Unregulated and Regulated Emissions from Biodiesel Fuelled CRDI SUV Engine

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Abstract

Use of biodiesel from non-edible vegetable oil as an alternative fuel to mineral diesel is attractive economically and environmentally. Diesel engines emit several harmful gaseous emissions and some of them are regulated worldwide, while countless others are not regulated. These unregulated species are associated with severe health hazards. Karanja biodiesel is a popular alternate fuel in South Asia and various governments are considering its large-scale implementation. Therefore it is important to study the possible adverse impact of this new alternate fuel. In this study, unregulated and regulated emissions were measured at varying engine speeds (1500, 2500 and 3500 rpm) for various engine loads (0%, 20%, 40%, 60%, 80% and 100% rated load) using 20% Karanja biodiesel blend (KB20) and diesel in a 4-cylinder 2.2L common rail direct injection (CRDI) sports utility vehicle (SUV) engine. Concentrations of regulated emissions namely CO, CO_2, HC and NO_X, in the engine exhaust were measured using raw exhaust gas emission analyzer. CO and THC emissions were emitted only at lower engine loads. Higher NO_X emissions were seen for KB20 compared to diesel, particularly at higher engine loads. Fourier transform infrared (FTIR) emission analyzer measured various unregulated emission species to gauge their possible environmental and health impact. Alkanes, ethylene, acetylene and propylene, aldehydes were found only at lower engine loads and with increasing load, almost negligible concentrations were detected. Most unregulated emissions such as n-butane, n-octane, ethylene, aldehydes (formaldehyde and acetaldehyde), formic acid, benzene, toluene, SO_2 etc. were observed to be lower for KB20 biodiesel blend compared to mineral diesel.

Introduction

Modernization and industrialization is changing the world energy scenario at a fast pace. Increased energy demand especially for automotive fuels has led to huge import of crude oil, which has resulted in increased environmental concerns as well as increased forex expenditure in developing world. In addition, fossil fuel combustion products cause global warming due to harmful emissions such as carbon dioxide (CO_2), sulfur dioxide (SO_2), and nitrogen oxides (NO_X). Before the industrial revolution, earth's atmosphere had 280 ppm CO_2, which has risen to 380 ppm till 2007 and is estimated to be increasing by 2 ppm annually [1]. Based on these projections and calculations, it will take only 28 years to reach the threshold value of 450 ppm CO_2 [1]. Biodiesel usage could possibly help reduce CO_2 emissions into the atmosphere. This will involve cultivation of feedstock, harvesting, conversions of oil seeds into fuel and combustion in power generating units. This is primarily due to low carbon cycle time of biodiesel, because any CO_2 released from biodiesel combustion will be recycled by the next generation of crops [2]. Biodiesel is composed of mono alkyl esters (C14 to C20) derived from fatty acids via transesterification process, using a catalyst and a primary alcohol. Thus biodiesel is a comparatively more homogeneous fuel than diesel, which contains very larger number of hydrocarbons [3].

Biodiesel is considered to be an environmental benign fuel because its application causes lesser net CO_2 addition to the atmosphere. Rapeseed, soybean, palm, sunflower, coconut, linseed, Jatropha and Karanja are some of the oils, which are used to produce biodiesel [4]. In India, non-edible oils such as Jatropha and Karanja are most preferred feedstocks for biodiesel production [5]. In addition, biodiesel does not contain aromatic hydrocarbons, or polycyclic aromatic hydrocarbons (PAHs) [3]. Thus biodiesel offers major environmental and energy security benefits in addition to agriculture development, and job and wealth creation [6].

Barik and Sivalingam [7] performed experiments for Karanja methyl ester (KME) and the biogas obtained from the anaerobic digestion of Karanja (*Pongamia pinnata*) de-oiled cakes in a single cylinder, four-stroke, air-cooled, direct-injection (DI) diesel engine. The results were compared with baseline mineral diesel. It was reported that CO and HC emissions were lower, but NO emissions were higher for KME than mineral diesel [7]. Similar observations were reported by Lingafa et al. [8] for non-edible vegetable oils such as Tung (*Aleuritesfordii*), Karanja and Jatropha (*Jatropha curcas*) methyl esters compared to diesel.

Apart from regulated emissions like HC, CO and NO_X, diesel engine exhaust consists of several unregulated species such as alkanes, aldehydes, BTX (benzene, toluene and xylene), alcohols, ketones etc. [9]. Although a number of studies are available on regulated species, there is a gap in studies related to unregulated emissions, emitted by combustion of biodiesel, and biodiesel blends. Since, utilization of biodiesel is likely to grow in near future; there is a need to characterize regulated as well as unregulated emissions present in the biodiesel exhaust.

For the 2009 SAE Clean Snowmobile Competition, in addition to regulated exhaust species, FTIR analyzer measured a variety of non-regulated exhaust species that are of particular interest to the regulatory agencies. It was reported that most of the four-stroke non-regulated emissions were very low [10]. Tan et al. [11] reported that for light duty diesel engines, HCHO was observed to be very low. They observed that acetaldehyde emission decreased with increasing engine load, while SO_2 emissions increased with increasing engine load.

Bermudez et al. [12] studied regulated and unregulated gaseous emissions for a 4-cy linder, light-duty EURO-4 diesel engine. Three different biodiesels obtained from soybean oil, rapeseed oil and palm oil, a Fischer Tropsch (FT) diesel and an ultra-low sulfur diesel (ULSD) were compared. The test was performed as per the New European Driving Cycle (NEDC). They concluded that the use of biodiesel reduced aromatic hydrocarbon emissions like benzene to negligible levels. They reported increasing CH_4 emission at higher loads.

Fontaras et al. [9] studied impact of biodiesel on carbonyl compound emissions. They used blended fuels from five different feed-stocks in a Euro-3 CRDI passenger car over various driving cycles. It was reported that use of biodiesel in low blend concentrations showed minor effect on carbonyl compound emissions. However, certain biodiesels resulted in significant increase while others led to reduction. Increased emissions were reported from biodiesels derived from rapeseed oil (approx. 200%) and palm oil (approx. 180%). Highest increase was observed in emission of formaldehyde and acroleine/ acetone. Agarwal [2] suggested that lack of aromatic hydrocarbon (benzene, toluene, etc.) in biodiesel is the main reason for lower non-regulated emissions such as ketone, benzene, etc.

Cheung et al. [13] conducted research for BTX emissions from a CI engine at five engine loads at 1800rpm using Euro V diesel, biodiesel (B100) and biodiesel blends with 5%, 10% and 15% methanol. Biodiesel showed lower BTX emissions compared to diesel because of higher oxygen content in biodiesel, which improved combustion and promoted the oxidation of benzene. They also observed that the BTX emissions decreased with increasing engine load.

Use of edible oils as alternate fuel has caused steep rise in its prices and created gap in its demand and supply. Therefore Asian countries are exploring non-edible oils such as Jatropha and Karanja as biodiesel feedstocks. These are wild plants/ trees, which can grow in arid, semi-arid and waste-land. Karanja is one of the tree-borne, nitrogen fixing trees (NFTs), which produces seeds with 30-40% oil content [14]. Its de-oiled cake is excellent organic manure, which helps retain soil moisture [15]. This plant has potential for large-scale vegetable oil production, required for a sustainable biodiesel industry. Panday et al. used a military engine (585 kW) fitted with a compression ignition diesel injection (CIDI) system and used Karanja oil methyl ester (KOME) and Jatropha oil methyl ester (JOME) as test fuel. They concluded that KOME performed better than JOME in terms of engine emissions [15].

