from both fuels [211]. Mikulski et al. [169] analyzed animal-fat based biodiesel namely swine lard methyl esters (SLME) blends (B25, B50 and B75) and mineral diesel in a modern CRDI high speed engine. An average 52% reduction of THC emissions was observed [169]. Lower calorific value of test fuel requires a larger fuel quantity of biofuel to be injected in the cylinder under identical operating conditions. Increase of biodiesel percentage in test fuel reduces the ignition delay though. In addition, presence of molecular oxygen in biodiesel improves combustion of the test fuel [169]. Cárdenas et al. tested three biodiesels (derived from rapeseed, sunflower and soybean oils) and their blends (30% v/v) with mineral diesel in a 4-cylinder CRDI engine under NEDC. Biodiesels and blends produced higher brake specific THC emissions in comparison with the reference fuel. Most important reason for these trends was the impact of fuel properties on the electronic control unit (ECU) response, which was tuned for diesel operation [212]. After ECU recalibration, it was possible to achieve lower THC emissions.

THC emissions reduced when 100% biodiesel was used instead of mineral diesel. THC emissions reduced with increasing biodiesel blend ratio. THC emissions are influenced by feedstock and fuel properties such as oxygen content and cetane number, which are affected by different chain lengths and saturation level of biodiesels. Addition of small fraction of alcohol to biodiesel blends further reduced THC emissions. Engine operating parameters such as increased FIP, retarded fuel injection timings etc. also reduced THC emissions. General trend suggests that usage of biodiesel and blends lead to substantial reduction in THC and CO emissions in lower FIP engines however this advantage of lower CO and THC emissions is rather limited in modern CRDI engines, which operate at relatively higher FIP. CRDI engines are ECU controlled engines and can be extensively optimized for the test fuel properties. Hence it is essential to recalibrate the ECU for improving the emission advantage of biodiesel and its blends vis-à-vis baseline mineral diesel.

4.2.3. NOx emissions

NOx formation in CI engines is dependent on peak in-cylinder temperature and duration of this high temperature (above 1700 K) environment in the combustion cycle, chemical structure of the fuels, and availability of oxygen in the high temperature zones. With addition of biodiesel to mineral diesel, physical parameters such as duration of high temperature window in the combustion chamber, concentration of oxygen in the high temperature combustion zones along with chemical composition of burning mixture also changes. In a review study, Lapuerta et al. [146] summarized four different types of effects of biodiesel on NOx emissions, ranging from increased NOx emissions to reuced NOx emissions by biodiesel fueling, at all operating points. However majority of papers on biodiesel emission characteristics reported increased NOx emissions with biodiesel from essentially unmodified engines [146,213]. Usta [158] reported that at part loads, NOx emissions from B20 were similar to mineral diesel. NOx increased slightly due to increased combustion chamber temperature and presence of fuel oxygen [158,214]. Alam et al. [162] reported that BSNOx emissions decreased with increasing engine load for all test fuels however biodiesel blends emitted higher NOx compared to baseline mineral diesel. They suggested that increased NOx emissions were due to relatively earlier start of fuel injection in biodiesel blends compared to mineral diesel, primarily due to differences in bulk modulus of compressibility [162]. There are numerous other studies in the open literature, which are summarized in Table 12 to show the effect of different biodiesels on NOx emissions compared to mineral diesel.

There are generally two diverse results from the experiments concerning NOx emissions from biodiesel. One group of experiments suggests relatively higher NOx emissions from biodiesel and the other group of experiments suggests relatively lower NOx emissions compared to baseline mineral diesel. Increase in NOx emissions are still not very well explained, but several influencing parameters, such as fuel type and quality, fuel spray characteristics, operating conditions, and engine technology are some of the possible reasons. NOx emissions depend strongly on the equivalence ratio, oxygen concentration and burned gas temperature; and they increase, when biodiesel and blends are used. This increase is mainly due to higher oxygen content of biodiesel/blends, resulting in a charge gas composition closer to stoichiometric (less rich) in the flame zone. Moreover, cetane number and different injection characteristics also have an impact on NOx emissions from biodiesel/ blends. The content of unsaturated compounds in biodiesel can have a greater impact on NOx emissions. In modern high speed diesel engines, use of biodiesel results in more advanced and faster overall combustion event, which leads to elevated in-cylinder temperatures and increased NOx formation. They also exhibit other NOx effects either positive or negative, depending on response of engine control systems to fuel property changes, such as relatively lower energy content of biodiesel compared to mineral diesel.

There are few other studies covering different aspects of NOx emissions from biodiesel fueled engines, which are covered individually. Suryawanshi et al. [179] reported higher NOx emissions from Pongamia biodiesel compared to mineral diesel. Retarding the start of injection (SOI) by 4° CA resulted in reduction in NOx emissions however NOx levels still remained higher than mineral diesel. Sharp et al. [216] reported that use of Soy biodiesel resulted in 10% increase in NOx emissions in a 6-cylinder, 14 L, turbocharged, intercooled, ECU controlled DI engine. Their investigations of correlation between NOx emissions and fuel properties showed that NOx emissions decreased with increasing fuel oxygen content of the test fuels and it increased with increasing carbon chain length (Fig. 17) [216]. H/C ratio and NOx emissions showed good correlation with a decreasing trend (Fig. 18) [216].

Table 12
Effect of different biodiesels on NOx emissions.

Test fuel	Change in NOx emissions (%)	Reference
B20 (Linseed biodiesel)	+5	Agarwal and Das [178]
B100 (Soy biodiesel)	+ 11.2	Canakci [174]
B100 (Soy biodiesel)	−5	Qi et al. [159]
B100 (Yellow grease biodiesel)	+11.6	Canakci and Van Gerpen [163]
B100 (Soy biodiesel)	+ 13.1	Canakci and Van Gerpen [163]
B17.5 (Mixture of Hazelnut soap-stock/ Waste sunflower biodiesels)	+3 to +6	Usta et al. [160]
B100 (Rapeseed methyl ester)	+ 20	Verhaeven et al. [177]
B20 (Rapeseed biodiesel)	~0	Baldassarri et al. [215]
B100 (Rapeseed methyl ester)	~0	Spessert et al. [200]
B100 (Mixture of Rapeseed biodiesel and Waste cooking oil methyl ester)	+40	Grimaldi et al. [155]
B10 (Palm biodiesel)	+ 6 to −4	Kousoulidou et al. [202]
B100 (Karanja biodiesel)	−26	Raheman et al. [161]
Ethanol: Methyl soyate: diesel blend (5:20:75)	+2 to +14	Shi et al. [201]
B50	+ 27.4	Xiaoming et al. [148]
B20	+6.8	Xiaoming et al. [148]

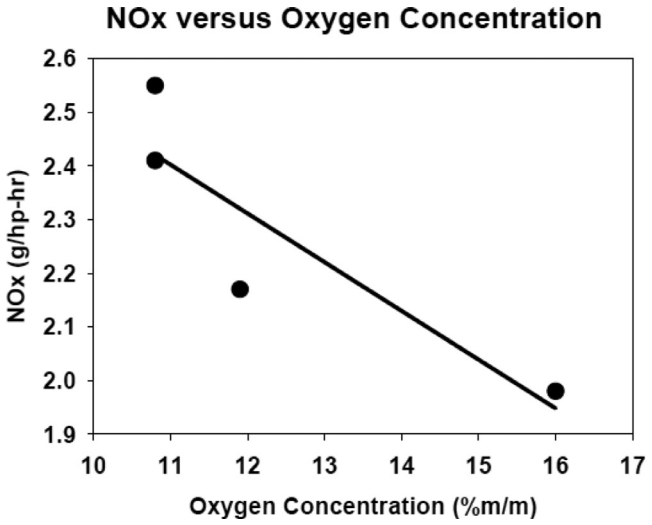


Fig. 17. NO_x vs. oxygen concentration of the test fuel (Reprinted from [216], with permission of SAE).

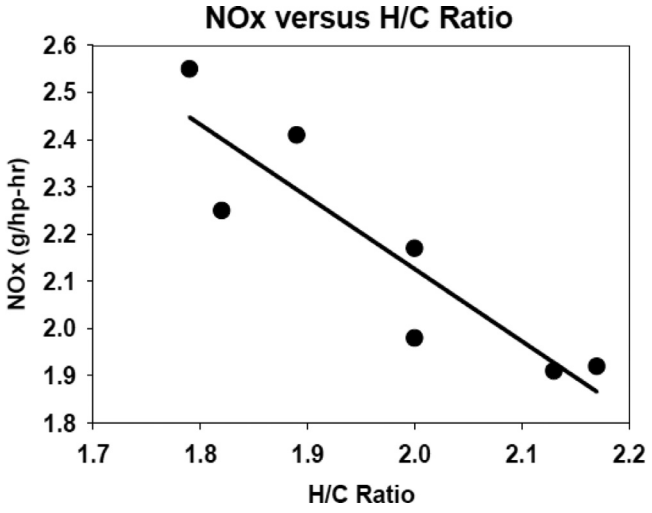


Fig. 18. NO_x emissions vs. H/C ratio of the test fuel (Reprinted from [216], with permission of SAE).

NOx emissions increase significantly for B100 and this increase varies with biodiesel feedstock. Unsaturated biodiesel (higher iodine value) produced relatively higher NOx emissions in an electronic unit injector equipped engine. In engine equipped with CRDI system, the effect of biodiesel unsaturation was relatively lower compared to engine equipped with unit injector. This suggests that higher bulk modulus of compressibility of biodiesel is not the only reason for increased NOx emissions from biodiesel [217]. Cetane improver additives in biodiesel had no effect on NOx emissions from any of the two engines. This suggested that NOx emissions were not dependent on the cetane number of the fuel either [217]. AL-Shemmeri et al. [218] reported linear relationship between adiabatic flame temperature and NOx emissions from different biodiesel blends. McGill et al. [219] reported increased NOx emissions from 100% biodiesel and blends at most operating conditions except some operating points at high speed and low load in comparison to mineral diesel in a DI engine equipped with electronically controlled mechanical fuel pump. Gumus et al. [182] reported that NOx emissions increased with increasing engine load due to higher peak combustion chamber temperature. NOx emissions increased with increasing biodiesel concentration in the test fuel. NOx emissions generally decreased with increasing FIP however the trend was not regular and significant (Fig. 19a-b) [182].

Wang et al. [198] tested nine vehicles using B35 and mineral diesel. They reported that differences in NOx emissions from B35 and diesel fueled engine were insignificant [198]. Particulate increased and NOx emissions decreased in a CI engine, when SoI timings were retarded [220]. Szybist et al. [221] also reported reduction in NOx emissions from biodiesel fueled engine by retarding the SoI timings. Yehliu et al. [176] reported that split injection reduced NOx emissions from both fuels but higher reduction was observed in case of B100 fueled engine, which showed 18% lower NOx compared to mineral diesel [176]. At all engine loads, an increase in FIP significantly increased NOx emissions from ultra-low sulfur diesel (ULSD) and Soybean methyl ester (SME) biodiesel (B40) in a CRDI engine [222]. Significant NOx emission reduction and a considerable smoke reduction was observed for B30 and B100 of different feedstocks in an engine fitted with CRDI system and an ECU with closed-loop combustion control [203]. Hwang et al. [223] showed that difference in NOx emissions from B100 and mineral diesel were insignificant at higher FIP (1600 bar) however at lower FIP, biodiesel emitted significantly higher NOx emissions. In modern ECU controlled engines, control parameters need to be re-optimized with changing fuel properties such as addition of biodiesel in mineral diesel. Anand et al. [224] reported ~37.3% reduction in NO emissions with addition of 10% methanol in Karanja biodiesel at full load. Zhu et al. [166] reported that BSNOx emissions from methanol/ ethanol-biodiesel blends were lower than mineral diesel and these emissions further decreased with increasing alcohol concentration in the test fuel. For the methanol/ ethanol-biodiesel blends, the mixture cooling effect of alcohols due to their higher latent heat of vaporization and relatively lower heating value reduced the peak combustion temperature hence the NOx emissions [166]. Lin et al. [164] suggested that NOx emissions from biodiesel were higher than mineral diesel but biodiesel produced by peroxidation process emitted lower NOx emissions than mineral diesel even though it has higher oxygen content than mineral diesel. This indicated that formation of NOx is probably more sensitive to biodiesel unsaturation than the oxygen content of the test fuel. Yoon et al. [225] reported lower NOx emissions from ethanol-biodiesel blends compared to mineral diesel for all test conditions due to higher latent heat of vaporization of ethanol and double injection strategy, which suppressed increase in peak combustion temperature and pressure. Szybist et al. [226] reduced the iodine value of Soybean biodiesel by increasing the concentration of methyl oleate (methyl ester of oleic acid). There was no increase in NOx emissions from Soybean biodiesel (B20) containing 76% methyl oleate, while ordinary Soybean biodiesel (B20) emitted 3–5% higher NOx compared to mineral diesel [226]. They concluded that NOx emissions were insensitive to cetane number [226]. A literature review on the effect of cetane number on NOx emissions concluded that NOx emissions generally decreased with increasing cetane number [227]. Many studies suggested that higher oxygen content of biodiesel is the main reason for higher NOx emissions but Lapuerta et al. [228] suggested that the oxygen content of biodiesel does not cause any increase in NO formation because diffusion combustion occurs mainly in regions with oxygen-fuel ratio around stoichiometric (2.81 for biodiesel and 3.58 for diesel). Fuel bound oxygen is not enough to compensate for such a difference. One study conducted on after-treatment of NOx emission by Sharma et al. [229] concluded that the effectiveness of Urea-SCR system in reducing NOx emissions from biodiesel (B20) was comparable to baseline mineral diesel.

