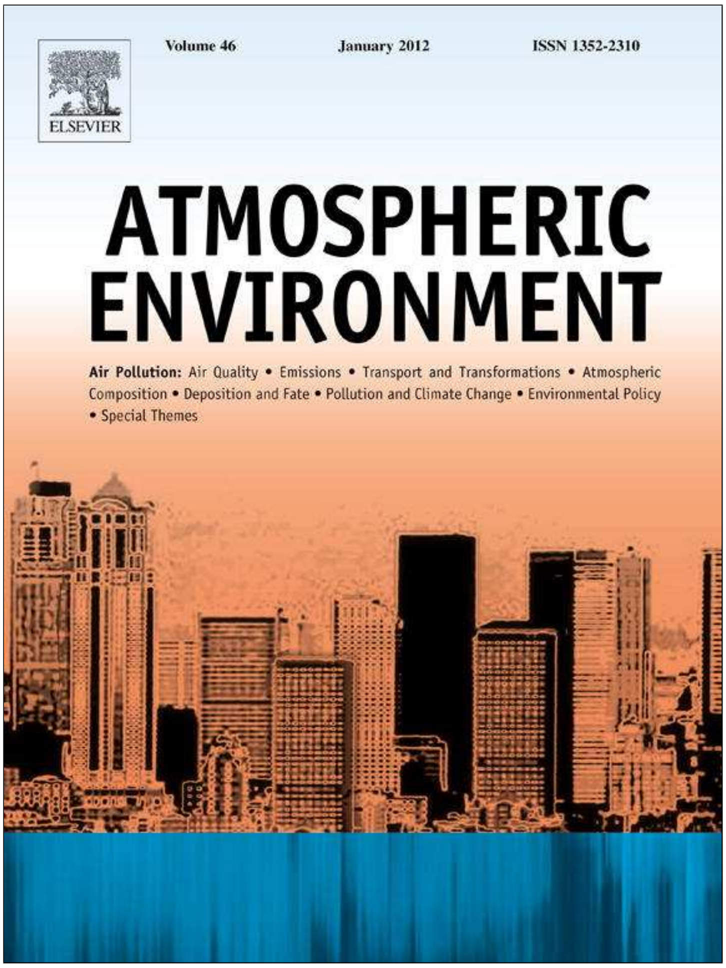

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Composition and comparative toxicity of particulate matter emitted from a diesel and biodiesel fuelled CRDI engine

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ABSTRACT

There is a global concern about adverse health effects of particulate matter (PM) originating from diesel engine exhaust. In the current study, parametric investigations were carried out using a CRDI (Common Rail Direct Injection) diesel engine operated at different loads at two different engine speeds (1800 and 2400 rpm), employing diesel and 20% biodiesel blends (B20) produced from Karanja oil. A partial flow dilution tunnel was employed to collect and measure the mass of the primary particulates from diesel and biodiesel blend collected on a 47 mm quartz substrate. The collected PM (particulate matter) was subjected to chemical analyses in order to assess the amount of Benzene Soluble Organic Fraction (BSOF) and trace metals using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). For both diesel and biodiesel, BSOF results showed decreasing levels with increasing engine load. B20 showed higher BSOF as compared to those measured with diesel. The concentration of different trace metals analyzed also showed decreasing trends with increasing engine loads. In addition, real-time measurements for Organic Carbon (OC), Elemental Carbon (EC) and total particle-bound Polycyclic Aromatic Hydrocarbons (PAHs) were carried out on the primary engine exhaust coming out of the partial flow dilution tunnel. Analysis of OC/EC data suggested that the ratio of OC to EC decreases with corresponding increase in engine load for both fuels. A peak in PAH concentration was observed at 60% engine load at 1800 rpm and 20% engine load at 2400 rpm engine speeds almost identical for both kinds of fuels. Comparison of chemical components of PM emitted from this CRDI engine provides new insight in terms of PM toxicity for B20 *vis-a-vis* diesel.