Although data is available on the effect of biodiesel on regulated emissions (i.e., HC, CO, NO_X, and particulates), most of this data was generated using older technology engines. Very few studies detailing exhaust characterization of biodiesel beyond regulated pollutants are available in open literature. Therefore in this study, exhaust emissions are characterized for regulated as well as unregulated emissions from a EURO-4 CRDI SUV diesel engine fuelled with mineral diesel and 20% blend of Karanja biodiesel with mineral diesel (KB20). Various unregulated gaseous emission species in the exhaust were analyzed by a Fourier Transform Infrared (FTIR) emission analyzer (Horiba; MEXA-6000FT-E). One of the primary advantages of an FTIR analyzer is its ability to measure a multitude of non-regulated exhaust species, which are of key interest to the regulatory agencies. These additional species include ammonia (NH_3), nitrous oxide (N_2O), alcohols (CH_3OH and C_2H_5OH) and aldehydes such as acetaldehyde (CH_3CHO) and formaldehyde (HCHO).

Experimental Setup

The engine experiments were performed on a EURO-4 CRDI SUV diesel engine. The technical specifications and features of the test engine are given in Table 1.

Table 1. Technical Specifications of the Test Engine

Make/ Model	Tata/ DICOR 2.2L (BS-4/ Euro-4)
Engine Type	16 valves, Water cooled, CRDI, Turbocharged with After-cooler, Diesel Engine with EGR.
No. of Cylinders	4, In-line
Valve Mechanism	DOHC
Bore/Stroke	85 mm/ 96 mm
Cubic Capacity	2179 cc
Max. Power	103 kW @4000 rpm
Maximum Torque	320 Nm @1700-2700 rpm
Compression ratio	17.5
Firing order	1-3-4-2
FIE System	CRDI with 1600 bar max. injection pressure
Timing and Governing	ECU controlled

Engine was tested with OEM fitted close coupled catalytic converter (CCC), diesel oxidation catalytic converter (DOC), turbocharger with variable nozzle turbine (VNT) and an after-cooler. Test engine was coupled to an eddy current dynamometer (Dynomerk; EC300) for controlling engine speed and load. The water supply to dynamometer was having a maximum pressure of 0.6 bars and a minimum flow rate of 1.6 lps. Figure 1 shows the schematic of the experimental setup. Tests were performed on the CRDI diesel engine fuelled with mineral diesel and KB20. Various regulated and unregulated gaseous emission concentrations in the engine exhaust were analyzed by using a raw exhaust gas emission analyzer (Horiba; EXSA-1500) and FTIR emission analyzer (Horiba; MEXA-6000FT-E) respectively.

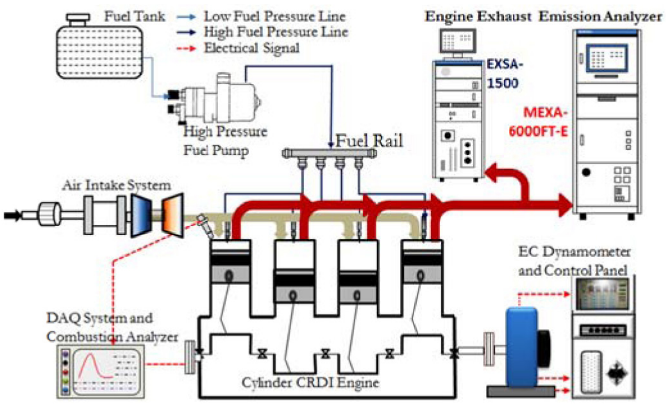


Figure 1. Schematic of CRDI diesel engine test setup.

In raw exhaust gas emission analyser, Total Hydrocarbons (THC) is measured by a Flame Ionization Detector (FID) analyzer. CO and CO_2 are measured by a Non-Dispersive Infrared (NDIR) analyzer. A Chemiluminescense Detector (CLD) was used to measure NOx emissions and a Paramagnetic Detector (PMD) was used for measuring O_2. In FTIR emission analyzer, a beam of infrared light is passed through the exhaust sample and the light intensity absorbed at each wavelength is recorded. MEXA-6000FT-E uses Fourier transform infrared spectrometry (FTIR) detection method for obtaining an infrared absorption spectrum of high resolution by a combination of an interferometer and high speed Fourier transform. Both the emission analyzers were equipped with a heated sampling line as per the specifications prescribed by Environmental Protection Agency (EPA) and have measuring accuracy of ± 1% of full scale for most species.

Emission Test Procedure

Engine was warmed up in order to ensure that the steady state condition of the test engine is attained before starting the exhaust sampling. Engine exhaust was sampled at six different engine loads (0%, 20%, 40%, 60%, 80% and 100%) at three engine speeds (1500, 2500 and 3500 rpm). After achieving the steady state, exhaust samples were drawn simultaneously for regulated and unregulated gas measurements. Emission measurements for various gaseous species were recorded through interface software of the instrument. The data was processed and analyzed for regulated and unregulated emission species. One data set per second was taken by the emission analyser and an average of 100 data points for a single test condition was reported for each data point.

Results and Discussion

Important physical properties of test fuels namely mineral diesel, KB100 and KB20 were measured in the laboratory (Table 2).

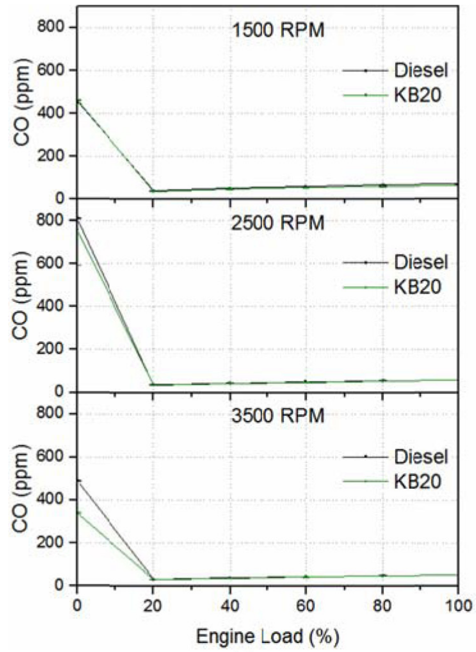
Table 2. Physical properties of test fuels

Test Fuel	Viscosity @ 40°C (cSt)	Density (g/cm^3)	LHV (MJ/kg)	Cetane Number
Diesel	2.71	0.822	43.06	51.2
KB20	3.31	0.835	42.52	--
KB100	5.79	0.887	40.36	50.8

Experimental results are discussed in two separate sections namely, regulated and unregulated emissions.

Regulated Emissions

Figure 2 shows the emission of CO and CO_2 in the exhaust from both test fuels. CO concentrations were nearly equal for both test fuels (approx. < 50 ppm) at all test conditions except no load. Therefore no statistical trend could be observed for CO emissions.



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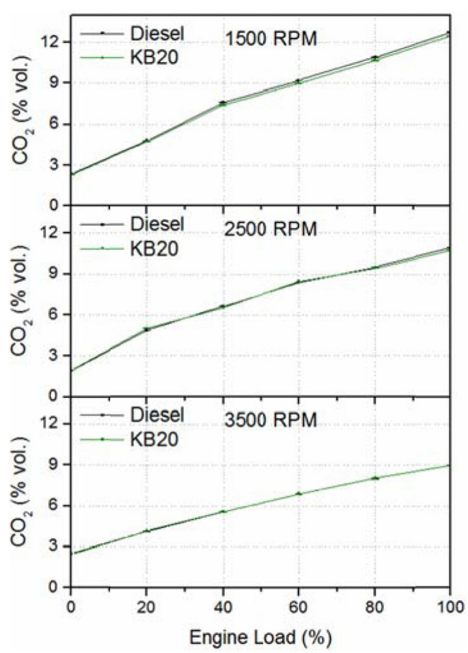

(b)

Figure 2. Emission of CO and CO_2.