Mueller et al. [230] suggested that NOx increase from biodiesel fuelled engines can't be quantitatively determined by a change in a single fuel property. Rather it is a result of a number of coupled mechanisms, whose effects reinforces or cancels one another under different conditions, depending on specific combustion and fuel characteristics. Fuel-air mixtures closer to stoichiometric at the time of ignition and in the premixed auto-ignition zone near the flame lift-off length appear to be a key factor in helping more NOx emissions

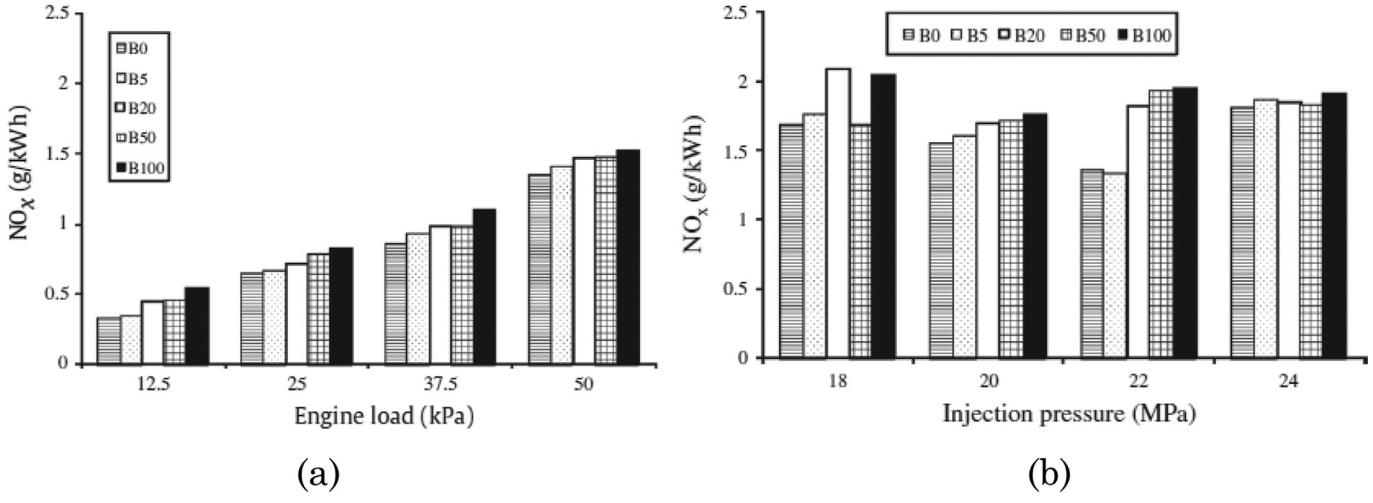


Fig. 19. (a) NOx emissions vs. engine load (b) NOx emissions vs. fuel injection pressure (Reprinted from [182], with permission of Elsevier).

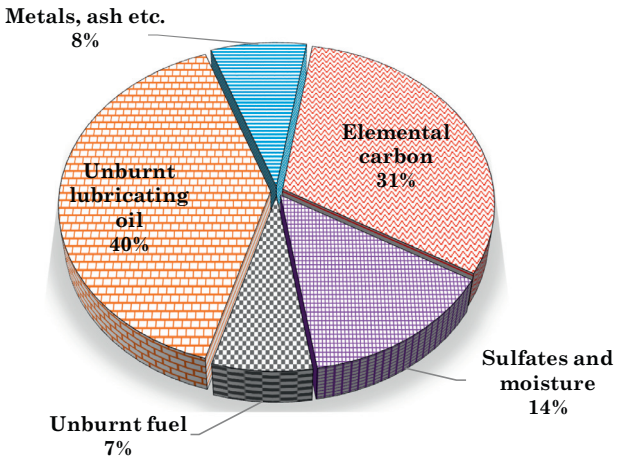


Fig. 20. Typical composition of diesel particulate matter (Reprinted from [7], with permission of Elsevier).

from biodiesel fuelled engine under all conditions. These differences are expected to encourage higher local and higher average in-cylinder temperatures, lower radiative heat losses, and shorter and more-advanced combustion event. All these factors increase thermal NOx emissions. Differences in prompt NO formation and species concentrations resulting from fuel and jet-structure changes also play important role in higher NOx formation from biodiesel.

4.2.4. Particulate emissions

Diesel engines are known for emitting carbonaceous particles, known as particulate matter (PM). PM comprises of carbon core with several organic compounds, nitrates, sulfates, metals and irritants (such as acrolein, ammonia, acids, fuel vapors, unburnt lubricants oils) adsorbed on to its surface [231]. These particles mainly originate from incomplete combustion of fuel, lubricating oil and engine wear. Typical composition of PM is shown in Fig. 20 [7].

The particle size-number distribution and chemical composition varies greatly, depending on engine type, engine speed, fuel composition, lubricating oil formulation, and emission control technology employed in the engine [232]. Diesel PM are respirable and have a very large surface area per unit mass, which makes them an excellent carrier for adsorbed inorganic and organic compounds [233]. Many of these adsorbed species are known to be toxic, mutagenic and carcinogenic [233].

PM produced by biodiesel combustion is of a different nature compared to the one from mineral diesel origin and is generally lower in mass comparatively, as well as the mean particle size and total numbers. This is attributed to suppression of soot formation and agglomeration due to lower soot precursor generation and increased in-cylinder pressure generated by biodiesel combustion. PM from biodiesel combustion has been shown to have an increased proportion of small nano-particulate (nuclei-mode particles) compared to baseline mineral diesel. This is a consequence of biodiesel spray characteristics, which creates an increased proportion of SOF (liquid part of the PM). Health studies to date have focused on the damage caused by solid particulate. For widening the range of fuels for CI engines in future, it has become increasingly important to study the health effects of the PM emitted by different fuels and substantial research in this area is yet to be done. This may also become an important database for evolution of future PM legislations as well.

Many studies of PM emissions from biodiesel fueled engines have been conducted by different researchers. Some of them are discussed individually while many of them are summarized in Table 13. Murali et al. reported that proper tuning of biodiesel fuelled engine resulted in 16% reduction in PM emission compared to 14% reduction in case of non-optimised engine [234]. Other researchers also reported reduction in PM emissions due to biodiesel fuelling of CRDI engnies [235–236]. Lapuerta et al. [237] tested four biodiesels and compared PM emissions with baseline mineral diesel on a four cylinder, 2.2 L, turbocharged, DI diesel engine operated under NEDC. All four test biodiesels showed sharp reduction in PM mass emissions compared to baseline mineral diesel. PM mass emissions decreased by 20% as the biodiesel unsaturation levels increased [237]. Xue et al. [10] concluded in their review article that biodiesel fueled engines generally emitted lower PM mass emissions than mineral diesel fueled engines. This observation is also consistent with the general trend observed in Table 13, wherein several studies on biodiesels from different feedstocks have been summarized.

Table 13
Effect of biodiesel on PM emissions.

Test fuel	Change in PM emissions (%)	Reference
B100 (Rapeseed biodiesel)	−40	Krahl et al. [238]
B100 (Soy biodiesel & waste cooking oil biodiesel)	−65% (For both)	Canakci and Van Gerpen [163]
B20	−45	Handbook of biodiesel [239]
B100 (Beef tallow methyl ester)	−75	Kado et al. [240]
B20 (Rapeseed methyl ester)	No difference	Turrio-Baldassarri et al. [215]
B20 (Soy soap-stock biodiesel)	−20	Haas et al. [241]
B25, B50, B75 and B100	-ve, Highest reduction for B25	Lapuerta et al. [242]
B30, B70, B100 (Methyl esters of waste cooking oil)	-ve, Highest reduction for B30	Armas et al. [243]
B100 (Soybean methyl ester)	−30	Last et al. [244]
B100 (Waste cooking oil methyl ester, Palm methyl ester, Cottonseed methyl ester, Rapeseed methyl ester, and Soybean methyl ester)	−53 to −69	Wu et al. [245]
B30, B50, B100 (by Simulation)	−32.3, −42.9, −53	Luján et al. [246]
B100 (Soy biodiesel at four different altitudes)	−33.33, −44.50, −56.92 and −69.21 at 4560 m, 3280 m, 2408 m and 1608 m altitude	Yu et al. [247]
B30 and B100 (Rapeseed methyl ester)	−16.36, −25.45	Sadiktsis et al. [248]
B100 (Rapeseed methyl ester)	−41.38	Rounce et al. [249]
B20 (Soy biodiesel)	−21.79	Alam et al. [162]
B100 (Rapeseed biodiesel)	+10	Bouche et al. [189]
B20, B100 (Rapeseed biodiesel)	−39.71, −54.41	Krahl et al. [206]
B20, B100 (Palm biodiesel)	−9.61, +21.11	Lin et al. [250]
B100 (Rapeseed biodiesel)	−27.75	Winsor et al. [251]
B100 (Soy biodiesel)	−33.04	Winsor et al. [251]
B100 (Soy biodiesel)	−77.98	Knothe et al. [252]

Diesel PM exists in two distinct submicron modes: nuclei-mode (7.5 to 56 nm) and accumulation mode (56 to 1000 nm) [253]. Accumulation-mode particles are chain agglomerates of primary carbon spheres and sulfates with adsorbed hydrocarbons. Nuclei mode particles are composed of elemental carbon (EC) and condensed organic carbon (OC) fractions. Several studies have indicated that higher fuel sulfur content results in higher nuclei-mode particle formation [254,255]. Generally, it is observed that addition of biodiesel in mineral diesel results in reduction in PM mass emissions and smoke opacity but PN concentration increases due to increase in number concentration of nuclei mode particles, which have smaller size. Increased nuclei mode particles are attributed to increased soluble organic fraction (SOF) formed due to relatively inferior evaporation characteristics of biodiesel compared to mineral diesel. Lower concentration biodiesel blends were effective in reducing PN concentration as well. Chemical composition of particulate emitted by biodiesel fueled engines need to be thoroughly investigated for understanding their toxicity potential and formation mechanism. This will also be helpful in suggesting changes in engine control strategies for reducing PN emissions along with other regulated pollutants, upon biodiesel/ blend usage.