1. Introduction

Diesel engine is the most efficient power source among all types of internal combustion engines. Diesel engine is advantageous in terms of lower CO and HC emissions vis-a-vis gasoline engines. However, diesel engines are disadvantaged in terms of high NO_x and particulate matters which are directly associated with adverse human health and environmental impacts. This study mainly focuses on particulate matter emitted in engine exhaust. PM in engine exhaust contains toxic species such as benzene and polycyclic aromatic hydrocarbons (PAHs), and trace metals (Gupta et al., 2010). Diesel particulates are a complex mixture of several organic compounds (OC), also known as soluble organic fraction (SOF), sulphate, nitrates, elemental metals, and irritants (such as acrolein, ammonia, acids, fuel vapours, unburnt lubricating oils, moisture, PAHs) mostly adsorbed onto an elemental carbon (EC) core.

The solid phase emissions are made up of small (10–80 nm) spherical carbon particles; these are termed as solids (SOL), solid particulate or soot. The liquid phase emissions are composed of the organic or hydrocarbon compounds and sulfates. The organic fraction of diesel particulate contains compounds such as aldehydes, alkanes and alkenes, aliphatic hydrocarbons, PAH and PAH derivatives (Johnson et al., 1994). Interaction of biodiesel with lubricating oil is quite different from interaction of mineral diesel with lubricating oil (Agarwal, 2005). The organic fraction comes from the unburnt fuel and lubricating oils, and from partially oxidized/pyrolysed fuel and oils (Williams et al., 1987). The National Research Council (1983) showed that approximately 25% of the particle mass may be extracted using organic solvent but, depending on the engine conditions and testing cycle (Williams et al., 1989). Organic fraction containing neutral and aromatic fraction of diesel soot has been found to be mutagenic and carcinogenic in nature (USEPA, 1995). PAHs are aromatic hydrocarbon with two or more (upto five or six) benzene

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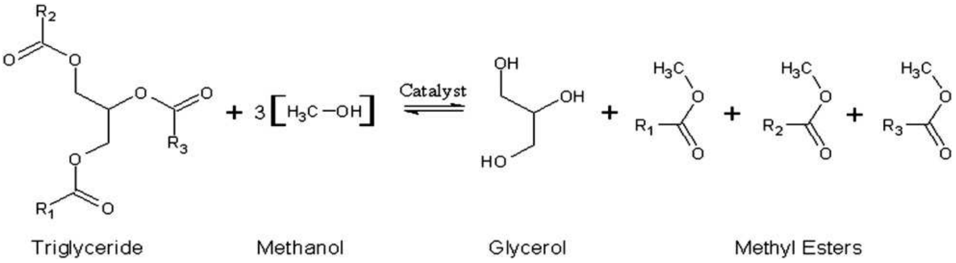
rings joined in various (more or less) clustered forms. Aromatic compound concentration in diesel varies between 1.5% and 2.5%. It is also believed that some of the heaviest PAH compounds are generated by pyrosynthesis of these aromatic compounds in the engine.