Cosseron et al. [16], Poitras et al. [17] also observed no significant difference in CO emission between the reference fuel (diesel) and biodiesel blends. However, biodiesel contains fuel oxygen, which improves combustion and reduces CO emission in KB20 exhaust compared to diesel [18]. Also, test engine (EURO-4) is having an OEM fitted close coupled catalytic converter (CCC) and a diesel oxidation catalytic converter (DOC), which oxidize CO to CO_2. At lower engine load conditions, insufficient oxygen and lower exhaust gas temperatures reduce effectiveness of DOC, which is reflected in higher CO emissions [19] (Figure 2).

CO_2 emission increased with increasing engine load (Figure 2b) and it ranges from 2% to 13% at all tested engine speeds for both test fuels. With increasing engine load and engine speed, induced air flow rate and fuel injected quantity to the engine also increases, which leads to increased CO_2 emissions. Both test fuels showed similar trends for CO_2 for similar operating condition. Poitras et al. [17] also reported no change in CO_2 emissions for all test modes using biodiesel (canola methyl ester) blends and mineral diesel. CO_2 emissions increase with increasing engine loads due to higher oxidation of CO to CO_2 by DOCs at higher exhaust gas temperatures [19].

NO_x emissions mostly comprise of NO, NO_2 and N_2O, which are measured separately by FTIR emission analyzer. Total NO_X concentration was measured by conventional CLD analyzer. NO, NO_2, and N_2O emissions for both test fuels are shown in Figure 3. It was observed that NO increases with increasing engine load and reached a maximum at full load at all engine speeds for both test fuels. NO formation in the combustion chamber is highly dependent on combustion temperature, oxygen availability, compression ratio and the retention time for the reaction. NO formation was observed to be higher for KB20 compared to mineral diesel at higher loads and higher speeds, possibly due to fuel bound oxygen with Karanja biodiesel blend, which results in higher NO formation. Barik and Sivalingam [7] reported 12.2% higher NO from biodiesel (Karanja methyl ester) compared to mineral diesel.

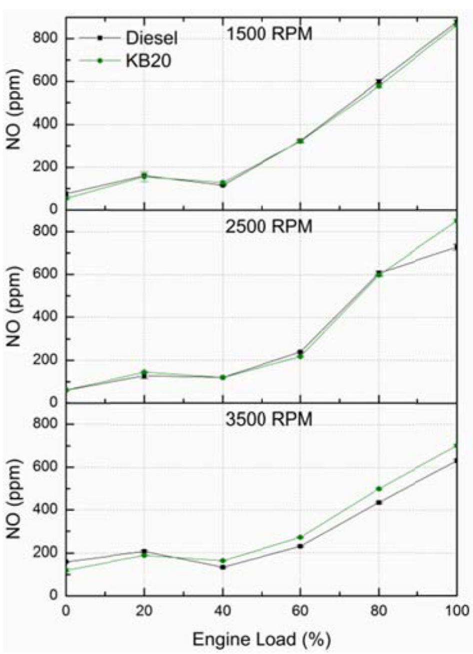

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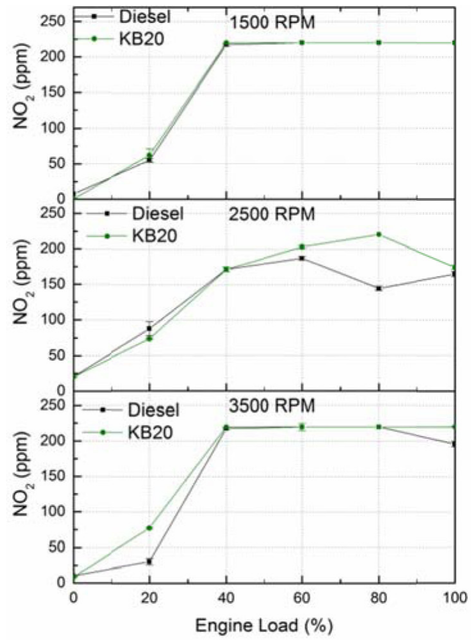
Figure 3.



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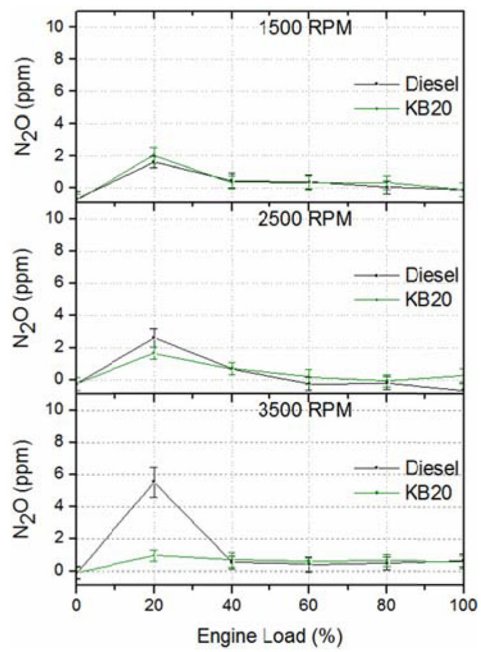


(c)

Figure 3. (cont.) Emission of NO, NO_2 and N_2O.

Figure 3b shows the NO_2 emissions for the two test fuels. It was observed that NO_2 formation increases with increasing engine load. Engine emitted NO_2 in range of 10 ppm at no load condition to 220 ppm at full load for both fuels at all engine speeds. NO_2 was observed to be over the measurement limit of the FTIR instrument. Poitras et al. [17] also reported that fraction of NO_2 does not vary significantly with biodiesel feedstock, or blend level. The effects of biodiesel on NO_2 emissions followed the same trends, as observed for NO_X emissions. Typical ambient N_2O concentration ranges from 3 to 3.5 ppm at most of the conditions, exhaust N_2O concentration was also observed to be in this range (Figure 3c). However, at 20% load, N_2O was observed to be higher for both fuels at all engine speeds.

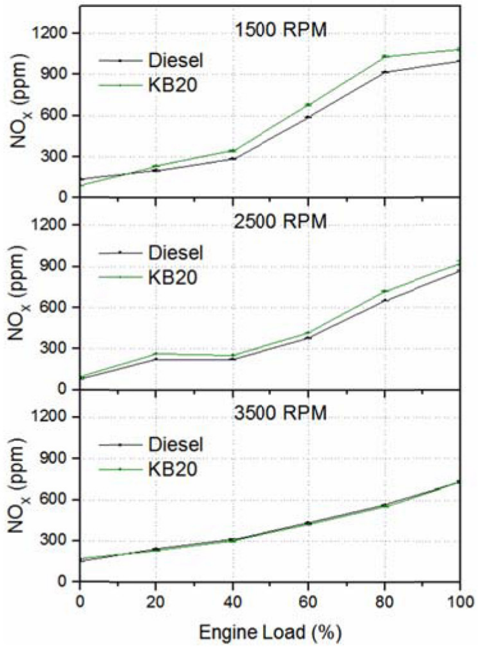


Figure 4. Emission of total NO_x.