Zhu et al. [256] conducted experiments using ULSD (< 1 ppm Sulphur) and two biodiesels blended with baseline mineral diesel (400 ppm Sulphur) using a direct injection diesel engine (Cummins). It was reported that with increasing proportion of biodiesel in the test blends, smoke opacity decreased, while total particle number concentrations increased [256]. ULSD also showed relatively lower smoke opacity and total PN concentration compared to baseline mineral diesel. In comparison to baseline mineral diesel, total nucleation mode particle number concentration was higher in case of biodiesel blends, and relatively lower in case of ULSD [256]. Tan et al. [257] reported that the number of nucleation mode particles at peak (6 to 16 nm) increased with increasing blending ratio of Jatropha biodiesel in a CRDI engine. However, there was reduction in accumulation mode particles at peak (30 to 61 nm) at most engine operating conditions [257]. Higher nucleation mode particulate formation was explained by three mechanisms, including super-saturation leading to formation of new particles by nucleation, increased SOF due to higher viscosity and lower volatility of biodiesel, and higher oxygen content of biodiesel causing carbonaceous particles to change from fine to ultrafine/ nano-particle sizes [257]. Di et al. [258] reported that with increasing oxygen content of the blends of diglyme (DGM) with ULSD, smoke opacity, PM mass emission, and geometric mean diameter of particles decreased. PN for sizes less than 100 nm and total particle numbers increased for diesel-DGM blend compared to baseline ULSD [258]. Zhang et al. [259] reported lower particle number emissions with no nucleation mode particles for B100 from a CRDI engine fueled with biodiesel blends. It was concluded that lower sulfur content of biodiesel (64 ppm) in comparison to mineral diesel (1135 ppm) was responsible for this absence of nucleation mode particles [259]. Sinha et al. [260] reported that the PN density increased and particulate mass decreased with increasing percentage of soybean biodiesel in test blend with ULSD. B100 reduced the accumulation mode particle numbers and produced higher nucleation mode particles compared to ULSD at higher FIP [260]. Higher nucleation mode particle formation was assumed to be because of higher SOF [260].

Agarwal et al. [261] conducted an experimental study to find particulate size-number distribution from B20 and B100 and they compared it with baseline mineral diesel fueled engine at different engine loads. In this study, B20 gave highest particle number concentration at no load however at most loads, higher number of smaller particles were emitted by B100 compared to baseline mineral diesel. They also reported that emission of particles of all size ranges was higher for B100 (Fig. 21) than other test fuels in most experimental conditions [261].

Several researchers studied the effect of fuel injection parameters and strategies on particulate number-size distribution using single cylinder research engine and reported that particulate number-size distribution reduced with increasing FIP [262,263]. Total PN emitted by Karanja biodiesel blends were lower than mineral diesel [256]. Agarwal et al. [263] reported lowest PN emitted by 10% Karanja biodiesel blend. Dhar and Agarwal [264] reported that total PN concentration emitted by B20 and B50 were lower than baseline mineral diesel. Particulate number-size distribution lowered with increasing FIP. At fixed pilot injection timing, particulate number-size distribution increased with retarded main injection for all test fuels [264].

There were some experimental studies looking at the response of exhaust gas after-treatment systems with biodiesel and blends, compared to baseline mineral diesel. Some of these studies are discussed here. In one such study, Lower nuclei mode particle numbers were emitted downstream of diesel oxidation catalyst (DOC) for both fresh cooking oil (FCO) and WCOB100 compared to baseline diesel. High proportion of liquid aerosol particles formed in the engine combustion chamber were eliminated by DOC and the presence of fuel oxygen in FCO and WCOB100 also helped reduce particulate emissions [236]. Vertin et al. [265] performed experiments using a medium-duty truck engine having DOC followed by a cordierite wall-flow type diesel particulate filter (DPF) using ULSD and 20% Soy biodiesel (B20). They reported that PM emissions reduced by 22–35% for B20 in the transient test cycle however no PM reduction was observed in steady-state test-cycle [265]. There were no statistical differences in post-DPF particulate emissions for B20 and ULSD [265].

Positive or adverse effects of biodiesel and blends on PM emissions vary significantly amongst vehicles, engine technology, and test cycles. These are mainly attributed to certain physico-chemical properties of biodiesel and in cold-start conditions.

4.2.5. Unregulated emissions

Fatty acids methyl esters (FAME) of biodiesels are chemically more reactive than hydrocarbon molecules of mineral diesel. This leads to possibility of formation of higher number of pollutant species in the combustion chamber of a biodiesel fueled engine. Many of these pollutant species are unregulated and have severe health effects. There are very few scientific studies in literature dealing with unregulated emissions from biodiesel [191,266–268]. Unregulated emission species in the engine exhaust may contain wide range of organic compound families such as alkanes, aldehydes, alcohols, ketones, aromatic and poly-aromatic hydrocarbons such as benzene, toluene and xylene (BTX) etc. It is extremely important to understand and evaluate the possible harmful health effects of these species on the human health and the environment [269] and this is an area where significant quantum of research needs to be done. Aromatics and poly-aromatic hydrocarbons are highly toxic and can have mutagenic effects. Use of biodiesel based on methyl esters has negligible effect on emission of unregulated emission species namely acrolein, propanol and acetone compared to baseline diesel. However use of biodiesel based on ethyl esters leads to increased emission of unregulated species such as acetaldehyde, acrolein, propanol and acetone; and to a lesser extent, formaldehyde compared to baseline diesel [270].

Aldehydes are one of the most harmful incomplete combustion products from hydrocarbon fuels. Aldehyde emissions reduced by ~30% for SME (B100) and ~8% for B20 compared to baseline diesel in ECU controlled high pressure unit injector equipped engines. In the same study, Aldehyde emissions reduced by ~50% for B100 and ~30% for B20 compared to baseline diesel, in a mechanically controlled engine using pump-line-nozzle (PLN) fuel injection system [271]. Three-quarters of total aldehyde emissions on mass basis comprise of formaldehyde, acetaldehyde, and acrolein, and the remaining are heavier aldehydes [271]. Karavalakis et al. [272]

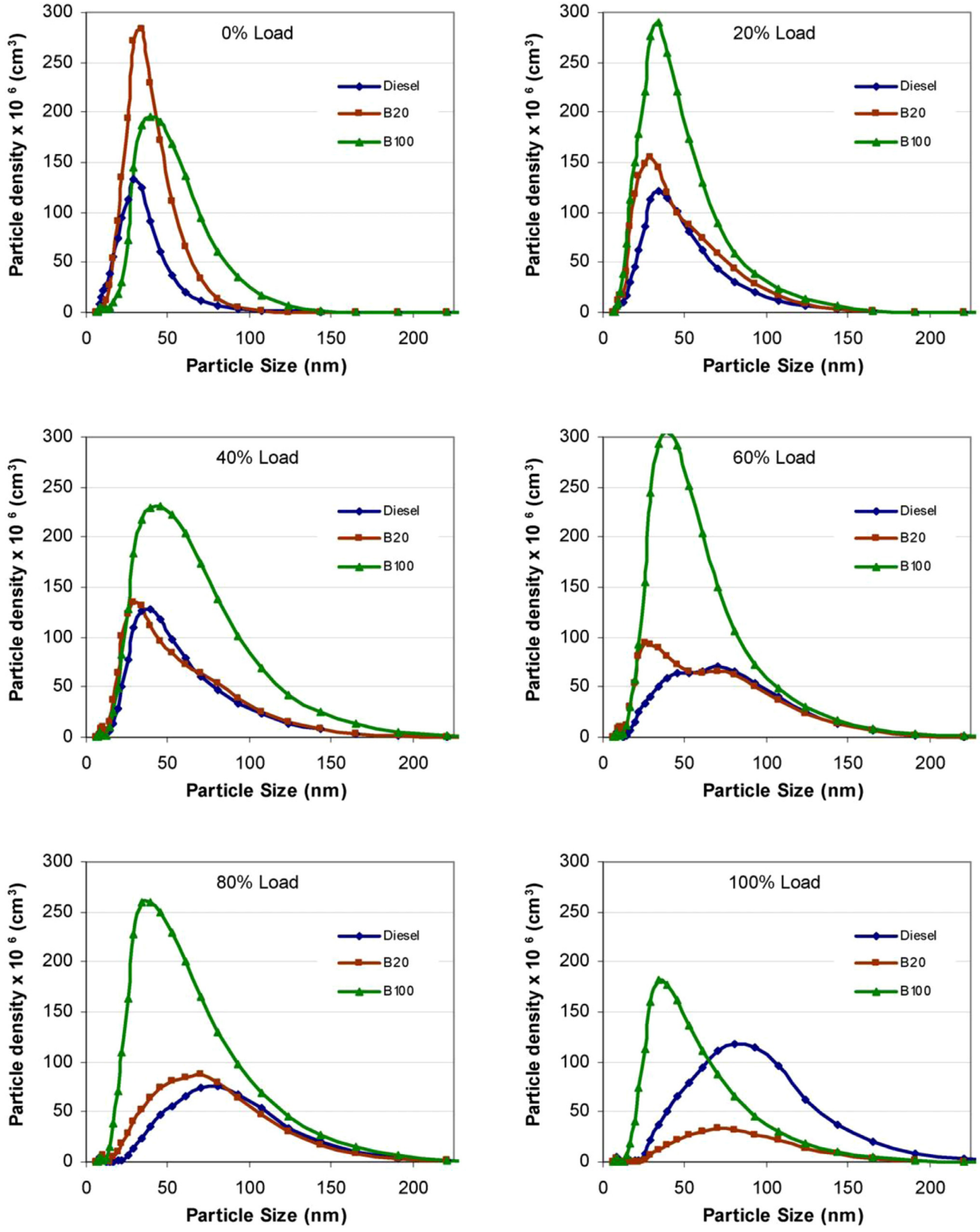


Fig. 21. Particle size-number distribution from biodiesel and blends at 1800 rpm for varying engine loads (Reprinted from [261], with permission of Elsevier).

reported formaldehyde and acetaldehyde as dominant aldehyde emissions from a 2.0 L TD, IDI diesel engine using biodiesel blends (RME5, RME10, RME20, PME5, PME10, PME20) compared to baseline low sulfur diesel over NEDC and Athens Driving Cycle (ADC). Reduced formaldehyde emission from biodiesel were also reported by Peng et al. [268] using WCOB (B20) and by Krahl et al. [191] using Rapeseed oil methyl ester (B100). No significant emission of alcohols was reported in the exhaust using any of these three test fuels in this study (B20, B100, and diesel) [271]. McGill et al. [219] reported very small differences in formaldehyde and acetaldehyde emissions

in all test conditions except at low loads (25% load @ 1900 rpm) for US #2 diesel, RME, SME, Swedish environmental class 1 reformulated diesel (RFD), SME 30-US diesel blend, RME 30-US diesel blend, 30% used vegetable oil methyl ester (UVOME30) blend in a Navistar 7.3 L DI medium-duty truck engine. For 1,3 butadiene emission, even this difference at low load condition was not apparent [219]. Karavalakis et al. [273] tested five test fuels, B5 and B10 of SME and animal fat (AFME) and compared them with baseline ULSD in a high speed CRDI Cummins engine and a Detroit Diesel Corporation (DDC) engine. Emissions tests were conducted as per Federal Test Procedure (FTP), Urban Dynamometer Driving Schedule (UDDS), and Supplemental Emissions Test (SET) cycles. They reported that formaldehyde and acetaldehyde were the predominant aldehydes in the exhaust, and the carbonyl emissions were not significantly affected by biodiesel feedstock [273].

Ballesters et al. [269] investigated regulated and unregulated emissions from a 4-cylinder, turbocharged, intercooled, CRDI 2.2 L diesel engine in urban mode and extra-urban mode cycles, representing European Transient Cycle (ETC), while using low Sulphur diesel (LSD), and sunflower oil biodiesel blends (B30 and B70). They reported that carbonyl emissions (aldehydes and ketones) increased with increasing biodiesel content in the test fuel, while paraffins (linked or branched alkanes) and aromatic compounds were detected only in the LSD and B30 because paraffins and aromatics are present only in reference fuels and absent in biodiesel [269]. Increase in formaldehyde and acetaldehyde emissions was reported in a Euro-V CI engine using biodiesel. Formaldehyde and acetaldehyde emissions were relatively higher in biodiesel-ethanol blends compared to baseline diesel [274]. Catalytic converters reduced heavier aldehyde emissions in the exhaust but increased formaldehyde and acetaldehyde emissions, regardless of the fuel used. Use of biodiesel–ethanol blends in addition to use of DOC reduced unregulated emissions from CI engines significantly [274]. WCOB and blends (having 2, 4, 6 and 8% oxygen w/w) with ULSD showed lower emissions of formaldehyde, 1,3-butadiene, toluene, xylene, but higher emission of acetaldehyde and benzene compared to baseline ULSD [266]. Formaldehyde emissions increased with increasing engine load and decreased with increasing biodiesel content in the test fuel [266]. Gupta and Agarwal [267] reported higher formaldehyde and acetaldehyde emissions at lower engine loads due to lower in-cylinder temperatures and leaner fuel-air mixture strength regions in a 2.2 L CRDI engine (Fig. 22). These emissions decreased with increasing engine load, and speed. Karanja biodiesel blend (KB20) emitted lower unregulated emissions compared to baseline mineral diesel [267].

Krahl et al. [191] detected aromatic emissions only at idling and low loads. Unsaturated hydrocarbons, ethene, ethylene and propene concentrations were also lower for RME compared to baseline diesel and other test fuels [191]. Total PAH and nitro-PAH emissions reduced with use of biodiesel, independent of feedstock [272].

Bermudez et al. [275] reported that use of biodiesel slightly reduced aromatic hydrocarbon emissions such as benzene but methane emission increased at higher loads [275].

Impact of unregulated emission species such as carbonyl compounds and PAHs from biodiesel and blends can be significant though there is limited data available in open literature, which is often contradictory. This contradiction is attributed to noticeable dependence on engine operating conditions, test cycle followed, and the chemical structure of fuel, all of which are usually acknowledged. Nevertheless, these unregulated emissions amongst others

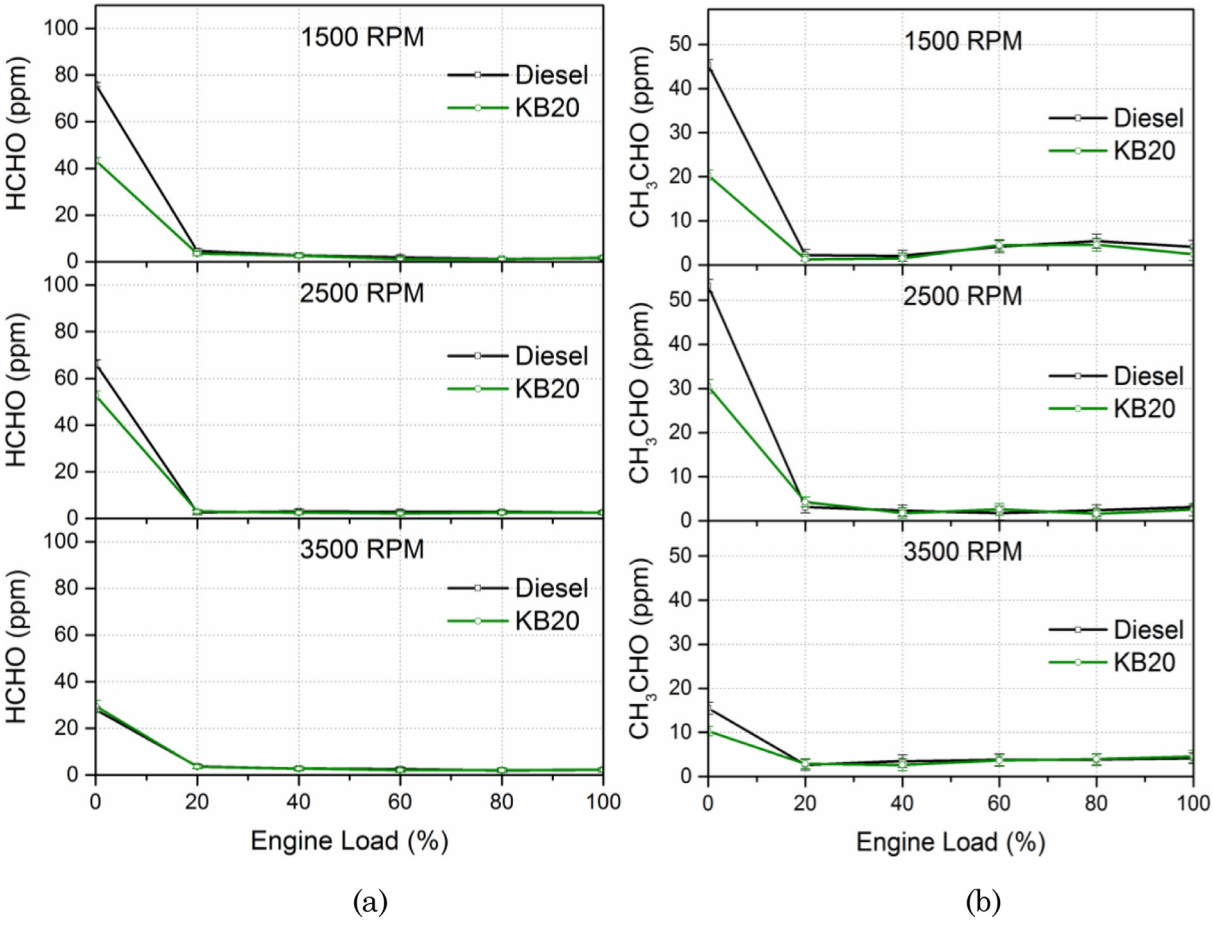


Fig. 22. Formaldehyde and Acetaldehyde emissions from biodiesel fueled engine (Reprinted from [267], with permission of SAE).

are of greater importance as some pollutant species are toxic, mutagenic, and even carcinogenic to the humans. Carbonyl compounds also play a critical role to the troposphere chemistry, as they are important precursors for the formation of free radicals (HOx), ozone, and peroxy-acyl-nitrates. While results of these emissions vary, it is widely accepted that use of biodiesel as an alternate fuel increases these emissions because of its higher oxygen content, significantly different vaporization characteristics and combustion chemistry. PAH emissions are released during incomplete combustion of diesel and biodiesel and are widely distributed in the atmosphere. Nitrate and oxygenated PAHs are of utmost concern due to their mutagenic and carcinogenic potential. Most research studies showed that emission of aromatic and polyaromatic compounds from biodiesel were relatively lower compared to mineral diesel however these were influenced by engine operating conditions such as engine load, driving cycle, and operating mode etc.

4.3. Combustion characteristics

Engine combustion characteristics of a test fuel are investigated using analysis of cylinder pressure-crank angle history. Combustion analysis is helpful in understanding the effect of fuel properties on engine performance and engine-out emissions. Several studies were reviewed to understand the effect of biodiesel on in-cylinder pressure, HRR, ignition delay, and combustion duration compared to baseline mineral diesel. Properties of test fuels used in these investigations along with the effect of biodiesel on the combustion characteristics are also discussed and an attempt has been made to find general trends.

Gumus investigated combustion characteristics of Hazelnut biodiesel, which had lower calorific value, and higher viscosity, density and cetane number compared to mineral diesel [276]. Combustion started earlier with increased biodiesel concentration in the test fuel, due to shortening of injection delay because of biodiesel's higher cetane number. Peak cylinder pressure decreased with increasing biodiesel concentration in the test fuel but it increased with advancing SOI, increasing FIP, increasing engine load and increasing CR. While increasing biodiesel content in the test fuel decreased HRR; advancing SoI, increasing FIP and CR increased the HRR from biodiesel and blends vis-à-vis mineral diesel and led to significant improvement in combustion characteristics [276].

Xiaoming et al. [148] compared combustion characteristics of biodiesel (density: 880 g/cc; cetane number: 50; CV: 37 MJ/m^3) and mineral diesel (density: 841 g/cc; cetane number: >45; CV: 42 MJ/m^3). Peak cylinder pressure for biodiesel was lower than mineral diesel at all operating conditions except lower engine speed and high load combinations [148]. Measured values of fuel line pressure showed advanced rise in fuel pressure and slightly higher maximum fuel line pressure in biodiesel compared to mineral diesel, which suggested advanced injection of biodiesel compared to mineral diesel in an unmodified mechanical fuel injection system equipped engine. Ignition delay was also shorter in case of biodiesel. Kwano et al. [149] compared the combustion characteristics such as in-cylinder pressure, HRR and needle lift for RME (density: 883 g/cc; cetane number: 52.8; CV: 36.9 MJ/m^3; viscosity: 4.31 cSt) and mineral diesel (density: 822 g/cc; cetane number: 58.3; CV: 43.1 MJ/m^3; viscosity: 3.35 cSt) in a CRDI, 4-cylinder, intercooled-turbocharged, modern high speed transportation engine. Relatively higher bulk modulus and density of RME didn't influence injection timing in the CRDI system. Ignition delay was not affected by the difference in cetane number of diesel and RME. Peak cylinder pressure and HRR for both, pilot and main injections of RME were slightly higher than mineral diesel, due to higher burning rate of RME. Due to this, mixing controlled combustion of RME completed slightly earlier than mineral diesel [149].

Variations of in-cylinder pressure and HRR for diesel, B25, B50 and B100 at two engine speeds 1500 and 2500 rpm (Fig. 23) shows that premixed combustion starts earlier in biodiesel and its blends at almost all engine speeds, due to their higher cetane number compared to mineral diesel [171]. HRR_{max} decreased by ~18% and 30% for diesel and biodiesel respectively, due to the reduction in premixed combustion phase caused by shortening of the ignition delay between 1500 rpm to 2500 rpm [171].

Sahoo and Das [277] also investigated combustion characteristics of Jatropha, Karanja and Polanga biodiesel blends and compared them to baseline mineral diesel. All biodiesel blends showed higher viscosity, and density and lower calorific value compared to mineral diesel. Ignition delay of 50% Karanja biodiesel blend (KB50) was comparable to mineral diesel. Alam et al. [162] reported that SoI occurred in the same order as the density of the test fuels i.e. higher the density, earlier will be the SoI. Highest premixed combustion heat release peak was observed for the fuel with lowest cetane number [162]. Qi et al. [159] reported that at lower loads, the maximum cylinder pressure (P_{max}), maximum rate of pressure rise ($RoPR_{max}$) and maximum HRR (HRR_{max}) were slightly higher for biodiesel compared to baseline mineral diesel. At higher engine loads, P_{max} for both fuels was similar, but $RoPR_{max}$ and HRR_{max} were relatively lower for biodiesel. The SoI and ignition delay for B100 were

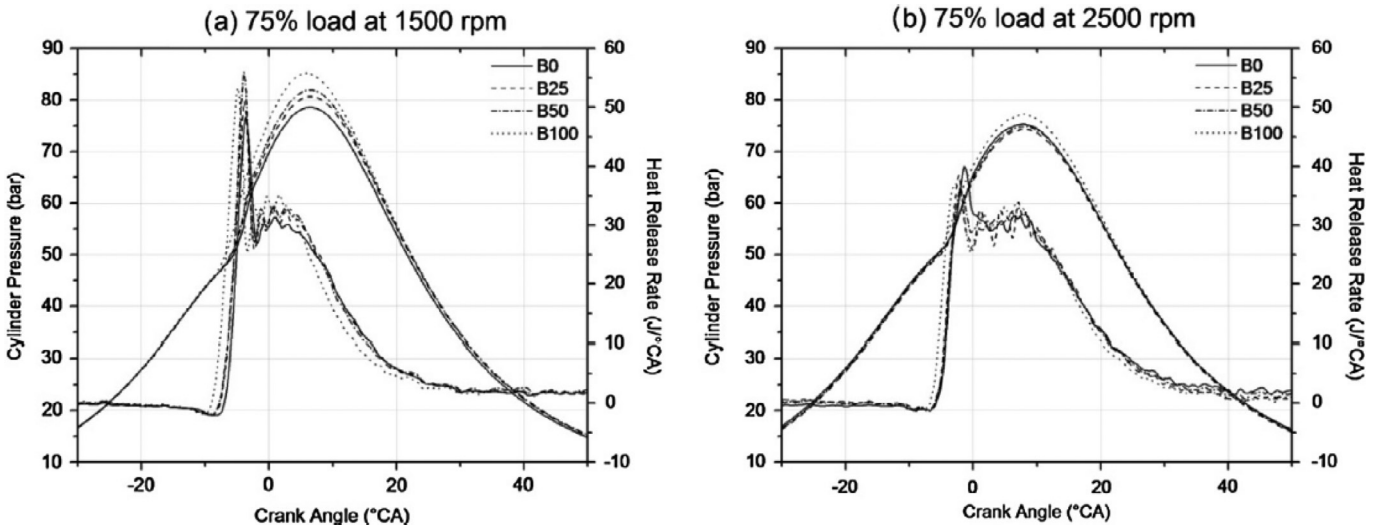


Fig. 23. Cylinder pressure and HRR of biodiesel/ blends compared to mineral diesel (Reprinted from [171], with permission of Elsevier).

relatively earlier and shorter than mineral diesel. This was probably due to combination of different physical properties of test fuels and fuel quantity related changes in the injection timings. Combined effect of advanced injection timing and shorter ignition delay of biodiesel led to relatively earlier start of combustion (SoC) compared to mineral diesel [159,174].