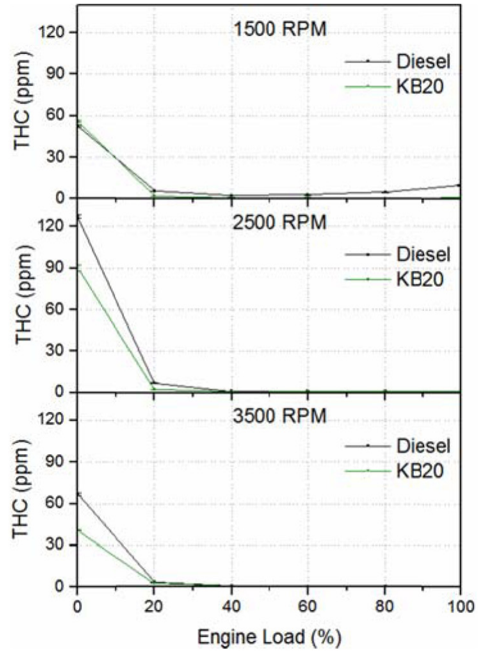


Figure 5. THC emission.

NO_X emissions increased with increasing engine load for all engine speeds for both test fuels (Figure 4). NO_X emission increases with increasing heat release rate. Comparison of NO_X emissions for KB20 and diesel shows almost similar trend. KB20 shows higher NO_X emissions, especially at low-to-medium speeds for equivalent operating conditions. Higher NO_X emissions produced in biodiesel combustion is influenced by many factors such as the physiochemical properties and molecular structure of biodiesel, adiabatic flame temperature, ignition delay time and injection timing. Thermal, prompt, and fuel NO_X are the common mechanisms for the formation of NO_X during combustion [20]. Among them, thermal and prompt are the dominant mechanisms of NO_X formation in biodiesel combustion. NO_X produced due to the reaction of atmospheric oxygen and nitrogen at elevated temperatures is termed as thermal NO_X [21]. Fenimore [22] suggested that the reactions of hydrocarbon radicals with molecular nitrogen are the main contributors to produce prompt NO_X. Garner and Brezinsky [23] found that the formation rate of CH radical is high for biodiesel combustion in diesel engine. As a result, it could be said that higher formation rate of free radicals is the prime reason for higher NO_X from KB20. At higher engine speed of 3500 rpm, NO_X emissions for both KB20 and diesel are almost similar. At higher engine speed, sufficient air is available for combustion, which compensates for the fuel bound oxygen of biodiesel. At high speeds, the time available for NO_X formation chemistry to take place also reduces, which results in reduced NO_X emissions. Also, EGR acts as additional diluent to the unburned gas mixture, thereby reducing the peak burnt gas temperature and NO_X formation rate. McGill et al. [24] also reported similar trend of higher NO_X emission with exception at higher speeds and at low load conditions. Poitras et al. [17] reported for all conducted test modes, canola biodiesel (CME) (B100) and soya biodiesel (SME) (B100) showed highest increase in NO_X emissions, while animal fat-based biodiesel, Tallow biodiesel (TME) (B100) on the other hand showed a reduction in all three test modes.

Figure 5 shows that for both test fuels and all test conditions except no load condition, THC concentrations were generally similar at or lower than the ambient THC concentrations. As such, the difference between the THC sample and ambient concentrations was very small, and often, below the detection limit of the HFID instrument of the emission analyzer. No statistical trends could be observed for THC emissions. The unburnt hydrocarbons (UHC) were produced due to incomplete combustion. The test engine was fitted with turbocharger, which ensures higher oxygen availability for complete combustion of fuels, which results in lower THC emissions. At no load, higher THC emissions were observed for diesel compared to biodiesel blend, possibly due to inherent fuel oxygen of biodiesel, which reduce THC emission from biodiesel blend.

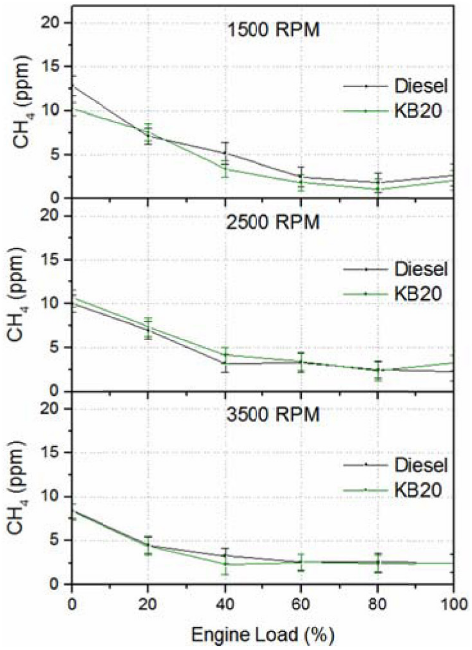
Similar trends were observed by Poitras et al. [17], and Agarwal et al. [25]. Barik and Sivalingam [7] also observed lower HC emissions with Karanja biodiesel compared to diesel. DOCs also oxidize hydrocarbons in the exhaust gas at higher engine loads [19]. However at lower engine loads, DOCs are not effective because of its temperature limitations therefore higher hydrocarbon emissions were observed in such conditions in the engine exhaust.

Unregulated Emissions

Saturated Hydrocarbons

Emission of methane (CH_4) and propane (C_3H_8) in the engine exhaust are shown in Figure 6. Methane is a strong greenhouse gas, which is thought to remain in atmosphere for 9-15 years [26].

CH_4 is 20 times more effective in trapping heat in the atmosphere than CO_2 over a 100-year period [26]. Lower combustion chamber temperature prevailing at lower engine load leads to formation of methane and propane. Methane can be generated by thermal cracking of paraffinic and olefin hydrocarbons [27]. At higher temperatures, there is a high probability of these emissions getting oxidized. Even though CH_4 and N_2O have a high global warming potential, both CH_4 and N_2O emission levels from the test engine operating on diesel and KB20 had a negligible GHG impact compared to total CO_2 emitted by these fuels.



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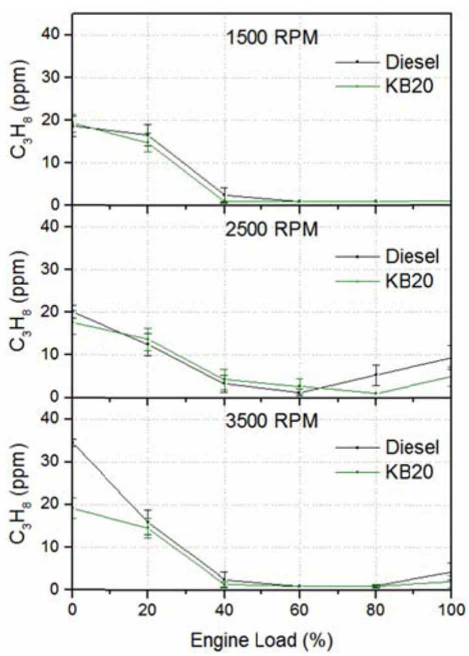
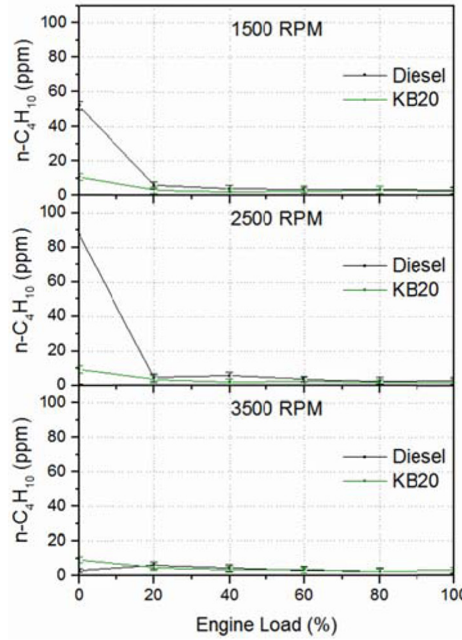


(b)

Figure 6. Emission of methane (CH_4) and propane (C_3H_8).