Grimaldi et al. [155] compared the combustion characteristics of biodiesel (mixture of 70% Rapeseed crude oil biodiesel + 30% Waste vegetable oil biodiesel) (density: 884 g/cc; cetane number: 55.9; CV: 37.4 MJ/m^3; viscosity: 4.43 cSt) with baseline mineral diesel (density: 834 g/cc; cetane number: 54.7; CV: 42.9 MJ/m^3; viscosity: 2.52 cSt) in a high speed direct injection (HSDI) engine equipped with CRDI system. They reported that after the pilot injection, cylinder pressure and average cylinder temperature curves of the CI engine showed faster increase compared to corresponding biodiesel curves. This significant difference in pilot combustion could be explained by relatively higher distillation temperature range and relatively lower calorific value of biodiesel compared to mineral diesel [155]. After the main injection, higher combustion rate of biodiesel was confirmed by higher HRR_{max} as well as by steeper slope of cumulative heat release (CHR) curve (Fig. 24) [155].

Canakci and Van Gerpen [163] compared the combustion characteristics of Yellow grease methyl ester (YGME) and SME blended with mineral diesel in a turbocharged diesel engine. Biodiesel exhibited relatively earlier SoI and SoC timings compared to mineral diesel. The SoI timings for SME and YGME advanced by 2.68° and 3.55° respectively compared to mineral diesel due to difference in bulk modulus of compressibility of the test fuels. SME and YGME started to burn ~3.4° and 4.2° earlier respectively compared to mineral diesel [163]. Advanced SoC was primarily due to relatively earlier SoI timings and higher cetane number [278]. Combustion characteristics of RME were rather inferior at low engine load [279]. RME experienced delayed vaporization in the combustion chamber because of higher middle distillation temperature, and relatively narrower distillation temperature range, which led to larger sauter mean diameter (SMD) of spray droplets compared to baseline mineral diesel. Premixed heat release was unsteady because of concurrent fuel spray vaporization and premixed combustion [279]. These combustion characteristics could be improved by increasing the FIP [279]. There is a strong correlation among fuel-air mixing, SoI timings and fuel properties. For satisfactory combustion characteristics, fuel

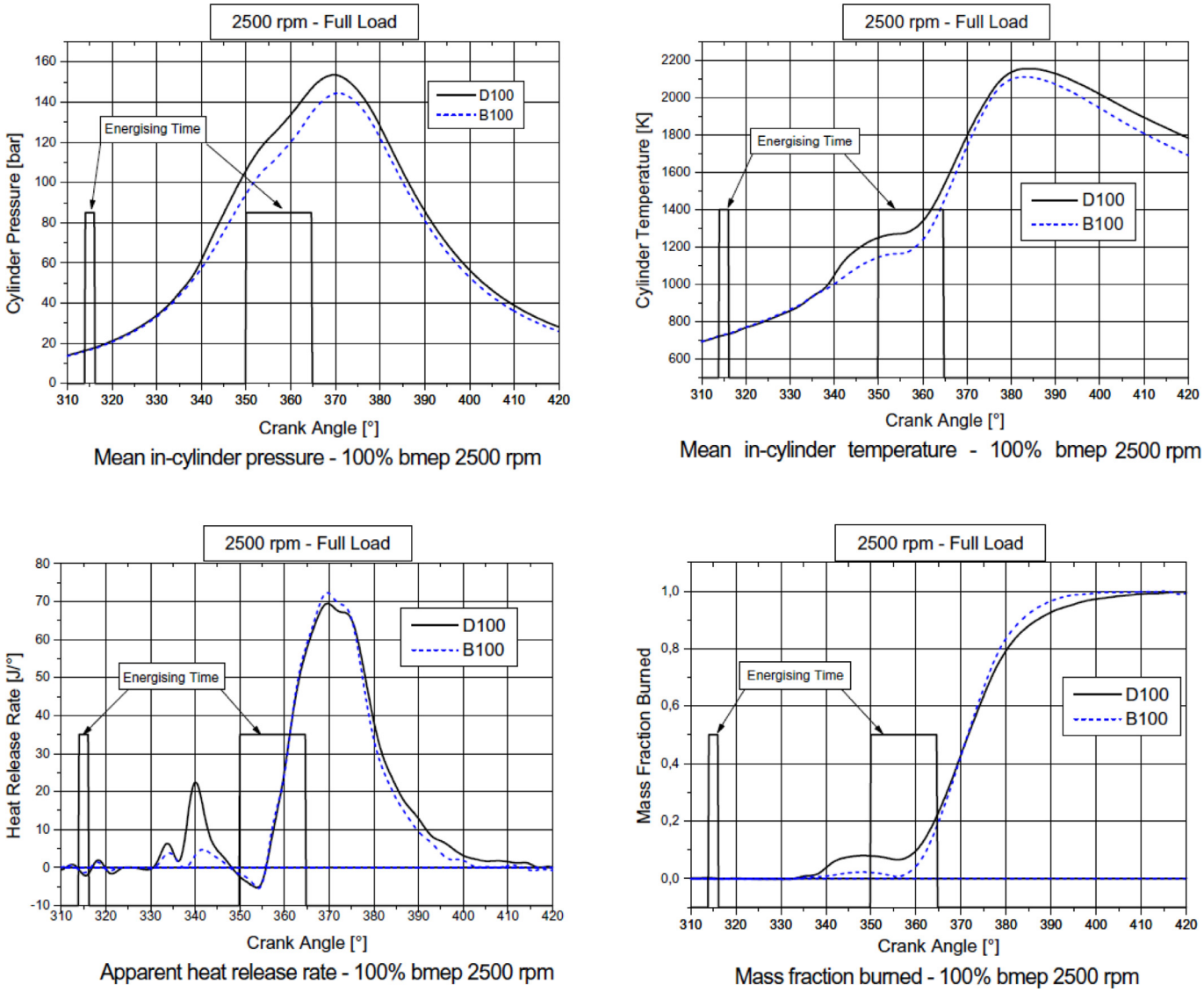


Fig. 24. (a) In-cylinder pressure, (b) In-cylinder temperature, (c) Heat release rate and (d) Mass fraction burned at 100% load, 2500 rpm in a CRDI HSDI engine using pilot injection (Reprinted from [155], with permission of SAE).

spray should disintegrate before the ignition starts and biodiesel blends up to B40 satisfy this criterion in an unmodified engine [280].

Yoon et al. [225] investigated the effect of double injection strategy on the combustion characteristics of a biodiesel-ethanol blend fueled engine and reported that fuel injected in the second injection pulse combusted rapidly with an extremely short ignition delay. P_{max} and HRR_{max} of biodiesel-ethanol blend were generally higher than mineral diesel due to their relatively shorter ignition delay [225]. HRR analysis of B40 (SME) blended with ULSD in a CRDI engine showed that for all loads, retarding SoI timing to aTDC side enhanced premixed combustion [222]. For the same SoI, higher FIP led to higher HRR and slightly advanced SoC because of improved fuel-air mixing [225]. At low loads, biodiesel exhibited advanced SoC and reduced premixed heat release. At moderate to high loads, biodiesel did not have any noticeable impact on the HRR [222].

Yamane et al. [281] reported that difference in the bulk modulus of compressibility of biodiesel and mineral diesel increased at lower temperatures and higher pressures. Very comprehensive experimental study on bulk modulus of compressibility and its effect on fuel injection characteristics of biodiesels was carried out by Van Gerpen et al. [282–285]. In a DICI engine, differences in the injection characteristics of biodiesel and mineral diesel became more significant at higher speeds and loads, when the mean FIP was also high [281]. Boudy and Seers [286] investigated the effect of fuel properties on the fuel injection quantity and duration in a CRDI engine. Fuel density is the main property, which influences the fuel mass injected. Pressure-wave velocity affects the fuel quantity injected in the second injection pulse during multiple injections. Fuel quantity injected decreased with increasing bulk modulus of compressibility of the test fuel and increased with increasing fuel density [286]. Kuti et al. [287] investigated the spray formation and combustion characteristics of Palm biodiesel and mineral diesel using a CRDI system in a constant volume spray chamber. They reported relatively longer liquid jet length in case of biodiesel compared to mineral diesel due to its higher boiling range [287]. Ignition delay was shorter in case of biodiesel due to its higher cetane number and it further reduced with increasing FIP and decreasing nozzle hole diameter [287].

Combustion characteristics of ULSD, B100 (SME), and a synthetic, practically free of sulfur and aromatic compounds Fischer-Tropsch (FT) diesel were investigated in a 2.5 L, CRDI turbocharged diesel engine [176]. Experiments were conducted at fixed equivalence ratio, BMEP and SoI. Needle lift measurements showed that SoI timings were constant for different test fuels [176]. Increased injection duration was observed due to increased fuel mass injected in case of B100, in addition to advanced SoC due to higher cetane number of biodiesel [176]. Anand et al. [224] reported that addition of methanol in Karanja biodiesel shortened the combustion duration.

Higher viscosity of biodiesel results in an increased combustion duration. Generally, higher kinematic viscosity of biodiesel significantly affects fuel spray, droplet size distribution, droplet evaporation rate, and spray atomization process, resulting in slower burning therefore having longer combustion duration. However the opposite trend can be realized by modifying certain fuel injection parameters, which can potentially lead to shorter combustion duration for biodiesel compared to mineral diesel at low, medium and high load conditions. The cloud and pour point of biodiesel are also higher than mineral diesel, which makes it sensitive to cold weather conditions, resulting in difficulty in cold starting. In combination with the effects resulting from ignition delay and combustion duration, the HRR of biodiesel (due to lower heating value of biodiesel) is relatively lower than mineral diesel, which reduces the peak pressure rise rate, peak cylinder pressure and power output.

4.4. Engine wear and durability

Before large-scale implementation of biodiesel as alternate diesel fuel in transport sector, there are concerns about its compatibility with contemporary engine materials, FIE, and components due to its significantly different chemical composition compared to baseline mineral diesel, which need to be addressed [146,288,289]. Fazal et al. [288] summarized comparative wear of engine components from biodiesel and mineral diesel in their review article. They observed either lower or similar wear in biodiesel/ biodiesel blend fueled engine components compared to mineral diesel fueled engine components. These observations were made in engine studies as well as vehicular field trial studies [288]. Agarwal et al. [178] carried out 512 h endurance test on a single cylinder CI engine using B20 (Linseed oil methyl ester) and another similar engine operating in parallel using mineral diesel. They concluded that biodiesel does not cause any specific adverse effect on wear of vital moving components of the engine. They reported that the problem of injector coking, lubricating oil dilution, carbon deposits, ring sticking, fuel pump failure etc., which exist with the use of straight vegetable oil in engines, were completely eliminated upon use of biodiesel as a full/ partial substitute of mineral diesel [178]. Verhaeven et al. [177] reported that there were no significant differences in the wear of injectors and other FIE components after a 100,000 km field-trial using RME and UVOME as substitute fuels. At the end of the project, investigators checked the engine condition by measuring compression pressure and conducting leak test in the combustion chamber. They reported good health of the engines and no specific wear of the engine components due to RME or UVOME [177]. Fraer et al. [290] studied the effect of biodiesel on engine durability after 4 years of operation and more than 600,000 miles accumulated on eight B20 fueled engines. They reported heavy sludge around rocker assembly in B20 engines, which was not seen in diesel fueled engines. It was suggested that probably out of specification biodiesel was a possible reason for the heavy sludge formation. They concluded that all engines that were investigated, exhibited normal wear according to their mileage, independent of the fuel used [290]. Sinha and Agarwal [291] reported that physical measurements of vital engine components showed relatively lower wear for B20 (Rice-bran biodiesel) fueled CIDI engine except the big end bearing, which showed slightly higher wear compared to baseline mineral diesel in a long-term endurance test. They reported slightly lower wear of cylinder liner in case of B20. For this, they performed surface roughness profiles at various locations as well as scanning electron microscopy (SEM) of the liner surface after the endurance test [291]. SEM micrographs of the liner segments (Fig. 25) from this study depicted that wear was relatively higher on the anti-thrust side at TDC compared to the thrust side for both diesel and B20. Overall liner wear was seen to be significantly lower in B20 fueled engine compared to mineral diesel fueled engine [270]. In another study, Dhar and Agarwal [292] investigated the effect of 20% Karanja biodiesel blend (KB20) on engine wear and durability vis-à-vis mineral diesel in a 250 h endurance test on a DICI engine. Wear characterization of liner surface showed that for both fuels, surface texture of cylinder liners remained in acceptable condition after the endurance test [292].

Dhar and Agarwal [292] also reported that physical wear measurement of engine components showed relatively lower wear of valves, pistons, piston rings, liners and small end bearing of the connecting rods for biodiesel fueled engine compared to mineral diesel fueled engine. Lower wear of piston rings was confirmed by measuring weight loss after the completion of the endurance test (Fig. 26) [292]. In another study, Agarwal et al. [293] investigated the effect of B20 (Linseed oil methyl ester) on durability of CI engine components

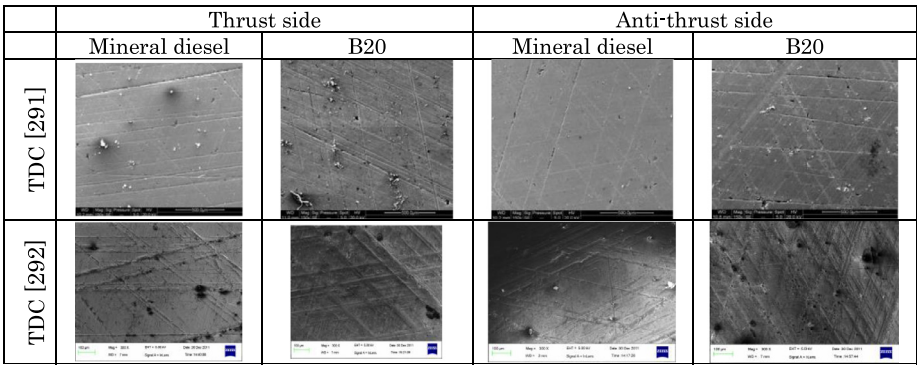


Fig. 25. SEM of liner surfaces for biodiesel and mineral diesel fueled engines (Reprinted from [291], with permission of ASME and from [292], with permission of Elsevier).

in a 512 h endurance test. Physical wear measurements in another experimental study from the same research group reported up to 30% reduction in wear of vital engine components because of additional lubricity properties of biodiesel [293].

4.5. Carbon deposits on engine components

In addition to wear of components, there are carbon deposits in the engine combustion chamber, which form upon long-term usage. Several investigators performed experiments to assess comparative levels of carbon deposits on vital engine components of the engines, fueled by biodiesels/ blends and mineral diesel. Çetinkaya et al. [156] reported same level of carbon deposits on the injectors of two vehicles fueled with WCOB and mineral diesel in the first phase of 7500 km road test during winter. Second phase of the study used viscosity improvers added to biodiesel. It was observed that the injectors were relatively cleaner than mineral diesel fueled engine's injectors [156]. Tziourtzioumis et al. [157] investigated an engine with CRDI fuel injection system for 30 h with B70 under steady-state and transient conditions, however they reportedly experienced starting problems. Biodiesel used in this study was a fatty acid methyl ester produced using 40% rapeseed oil, 30% soybean oil and 30% recycled cooking oil. They reported existence of significant quantity of dense slurry, rich in fatty esters in the fuel filters. They also reported that injector nozzle holes were covered by heavy and oily carbonaceous deposits, making them function in an erratic manner [157]. Armas et al. [294] compared the effect of ethanol–biodiesel–diesel blend (7.7%–27.69%–69.61%) and baseline mineral diesel in a CRDI system equipped engine in a 600 h accelerated durability test. This study showed that use of ethanol–biodiesel–diesel blend and baseline diesel had similar effect on durability of the fuel injection pump components and injector nozzle [294]. Pehan et al. [295] also reported identical carbon deposits in the combustion chamber of biodiesel and diesel fueled engines. Sem [296] reported piston skirt deposits and ring groove deposits in four biodiesel fueled engines and these deposits were absent in diesel fueled engines.

Dhar and Agarwal [292] reported higher carbon deposits on piston top, cylinder head and injector tip for B20 fueled engine compared to diesel fueled engine during the endurance test, primarily due to higher carbon residue and lower volatility of biodiesel (Fig. 27). Results for higher carbon deposits on piston top were also confirmed by measuring the weight of carbon deposited on the piston tops (Fig. 28).

It was reported that lower volatility of biodiesel increased the heat release during late combustion phase, leading to lesser time available for in-cylinder combustion/ oxidation of soot. This resulted in condensation of unburned/ pyrolyzed combustion product deposits on the combustion chamber walls, piston top and injector, as seen in Fig. 28 [292]. In another experimental study, Agarwal et al. [293] reported substantial reduction in carbon deposits on the piston top of B20 fuelled engine compared to mineral diesel fuelled engine.

4.6. Material compatibility

Automotive manufacturers face a major challenge related to compatibility of automotive engine components with biodiesel. Its different chemical structure (influenced by both feedstock and remnants of the production process) than mineral diesel renders it with certain undesirable properties such as auto-oxidation, hygroscopic nature, higher electrical conductivity, polarity and solvency, which can potentially enhance corrosion of metallic parts and degradation of elastomers. This leads to failure of engine parts, both static and dynamic, made from ferrous and non-ferrous metals along with elastomers and coatings. These negative aspects related to corrosion, tribo-corrosion, and instability of biodiesel upon exposure to metals, combined with other environmental factors are some of the main challenges yet to overcome, because use of biodiesel is expected to improves durability of engines primarily due to lower soot deposition on components and inherent lubricity, compared to mineral diesel. However, further studies on biodiesel engine endurance need to be carried out in order to clearly elucidate mechanisms of wear, since these aspects are not yet sufficiently understood based on information available in open literature. Some studies are summarized in the following paragraph.

Fazal et al. [297] compared corrosive characteristics of mineral diesel and Palm biodiesel for automotive materials. They carried out measurements of weight loss and corrosion rates and reported that Palm biodiesel was more corrosive to copper and aluminum components compared to mineral diesel [297]. Stainless steel was found to be compatible with biodiesel [297]. Kaul et al. [298] compared the corrosiveness of biodiesels (Jatropha, Karanja, Mahua and Pilu) vis-à-vis mineral diesel on piston and liner materials. They concluded that biodiesel derived from Pilu was most corrosive, followed by Jatropha, while Karanja and Mahua biodiesels showed lesser corrosion than mineral diesel [298]. Besee and Fay [299] reported that biodiesel was not compatible with nitrile rubber, nylon 6/6 and high density poly-propylene. However Teflon and Viton showed reasonably good compatibility with B100 [299]. Van Gerpen et al. [300] reported hydro-peroxides formation during oxidation of biodiesel, which were unstable compounds and attacked elastomers. Schumacher et al. [301] also reported degradation of rubber components of the FIE upon exposure to biodiesel and confirmed compatibility of biodiesel with Viton (fluorinated rubber), steel, aluminum and nylon reinforced tubing.

4.7. Lubricating oil degradation

Lubricating oil properties vary with usage due to thermal and mechanical stressing, which alters the chemical composition of

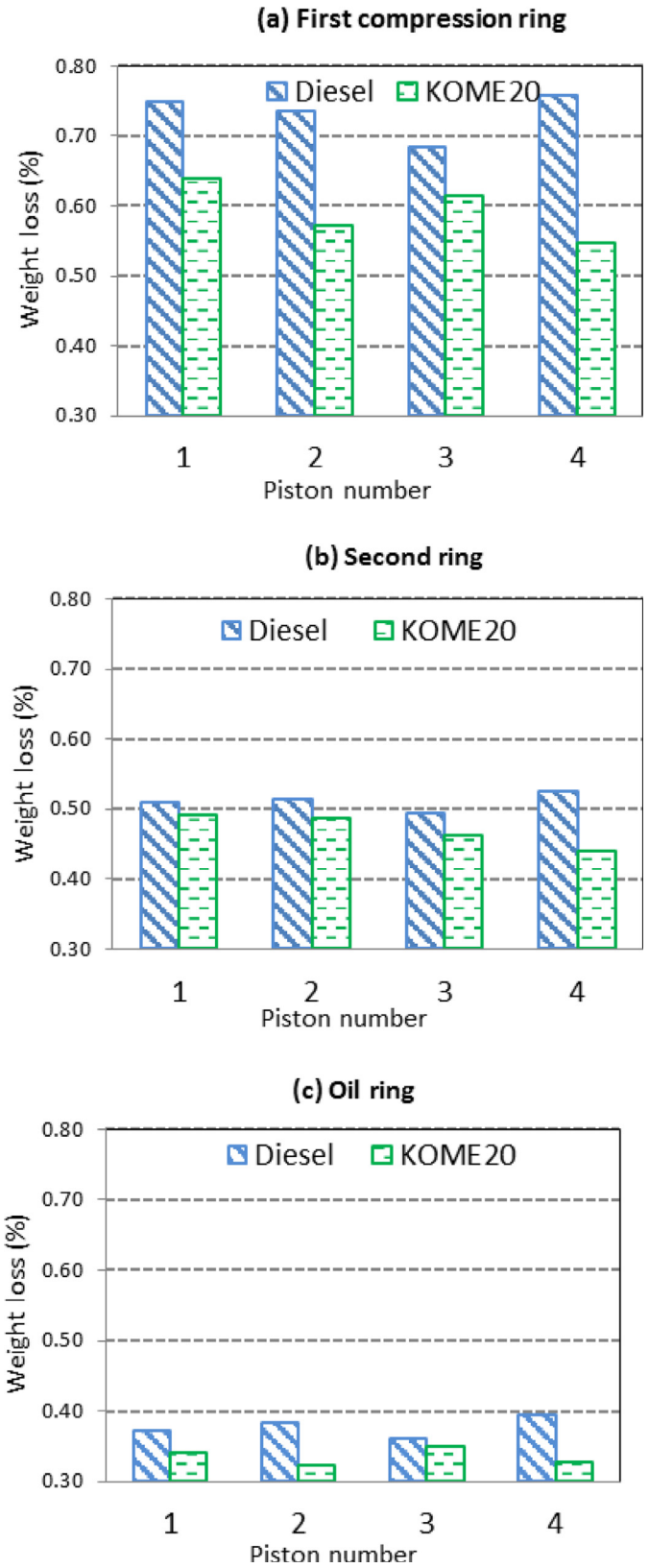


Fig. 26. Piston ring weight loss due to wear for (a) First compression ring (b) Second compression ring, and (c) Oil ring from mineral diesel and B20 fueled engines (Reprinted from [292], with permission of Elsevier).

lubricating oil and adds contaminants. These contaminants include (i) chemical constituents such as oxidation products and acids formed due to combustion, (ii) particles such as ambient dust and dirt, (iii) metallic wear debris, and (iv) combustion generated soot

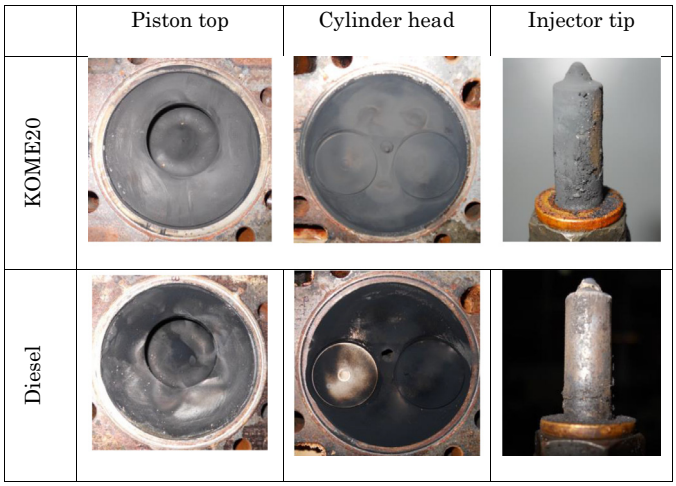


Fig. 27. Carbon deposits on the piston top, cylinder head and injector tip of mineral diesel and B20 fueled engines (Reprinted from [292], with permission of Elsevier).