Figure 7 shows emissions of n-butane (n-C_4H_{10}) and isobutene (iso-C_4H_{10}). n-butane was observed to be relatively higher for diesel at no load condition for all engine speeds compared to KB20. Possible reason for this may be the presence of fuel oxygen molecules in biodiesel, which helps break long chain of hydrocarbons (C_{16} or bigger) present in mineral diesel.



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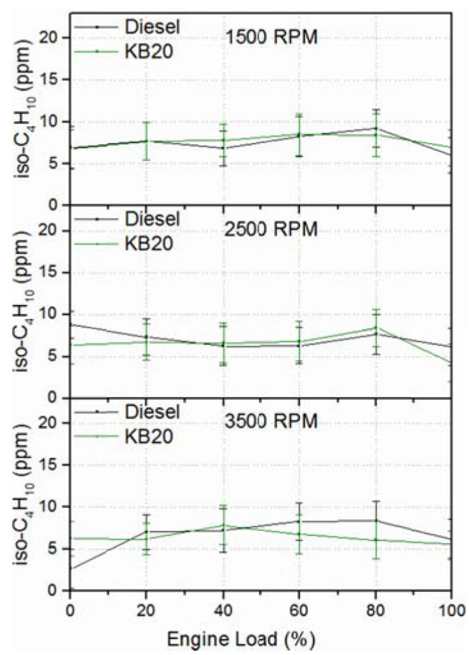

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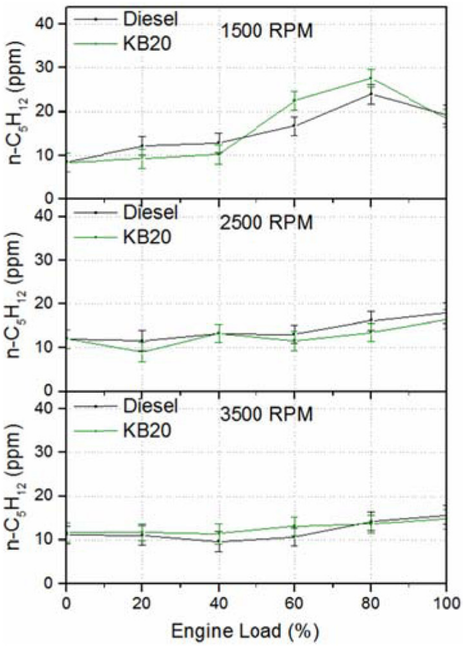
Figure 7. Emission of n-butane (n-C_4H_{10}) and isobutene (iso-C_4H_{10}).

At higher engine loads, increased combustion chamber temperatures lead to oxidation of n-butane, resulting in its low emission. Isobutene emission was obtained varying in the range of 3-9 ppm at all engine loads and speeds (Figure 7b). Emission levels are almost equal for most of the operating conditions for both test fuels.



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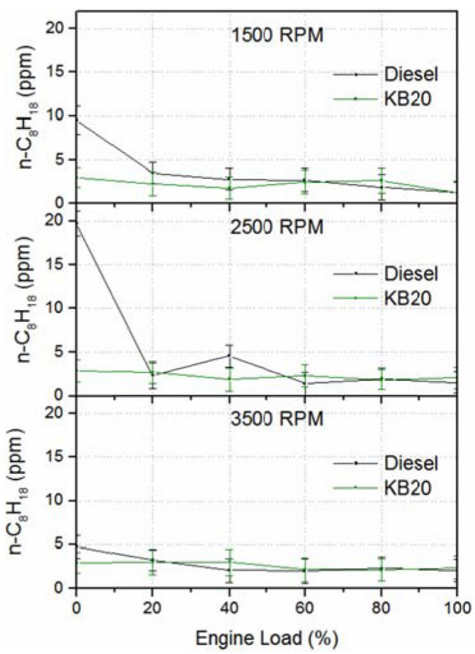

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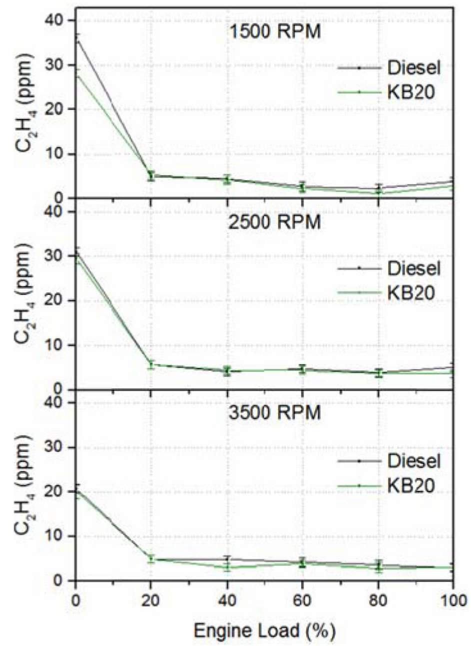
Figure 8. Emission of n-pentane (n-C_5H_{12}) and n-octane (n-C_8H_{18}).

It can be seen from figure 8a that n-pentane emission increased with increasing engine load. At no load and full load conditions, n-pentane emissions were almost similar for both test fuels. At intermediate loads, no exact trend was observed for both test fuels at different engine loads and speeds. It was observed from figure 8b that n-octane emissions were higher at no load for all engine speeds for diesel, which reduce to approximately 2-3 ppm at full load. The reduction in n-octane may be due to higher in-cylinder temperature at higher engine loads, which helps in superior oxidation of hydrocarbons. KB20 showed lower n-octane emissions compared to diesel at most engine operating conditions.

Unsaturated Hydrocarbons

Ethylene (C_2H_4), acetylene (C_2H_2) and Propylene (C_3H_6) emissions in the engine exhaust from the two test fuels are shown in Figure 9. These emissions were seen to be present in significant quantities only at no load condition and at medium loads. At higher engine loads, these emissions were negligible. Ethylene was present in higher concentration compared to acetylene and propylene. Ethylene plays an important role in ozone formation [28]. KB20 showed relatively lower emissions of these three species compared to mineral diesel. Ethylene, acetylene and propylene are the products of thermal decomposition of fuel, which lead to formation of polycyclic aromatic hydrocarbons (PAH), which is considered to be an important soot precursor [29].