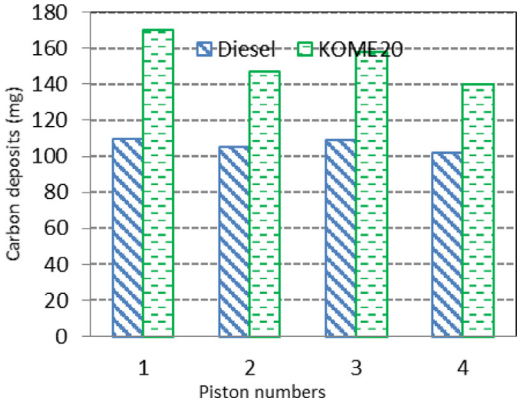


Fig. 28. Carbon deposits on the piston top of mineral diesel and B20 fueled engines (Reprinted from [292], with permission of Elsevier).

[302]. Lubricating oil dilution by fuel is affected by variations in physical properties of the test fuel, such as biodiesel or mineral diesel. Biodiesel, which contains oxygen and double bonds in its molecular structure, is more reactive than mineral diesel. Therefore, effect of biodiesel on lubricating oil degradation needs to be evaluated in a long-duration engine endurance study. Some studies experimentally evaluated lubricating oil degradation in long-duration tests in static engine tests as well as vehicle tests [177,291,296,303–307].

There are few studies, which explored the effect of biodiesels on the lubricating oil degradation in vehicles. Experiments were conducted to investigate the effect of RME and UVOME on engine durability in field trials of ten vehicles spanning over 100,000 km [177]. Lubricating oil samples were drawn and analyzed at a regular interval after every 7500 km. No difference in degradation of the lubricating oil was observed [177]. Staat et al. [303] conducted field trials spread over 3 years on 2000 vehicles in France, which were using RME. For the vehicles operating with more than 50% RME in the test fuel, slightly higher reduction in lubricating oil viscosity with usage was reported however there was no significant effect of RME blending on oil change intervals [303]. They also reported that for more than 30% RME blends, although reduction in lubricating oil viscosity was observed but wear and cleanliness of RME fuelled engines were as good as the reference fuel (Baseline diesel) or even better [303]. Lin et al. [308] investigated the effect of test fuels on lubricating oil degradation over 300 h (18,000 km) operation of a heavy-duty diesel engine/ vehicle fuelled with Palm biodiesel blends. Lubricating oil viscosity at 40 °C for diesel fuelled engine after 300 h reduced to

95.1 cSt from the initial value of 107 cSt. Total alkaline number (TAN) increased to 8.24 mg KOH g^{-1} from the initial value of 7.89 mg KOH g^{-1}. For B100 and B20, viscosity of lubricating oil reduced to 96.8 and 96.1 cSt respectively after 300 h [308]. Total alkaline numbers of B100 and B20 fuelled engine's lubricating oils were 8.26 and 8.05 mg KOH g^{-1} respectively. There was no significant negative influence of Palm biodiesel on the lubricating oil degradation [308]. Reece and Peterson [309] reported acceptable levels of trace wear metal concentrations in the lubricating oil samples drawn from mineral diesel and B20 (RME) fuelled vehicles in 80,000 km field trial of two pickups.

There are several studies reported in open literature, which also explored the effect of biodiesels on the lubricating oil degradation in engines. Agarwal [306] studied for the effect of B20 (Linseed oil methyl ester) on the tribological properties of lubricating oil in a 512 h endurance test. Lower fuel dilution was observed in lubricating oil sample drawn from biodiesel fuelled engine, which was also confirmed by measurement of viscosity and flash point of the lubricating oil samples [306]. Differential scanning calorimetry (DSC) studies of the lubricating oil samples indicated higher oxidation of lubricating oil samples drawn from B20 fueled engine [306]. In another experimental study, Agarwal et al. [293] confirmed lower wear of B20 fuelled engine by analyzing the lubricating oil samples. Lower ash content of used lubricating oil drawn from B20 fuelled engine indicated lower wear debris [293]. Sinha and Agarwal [305] also reported lower fuel dilution of lubricating oil in case of B20 fuelled engine vis-à-vis mineral diesel fuelled engine. They reported higher lubricating oil density and lower moisture content in the lubricating oil samples drawn from B20 fuelled engine compared to samples drawn from diesel fueled engine [305]. Resinous content in the lubricating oil samples was calculated by finding the difference in pentane and benzene insoluble [310]. Lower resinous content in B20 fuelled engine suggested relatively lower lubricating oil degradation over time. Thornton et al. [310] reported comparatively higher fuel dilution of lubricating oil in B20 (soy biodiesel) fuelled engine compared to mineral diesel fuelled engine but there was no trace of any biodiesel related additional wear [310].

Analysis of trace metals present in lubricating oil provide useful information about wear of engine components [303,311]. Sinha and Agarwal [291] reported relatively lower trace metals (Fe, Cr, Cu, Zn, Ni and Mg) in the lubricating oil samples drawn from B20 (Rice bran oil methyl ester) fueled engine (4-Cylinder transportation engine) compared to mineral diesel fueled engine in a 100 h endurance test (Fig. 29). However, Pb and Al were found to be in slightly higher concentration in the lubricating oil drawn from B20 fueled engine, which may be due to attack of biodiesel on paints and bearings [291, 311].

Agarwal et al. [312] reported relatively lower concentration of trace metals namely Fe, Cu, Zn, Mg, Cr, Pb, and Co in the lubricating oil samples drawn from B20 (Linseed oil methyl ester) fueled engine (Single cylinder constant speed engine) compared to mineral diesel fueled engine. In another study, Dhar and Agarwal [313] reported higher concentration of trace metals namely Fe, Cu and Mg in the lubricating samples drawn after 200 h from B20 (Karanja oil methyl ester) fueled engine (Variable speed MUV engine), compared to baseline mineral diesel fueled engine (Fig. 30).

Schumacher et al. [301] compared trace metals in the lubricating oil samples drawn from a B100 (SME) fueled engine and baseline mineral diesel fueled engine. They reported lower concentration of Pb, Fe and higher concentration of Si in the lubricating oil samples drawn from biodiesel fueled engine [301]. Concentrations of Cu and Cr were comparable in the lubricating oils samples though [301]. Raadnui and Meenak [314] reported same level of trace metals in the lubricating oil samples drawn from the engine using refined Palm oil and mineral diesel. Replacing diesel with biodiesel reduced wear of Al, Fe, Cr and Pb containing components in the engine [315].

Sem [296] also evaluated the performance of different lubricating oils in biodiesel fueled engines. They reported that synthetic lubricating oils were more stable, and more responsive to the additives used for extending the residual useful life of the lubricating oil. Higher additive levels in the lubricating oils contributed to reduction in piston skirt deposits in B100 fueled engine [296].

Biodiesel has many advantages and at the same time, some disadvantages. Amongst the advantages, biodiesel can be used in CI engines without any major hardware modifications, however there are some issues (disadvantages) because of properties of biodiesel, which are significantly different from mineral diesel. Some of the disadvantages are attributed to dilution of lubricating oil by fuel (biodiesel), which may consequently lead to oil related failures in the engine. Engine oil dilution by biodiesel is caused by its relatively lower volatility and lower oxidation stability compared to mineral diesel. With breakdown of biodiesel molecules, both oxidation and polymerization of unsaturated constituents of fuel and lubricating oil base-stock increases. There is always a possibility of unburnt biodiesel entering the lubricating oil sump along with blow-by gases, which eventually gets oxidized, promoting lubricating oil thickening and consequent degradation. This is often followed by severe sludge precipitation and significant loss of dispersion of carbon deposits. On the other hand, lubricating oil thinning can also take place, which may be due to excessive fuel dilution of lubricating oil or shear of polymers (additives) used as viscosity modifiers. Apart from this, certain trace metals such as Cu and Pb may leach out from the bearings due to effect of biodiesel and contaminate the lubricating oil. Since the extent of oil deterioration depends on engine operating conditions, oil performance grade, engine type, and engine condition, hence the service life span of lubricating oil while using biodiesel is not well understood. Possible incompatibility issues between lubricating oil and biodiesel need to be studied and suitable

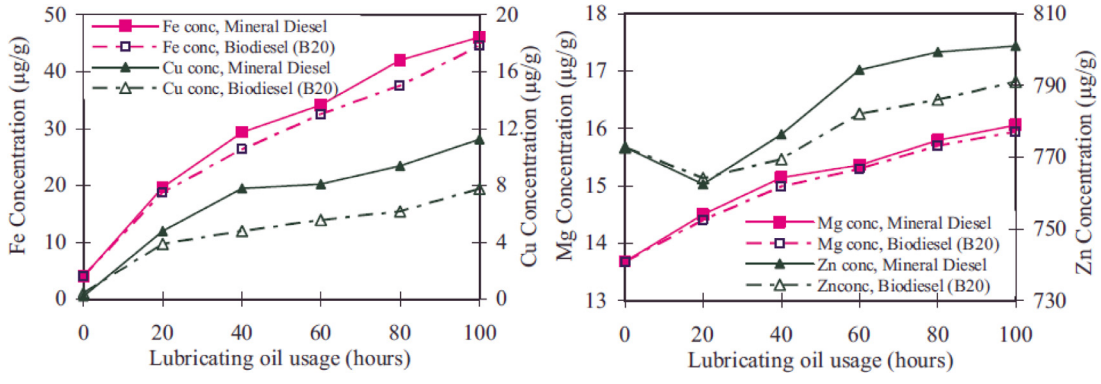


Fig. 29. Concentration of trace metals in lubricating oil in a 100 h test (Reprinted from [291], with permission of ASME).