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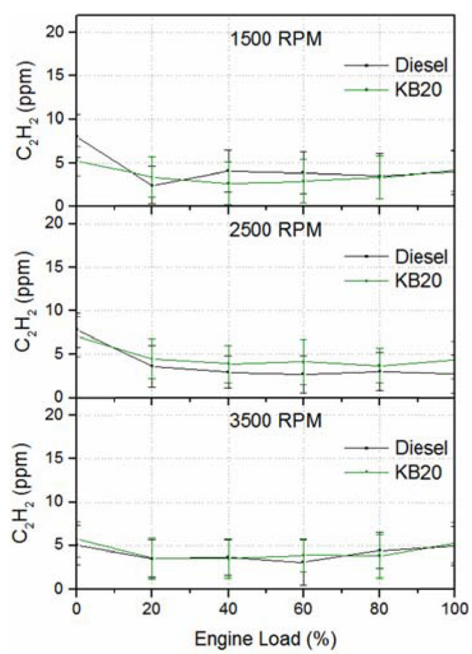

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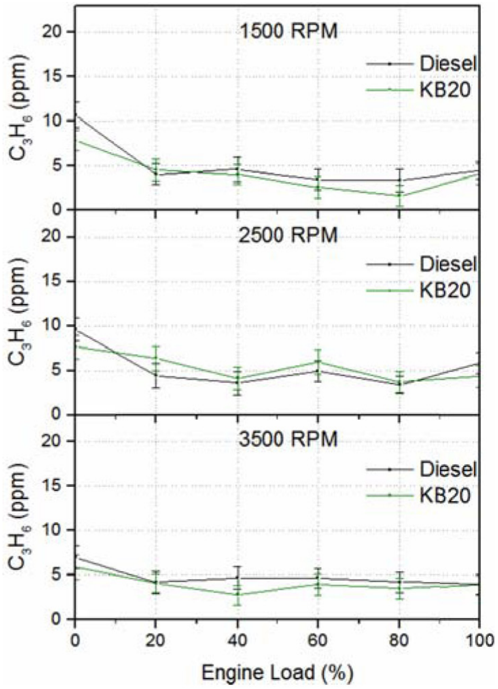
Figure 9. Ethylene (C_2H_4), Acetylene (C_2H_2) and Propylene (C_3H_6).



(c)

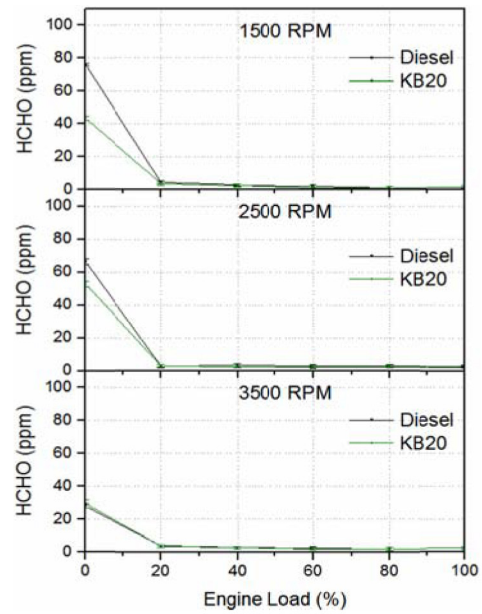
Figure 9. (cont.) Ethylene (C_2H_4), Acetylene (C_2H_2) and Propylene (C_3H_6).

Thermal cracking affects all long-chain paraffins. Thermal cracking involves breaking of bonds and formation of radicals. This subsequently leads formation of pairs of paraffins and olefins because the long chain hydrocarbons are shortened [30]. Olefins have greater tendency to split compared to paraffins, hence higher ethylene (C_2H_4) levels are emitted in the exhaust compared to lighter paraffin such as propylene (C_3H_6) [27]. Emissions of C_2H_4, C_2H_2 and C_3H_6 are strongly related to the combustion chamber temperature and fuel/air ratio.

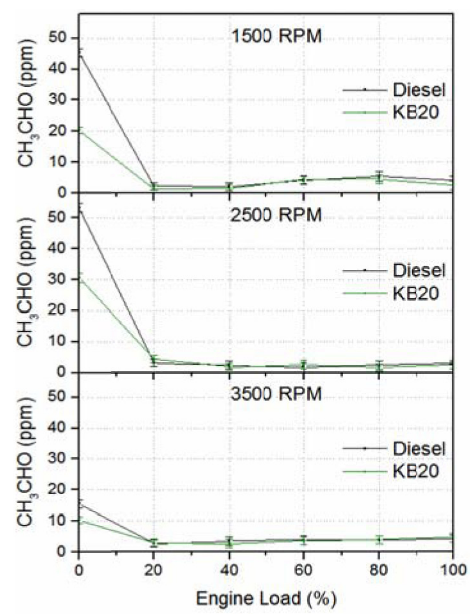
At high engine loads, higher combustion chamber temperature contributes to oxidization of the pyrolysis products, while higher fuel/air ratio leads to increase in formation of pyrolytic products [31]. Combined effect of these factors lead to lower emissions of these species at higher engine loads.

Concentrations of formaldehyde above 0.1 ppm in ambient air causes irritation in the eyes and mucous membrane, and can result in headache, watery eyes, burning sensation in throat, and difficulty in breathing [32]. These emissions are extremely important from human health point of view and because of their public nuisance value, especially in urban areas. Formaldehyde and acetaldehyde emissions from these two test fuels are shown in Figure 10. There was negligible difference observed in aldehyde emissions among these two test fuels except at the lowest engine loads. At low load conditions, aldehyde emissions were observed in significant quantity, which decreased with increasing engine speed as well as engine load. These were relatively lower for KB20 then mineral diesel. This indicates that relatively lower in-cylinder temperature and leaner fuel-air mixture regions at lower engine loads may lead to formation of formaldehyde and acetaldehyde. Aldehydes are intermediate combustion product originating from hydrocarbons or oxygenated compounds present in the fuel, and they decrease sharply as the engine load and the in-cylinder temperature reaches above a certain threshold value [11, 33]. Similar trend for aldehyde (Formaldehyde and acetaldehyde) emissions were also reported by McGill et al. [24], Cosseron et al. [16].

Ethanol emission from both test fuels is shown in Figure 11. No methanol emission was detected for these test fuels. Ethanol emission was seen in detectable quantity however their concentration was less than 10 ppm at all test conditions for both test fuels. Ethanol emission increased with increasing engine load, which indicates that there is ethanol formation during combustion at higher engine loads. KB20 showed slightly higher ethanol emission compared to mineral diesel at higher engine loads. The trend was not very clear though.



(a)



(b)

Figure 10. Emission of formaldehyde (HCHO) and acetaldehyde (CH_3CHO).

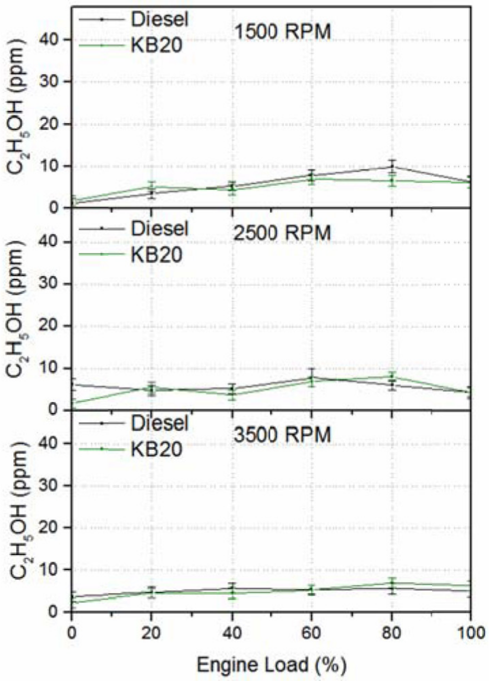
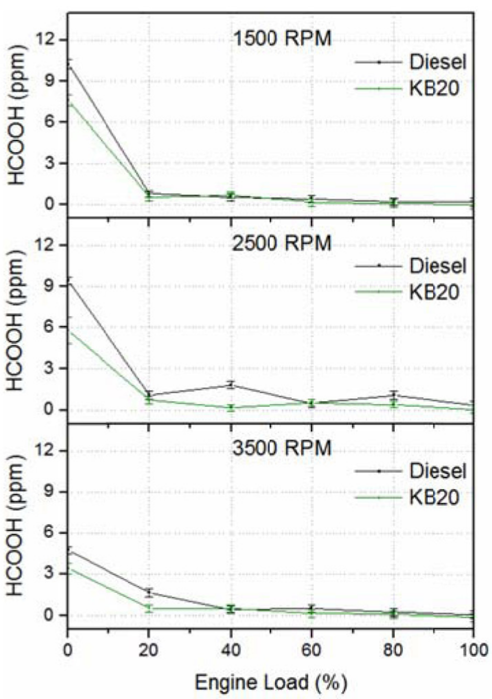