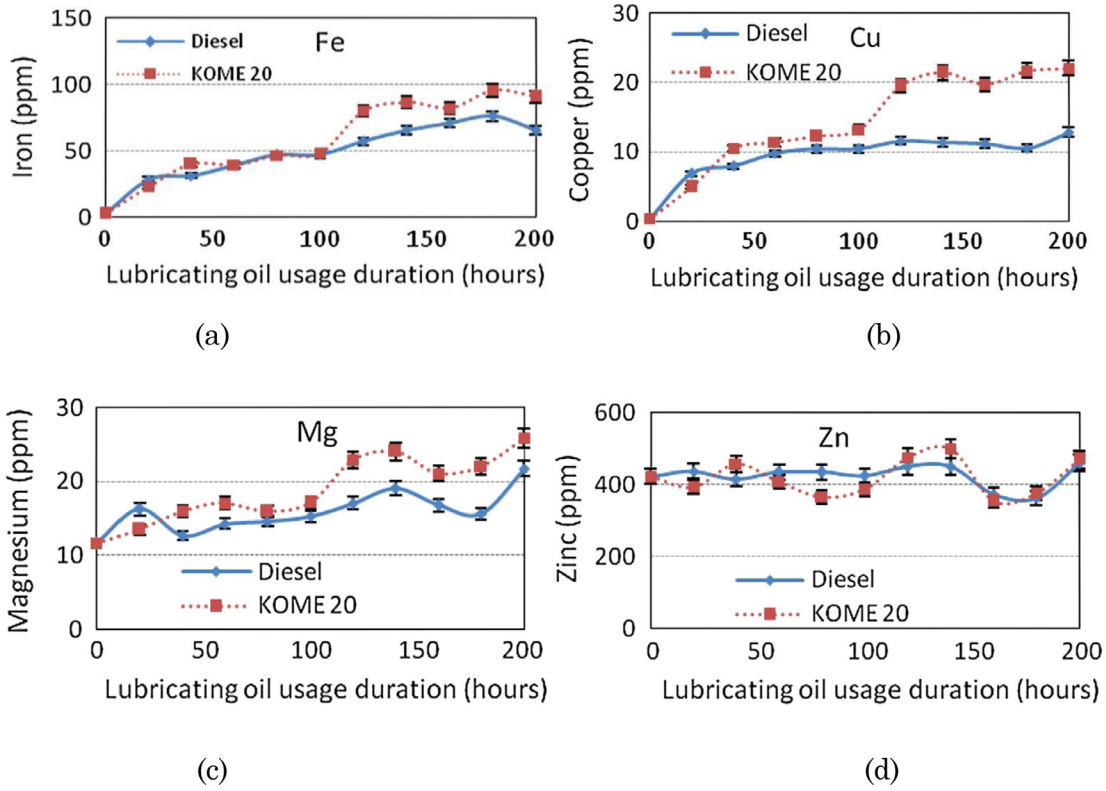


Fig. 30. Variation of trace metals in lubricating oil in a 200 h test (Reprinted from [313], with permission of Elsevier).

biodiesel specific additive package need to be developed. For this, experimental studies to understand complicated physico-chemical processes between modern engine lubricating oils and biodiesel need to be understood well.

5. Conclusions

This review article is an attempt to provide a comprehensive and updated scenario in biodiesel research space covering several aspects related to biodiesel production, utilization in IC engines, engine performance, and combustion studies, and emission characteristics, both gaseous and particulate. This article also provides a more complete picture of research undertaken in past three decades related to long-term engine durability investigations of biodiesel, effect of biodiesel on fuel injection system, carbon deposits, material compatibility, wear and lubricating oil degradation, in addition to economic analysis. Approx. 95% of biodiesel in the world is produced using edible vegetable oils, which increases its cost as well as the cost of food due to reduced availability of vegetable oils. Non-edible crops can be potentially cultivated in many parts of the world, on huge swaths of waste land available. This will reduce deforestation rate and avoid competition of biofuels with the food crops. With global targets of at least 10% biodiesel usage by 2020, it makes economic sense to carry out research and exploit biofuels derived from waste cooking oils, non-edible oils, and algal biomass to offset its production costs compared to mineral diesel.

Base-catalyst transesterification process has emerged to be superior to acid catalyzed transesterification and enzymatic transesterification processes for large-scale biodiesel production. Homogeneous alkali catalyzed transesterification, homogeneous acid catalyzed transesterification and two-step transesterification process involving acid-catalyzed esterification followed by base-catalyzed transesterification are the three most popular methods of biodiesel production using homogeneous catalysts. For improving the process economics and making the production process more environment friendly, research efforts are focusing on development of recyclable heterogonous solid catalysts. Use of enzymatic catalysts for transesterification of triglycerides for biodiesel production is still in research phase and the technology is not matured enough to be deployed for commercial production of biodiesel economically. The future of this route of biodiesel production is essentially dependent on reducing the production cost of enzymatic catalysts, which could deliver higher biodiesel yield. Biodiesel production using transesterification of triglycerides requires purification steps for catalyst removal, which increases the production cycle time, reduces biodiesel yield and generates large quantity of contaminated waste water. All these factors increase the cost of final product i.e. biodiesel. Supercritical alcoholysis is another method of biodiesel production, which can potentially overcome some of these issues. Absence of pre-treatment steps, soap removal step and catalyst removal step significantly reduce the cost of biodiesel plant however the operating cost of the plant increases because of use of high temperature and high pressure process, which is the main drawbacks of using supercritical alcoholysis for commercial biodiesel production. However, there is by and large agreement in the scientific community that supercritical alcoholysis process has great potential for production of high quality biodiesel at cheaper cost therefore more intense research effort is required to bring down the process temperature and pressure, thereby the energy input for biodiesel production at a commercial scale. Biodiesels produced from various feedstocks have almost identical physical, chemical and thermal properties as that of mineral diesel. However, production cost of biodiesel from vegetable oils remains the main barrier for large-scale replacement of mineral diesel by biodiesel. Hence the immediate research focus should be on process improvements and innovations; and making the feedstocks available in larger quantities economically for long-term energy sustainability. In the interim period, animal fat and waste cooking oils offer an opportunity to reduce biodiesel production cost however their availability is far below the demand for biodiesel. Therefore with limited land resources, it is important to consider

deployment of more productive crops, which can accrue oil and can be grown on nutrient deprived soils, fallow and marginal lands. LCA studies showed that generally biodiesel usage positively contributes to GHG emission reduction and it had net energy ratio higher than 1.3, which is favorable.

Almost all experimental studies reported successful operation of CI engines with biodiesel derived from a variety of feedstocks and their blends with mineral diesel in short duration engine tests. There are several scientific studies, which covered long-duration endurance tests on biodiesels and blends as well. Variations in performance, emissions and combustion characteristics of the engines using biodiesel with respect to conventional mineral diesel considerably depends on biodiesel properties, biodiesel blend percentage and engine technology used, with special emphasis on fuel injection technology, FIP and possibility of having split injection. Brake power output/ torque generated by the engines fueled by biodiesel produced from different feedstocks is reportedly lower than baseline mineral diesel fueled engines, barring few exceptions. BSFC of biodiesels and blends is generally slightly higher than mineral diesel in most experimental studies and it depends on the FIP, injection strategy and fuel injection technology employed in the engine to a great extent. Biodiesel derived from different feedstocks and their blends with mineral diesel and/ or alcohols can deliver slightly higher BTE than baseline mineral diesel, except very few studies, which showed lower BTE of biodiesel. Nevertheless, engine performance of biodiesels is conclusively comparable to that of baseline mineral diesel.

CO emission was generally lower for biodiesel and blends compared to baseline mineral diesel. The extent of reduction remained a function of biodiesel feedstock, C/ H ratio of the test fuel (compared to mineral diesel), fuel viscosity, oxygen content, cetane number, FIE type, FIP, fuel injection strategy and engine operating parameters. General trend suggests that usage of biodiesel and blends lead to substantial reduction in THC and CO emissions in lower FIP engines however this advantage of lower CO and THC emissions is reduced in modern CRDI engines, which operate at relatively higher FIP. CRDI engines are ECU controlled engines and can be extensively optimized for the test fuel properties. Hence it is essential to recalibrate the ECU for improving the emission characteristics of biodiesel and blends vis-à-vis baseline mineral diesel. NOx emission increase from biodiesel fueled engines can't be quantitatively determined by a change in a single fuel property. Rather it is a result of number of coupled mechanisms, whose effects reinforces or cancels one another under different engine operating conditions, depending on specific combustion and fuel characteristics. Fuel-air mixtures closer to stoichiometric at the time of ignition and in the standing premixed auto-ignition zone near the flame lift-off length appear to be a key factor in helping NOx increase from biodiesel fueled engine under all conditions. These differences result in higher local and average in-cylinder temperatures, lower radiative heat losses, and shorter and more-advanced combustion. All these factors increase thermal NOx formation. Differences in prompt NO formation and species concentrations resulting from fuel and jet-structure changes also play important role in higher NOx formation from biodiesel. The particle size-number distribution and chemical composition of particulate varies greatly, depending on engine type, engine speed, fuel composition, lubricating oil formulation, and emission control technology employed in the engine. Generally, biodiesel fueled engines emitted lower PM mass emissions than mineral diesel fueled engines. B100 reduced the accumulation mode particle numbers and produced higher number of nucleation mode particles compared to ULSD at higher FIP. Higher nucleation mode particle formation was assumed to be because of higher SOF. Long-chain fatty acids methyl esters (FAME) of biodiesels are chemically more reactive than hydrocarbon molecules of mineral diesel. This leads to possibility of formation of higher number of pollutant species in the combustion chamber of biodiesel fueled engine. Many of these pollutant species are unregulated and have severe health effects. Impact of unregulated emission species such as carbonyl compounds and PAHs from biodiesel and blends can be significant though there is limited data available in open literature, which is often contradictory. Nevertheless, these unregulated emissions amongst others are of greater importance as some of the species are toxic, mutagenic, and even carcinogenic to humans. Most research studies showed that emissions of aromatic and polyaromatic compounds from biodiesel were lower compared to mineral diesel however they were influenced by engine operating conditions such as engine load, driving cycle, and operating mode etc.

Higher viscosity of biodiesel results in relatively longer combustion duration. Higher kinematic viscosity of biodiesel significantly affects fuel spray, droplet size distribution, droplet evaporation rate, and spray atomization process, resulting in slower burning therefore leading to longer combustion duration. However, the opposite trend can be realized by modifying certain fuel injection parameters, which can lead to shorter combustion duration in case of biodiesel compared to mineral diesel at low, medium and high load conditions. Lower energy content of biodiesel combined with the effects resulting from ignition delay and combustion duration, the HRR of biodiesel (due to lower heating value of the biodiesel) is relatively lower than mineral diesel, which reduces the peak pressure rise rate, peak cylinder pressure and power output.

Before large-scale implementation of biodiesel as alternate diesel fuel in transport sector, there are concerns about its compatibility with engine materials, FIE, and components due to its significantly different chemical composition compared to baseline mineral diesel, which need to be addressed. Physical wear measurement of engine components showed relatively lower wear of valves, pistons, piston rings, liners and small end bearing of the connecting rods in case of biodiesel fuelled engine compared to mineral diesel fuelled engine. Lower wear of piston rings was also confirmed by measuring weight loss after the completion of the endurance test. Up to 30% lower wear of vital engine components of biodiesel fuelled engine was attributed to additional lubricity properties of biodiesel. In addition to wear of components, there are carbon deposits in the engine combustion chamber, which form upon long-term usage. Higher carbon deposits on the piston top, cylinder head and injector tip for B20 fuelled engine compared to diesel fuelled engine during the endurance test, form primarily due to higher carbon residue and lower volatility of biodiesel. Biodiesel's different chemical structure (influenced by both feedstock and remnants of the production process) than mineral diesel renders it with certain undesirable properties such as auto-oxidation, hygroscopic nature, higher electrical conductivity, polarity and solvency, which potentially causes enhanced corrosion of metallic parts and accelerated degradation of elastomers. This leads to failure of costly engine parts, both static and dynamic, made from different ferrous and non-ferrous metals along with elastomers and coatings. These negative aspects related to corrosion, tribo-corrosion, and instability of biodiesel due to exposure of metals combined with other environmental factors are some of the huge challenges to be overcome before its large-scale implementation globally. Use of biodiesel improves durability of engine components though due to lower soot deposition and inherent lubricity, compared to baseline mineral diesel.

Experimental evaluatation of lubricating oil degradation in long-duration tests in static engines as well as vehicles showed that synthetic lubricating oils were more stable, and more responsive to the additives used for extending the residual useful life of the lubricating oil for biodiesel usage. Extent of oil deterioration depends on engine operating conditions, oil performance grade, engine type, engine condition, and life span of lubricating oil. Possible incompatibility issues between lubricating oil and biodiesel need to be studied and suitable biodiesel specific additives need to be developed. Experimental studies to understand complicated physico-chemical

processes taking place between modern engine lubricating oils and biodiesel need to be undertaken.

In summary, biodiesel has emerged as an environment-friendly alternative fuel candidate globally, which can be successfully and efficiently used in existing CI engines with slight modifications in engine hardware and ECU recalibration, depending on the engine technology used. Biodiesel delivers satisfactory engine performance such as superior thermal efficiency, fuel economy and reduced regulated, unregulated and particulate emissions compared to mineral diesel. However more research is required for understanding biodiesel's compatibility with modern engines using flexible FIE using higher FIP, developing dedicated lubricants, interaction of biodiesel with exhaust gas after-treatment technologies and developing cheaper commercial biodiesel production processes.

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