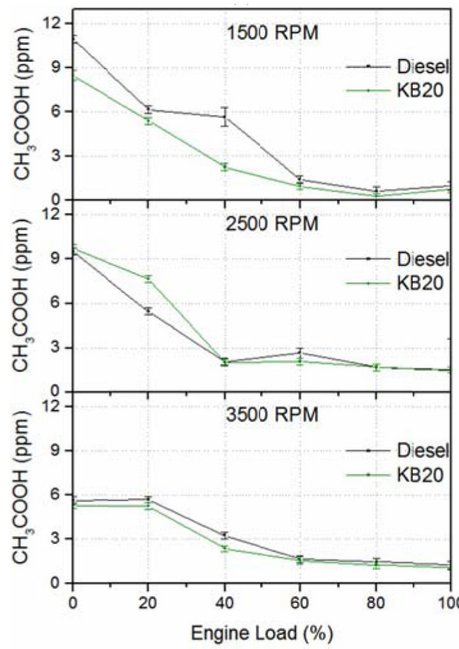
Figure 11. Emission of ethanol (C_2H_5OH).

Sharp et al. [3] also reported that no significant alcohol emissions in the engine exhaust from diesel, 100% soybean biodiesel and its 20% blend with diesel, while doing experiments on three different engines (Cummins N14, DDC Series 50, Cummins B5.9).



(a)

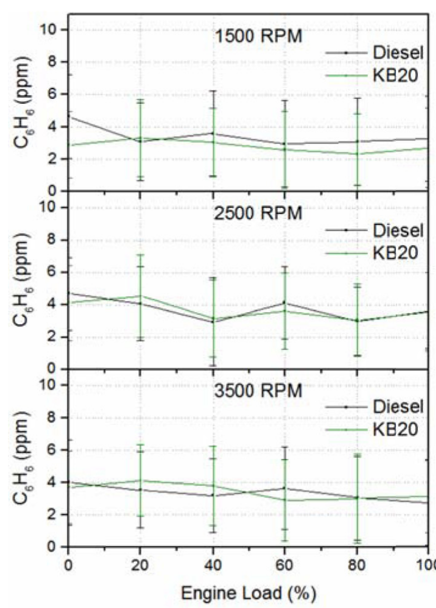
Figure 12.



(b)

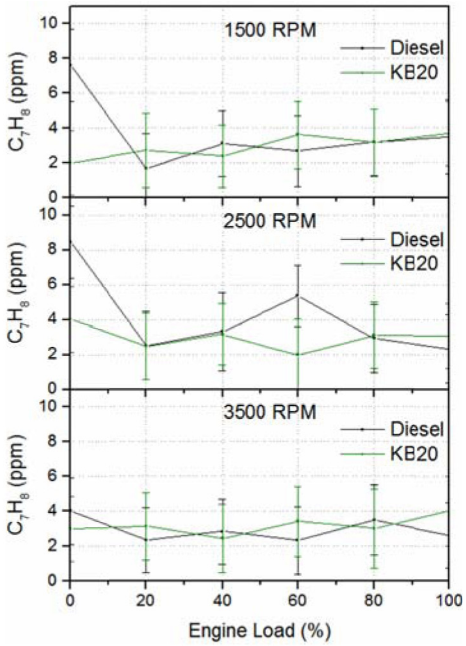
Figure 12. (cont.) Emission of formic acid (HCOOH) and acetic acid (CH_3COOH).

Emission of formic acid (HCOOH) and acetic acid (CH_3COOH) from the two test fuels are shown in Figure 12. Formic acid formation mechanism in the engine exhaust is not found in the open literature. There is no scientific proof whether organic acids in the exhaust are formed during combustion or they are products of post combustion oxidation of active species or they originate from recombination of radicals during cooling of exhaust gas [27]. One possible pathway for acids formation is further oxidation of aldehydes, and known products of hydrocarbons oxidation [27]. Poulopoulos et al. [34] stated that acetic acid has a very typical and annoying odor and it is mainly composed over a catalyst. Similar tendencies of acetaldehyde formation have been detected for the organic acids (HCOOH and CH_3COOH) in engine emissions (Figure 12).



(a)

Figure 13. Emission of benzene (C_6H_6) and toluene (C_7H_8)



(b)

Figure 13. (cont.) Emission of benzene (C_6H_6) and toluene (C_7H_8)

Benzene and toluene emissions in the engine exhaust are considered as carcinogenic, mutagenic and teratogenic in nature. These emissions from the two test fuels are shown in Figure 13. Benzene emissions were observed at all engine loads (<5 ppm) however their quantity decreases slightly with increasing engine load, due to higher combustion temperature at higher engine load. Takada et al. [33] also reported benzene emissions at lower engine loads and lower exhaust gas temperatures, and suggested that benzene got oxidized at higher exhaust gas temperature. As seen in Figure 13a, biodiesel emits slightly lower benzene emission than diesel. The main source of benzene, toluene and xylene in the engine exhaust is the pyro synthesis reaction, which leads to structural modifications in the unburned fuel molecules during combustion [35]. Since biodiesel has lower aromatic content in the fuels, it leads to lower benzene emissions in the engine exhaust.

Toluene is a light aromatic hydrocarbon. At medium concentrations in the ambient air, toluene causes irritation in the skin, eyes, mucous membrane, throat and respiratory tract. Symptoms of short-term exposure to higher levels of this compound include nausea, vomiting, headache, dermatitis and pulmonary edema [36]. Toluene emissions are relatively higher at lower engine loads, which decrease with increasing engine load (Figure 13b). When mineral diesel is used, toluene emissions are higher at lower engine load compared to KB20. Absence of aromatics in biodiesel is an important reason for this trend as has also been reported by Hansen and Jensen [37]. Another factor responsible for this trend is higher oxygen content of biodiesel compared to mineral diesel, which reduces aromatic emissions [36].

Figure 14 compares SO_2 emissions for both test fuels. SO_2 emissions were observed to be significant only at no load to low load. Relatively lower SO_2 emissions were observed for KB20, because of no sulfur presence in biodiesel. Sulfur present in the fuel leaves the combustion chamber as SO_2. SO_2 is further oxidized by DOC to SO_3, which may combine with moisture to form H_2SO_4 aerosol [19]. Since DOCs are not effective at lower exhaust temperature, therefore higher SO_2 emissions were observed at ‘zero to low loads’ compared to ‘intermediate to higher engine loads’ [19]. From intermediate to high loads, the high exhaust temperature of engine was helpful in oxidation of SO_2 and formation of sulfates [11]. SO_2 finally gets converted into sulfates, and leads to formation of particulate matter (PM) and smoke [11].

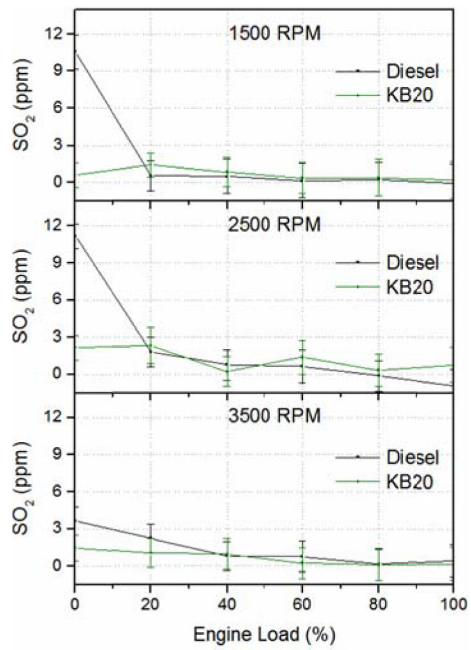
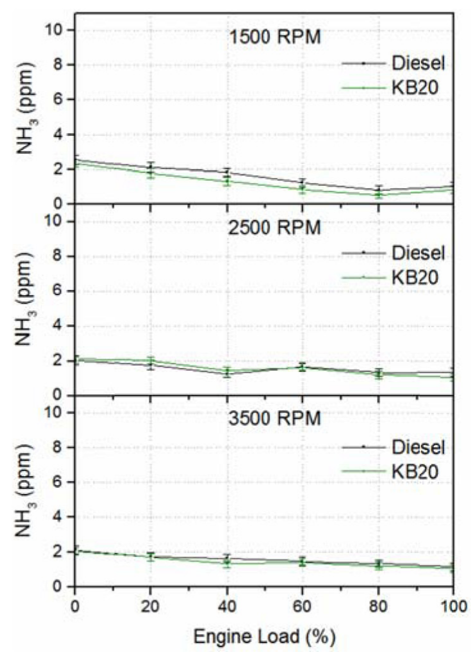
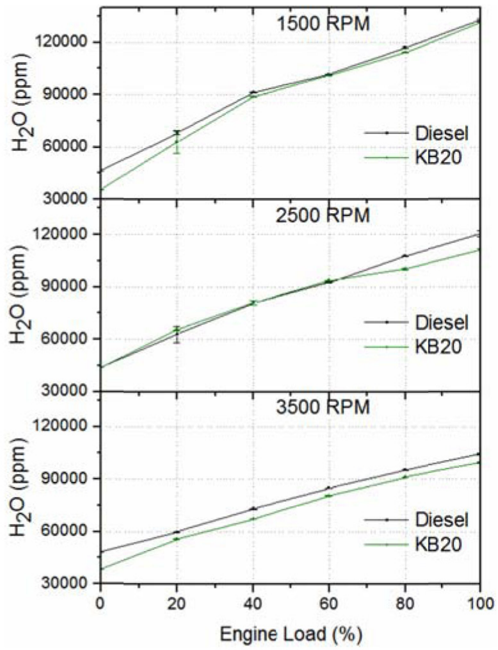


Figure 14. Emission of sulfur dioxide (SO_2)



(a)

Figure 15. Ammonia (NH_3) and H_2O Emission



(b)

Figure 15. (cont.) Ammonia (NH_3) and H_2O Emission

Ammonia (NH_3) and water (H_2O) in the engine exhaust for both test fuels are shown in Figure 15. Ammonia was found to be lower than 3 ppm at all loads for both test fuels. H_2O is a product of combustion in the engine. All test fuels show same trend for H_2O. With increase in engine load, increased H_2O in the exhaust is observed. However, water content was relatively lower for KB20.

Apart from the species discussed above, emission of ethane (C_2H_6), 1,3-butadiene (1,3-C_4H_6), isobutylene (iso-C_4H_8), iso-Pentane (iso-C_5H_{12}), Isocynic acid (HNCO) were also measured. These results are not reported in this paper because the concentration of these species in engine exhaust from these two test fuels were observed to be either statistically insignificant or below the accuracy limit of the measuring instrument.

Conclusions

In addition to the regulated exhaust species, FTIR analyzer measured a large number of non-regulated exhaust species, which may be of particular interest to the regulatory agencies. These species include formic acid (HCOOH), n-butane (n-C_4H_{10}), n-pentane (n-C_5H_{12}), ammonia (NH_3), nitrous oxide (N_2O), isocyanic acid (HNCO), alcohols (methanol and ethanol) and aldehydes (formaldehyde and acetaldehyde). On the basis of results obtained, following conclusions can be drawn:

1. Oxides of nitrogen (NO_X) were observed to be higher for KB20at 1500 and 2500 rpm however at 3500 rpm, their concentration was observed to be similar for both test fuels.
2. NO_X emissions were found to increase with the increasing engine load however nitrogen dioxide (NO_2) contribution in NO_X was lower at lower loads and higher at higher loads.
3. CO, CO_2 and THC emissions sowed almost similar trend for diesel and KB20. However, CO and THC emissions were observed to be in significant quantity at lower engine loads only.
4. Methane, propane, n-butane, ethylene, acetylene and propylene, formaldehyde and acetaldehyde were observed only at lower engine loads and were found to be almost negligible with higher engine load. Possibly, lower in-cylinder temperature and lean fuel-air mixture regions at lower loads cause formation of these species.
5. No methanol emission was detected in the exhaust for both test fuels however, ethanol emission was observed to be less than 10 ppm at all test conditions for both test fuels.
6. Engine exhaust acetic acid concentration (<10 ppm) was observed to be slightly higher than formic acid concentration for both test fuels at all engine operating conditions.
7. Biodiesel (KB20) showed lower emission for several harmful emission species such as CO, THC, n-butane, n-octane, ethylene, aldehydes (formaldehyde and acetaldehyde) and formic acid.

This study conclusively suggests that biodiesel blends are comparable to mineral diesel, as far as toxicity of the unregulated gaseous emissions is concerned.

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Definitions/Abbreviations

KB20 - 20% Karanja biodiesel blend with diesel

CO - Carbon monoxide

CO_2 - Carbon dioxide

NO - Nitric Oxide

NO_2 - Nitrogen Dioxide

N_2O - Nitrous Oxide

H_2O - Water

NH_3 - Ammonia

SO_2 - Sulfur dioxide

HCHO - Formaldehyde

HCOOH - Formic Acid

CH_4 - Methane

C_2H_4 - Ethylene

C_2H_6 - Ethane

C_3H_6 - Propylene

C_3H_8 - Propane

1,3-C_4H_6 - 1,3-Butadine

CH_3COOH - Acetic acid

C_2H_2 - Acetylene

C_2H_5OH - Ethanol

CH_3CHO - Acetaldehyde

CH_3OH - Methanol

ISO-C_5H_{12} - iso-Pentane

n-C_5H_{12} - n-pentane

n-C_8H_{18} - n-octane

HNCO - Isocynic acid

iso-C_4H_8 - iso-Butylene

n-C_4H_{10} - n-butane

iso-C_4H_{10} - Isobutene

C_6H_6 - Benzene

C_7H_8 - Toluene

BTX - Benzene, Toluene and Xylene

NEDC - New European Driving Cycle

PAH - Polycyclic Aromatic Hydrocarbons

KME - Karanja methyl ester

CME - Canola methyl ester

SME - Soybean methyl ester

TME - Tallow/waste-fry oil methyl-ester

CRDI - Common-rail direct injection

NFTs - Nitrogen fixing trees

KOME - Karanja oil methyl ester

JOME - Jatropha oil methyl ester

FTIR - Fourier transform infrared spectrometry

DOHC - Dual overhead cam

OEM - Original equipment manufacturer

CCC - Close-coupled catalytic converter

DOC - Diesel oxidation catalytic

lps - Liter per second

FID - Flame ionization detector

NDIR - Non-dispersive infrared

CLD - Chemiluminescense

PMD - Paramagnetic detector

EPA - Environmental Protection Agency

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