A four-stroke heavy-duty engine emits various trace metals such as silicon, calcium, zinc and phosphorus (Hare, 1997). Calcium was found to be a dominant metal in PM with levels ranging from 0.01 to 0.29% ($w/w_{particulate}$) (Springer, 1997). Phosphorus, silica and zinc were next most abundant metallic element found and sodium, iron, nickel, barium, chromium and copper were present either in small concentrations or were below detection limits (Agarwal et al., 2010; Kothari, 2009). In contrast with diesel emissions, scientists are constantly working on alternative fuels, to help address energy cost, energy security and global warming concerns associated with liquid fossil fuels. Biofuels contribution to greenhouse effect is almost negligible, since carbon dioxide (CO_2) emitted during combustion is recycled in the photosynthesis process in the plants (Agarwal & Agarwal, 2007; Bona et al., 1999; Agarwal, 1998; Narayan, 1992). Amongst alternative fuels, biodiesel has shown a great potential, especially to address the problem of CO_2 emissions and need for decentralized power, especially in rural areas (Wedel, 1999). A number of studies of larger heavy-duty engines and heavy-duty vehicles have concluded that biodiesel can provide emission reductions in terms of hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM), with some increase observed for nitrogen oxides (NO_x) (Amann et al., 1980). Biodiesel has higher cetane number than mineral diesel because of its higher oxygen content. It reduces the ignition delay thus combustion starts earlier and therefore emissions of HC, CO and PM are reduced due to higher degree of premixed combustion. Biodiesel can be used in neat form (B100) or can be blended with petroleum diesel in any proportions (CARB, 1998; Agarwal et al., 2006). Biodiesel has advantages of being virtually free from sulphur and aromatic compounds (Turrio-Baldassarri et al., 2004), therefore the possibility of its particulate being less toxic is contemplated, however it needs to be experimentally verified. For this purpose, it is essential to collect the samples of particulates from biodiesel fuelled engine and carry out detailed chemical characterisation including their trace metal content *vis-a-vis* diesel fuelled exhaust particulates. Therefore the objective of this paper is to comparatively assess and characterize the particulate emissions from a CRDI engine fuelled with diesel and B20 (20% biodiesel blend) in terms of (i) Particulate mass (ii) BSOF (iii) PAHs and (iv) Elemental carbon, organic carbon and total carbon and (v) Trace elemental metals.

2. Materials and methods

Biodiesel (20%) blended with diesel (80%) is one of the most popular biodiesel blend investigated and recommended world over. Biodiesel for the present experimental study was produced from Karanja oil using transesterification (Agarwal, 1998; Agarwal et al., 2006).



2.1. Fuel preparation and characterization

Four important tests were conducted according to ASTM standards on diesel, biodiesel (B100), and biodiesel blend with diesel (B20) to analyze their main properties namely kinematic viscosity, flash point temperature, density and calorific value. Viscosity is measured by ASTM D 445 procedure using a kinematic viscometer (83541-3, Stanhope-Seta, UK). The flash point of the test fuels was measured according to ASTM D93 using a flash point apparatus (33000-0, Stanhope-Seta, UK). A bomb calorimeter (6200, Parr, USA) was used to measure the heat of combustion (calorific value) of biodiesel and diesel samples. Specific gravity was measured by ASTM D4052 procedure using a high precision digital density meter (DA-130 N, Kyoto Electronics, Japan). The physical properties of biodiesel and diesel are shown in Table 1.

For the comparative study of biodiesel and diesel, a modern automotive common rail direct injection (CRDI) diesel engine (Safari DICOR 3.0 L, Tata India) typically used in sports utility vehicles (SUV) was employed. The engine uses a high pressure fuel pump and a common rail for supply of fuel to all cylinders at very high fuel injection pressures up to 1600 bar. The injectors were controlled electronically using an electronic control unit (ECU).

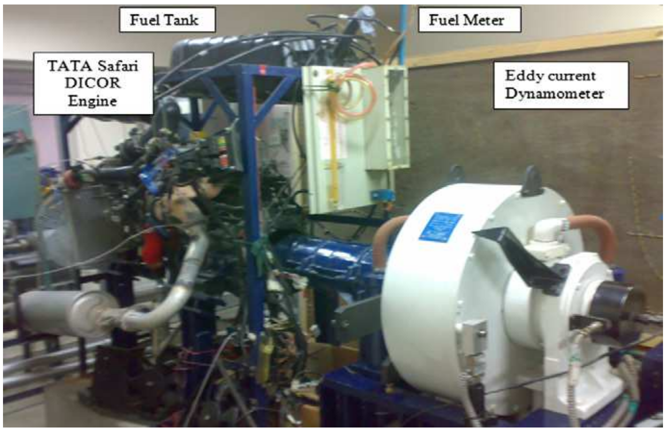


Fig. 1. Tata Dicor CRDI engine coupled with eddy current dynamometer.

Table 1
Physical properties of diesel and biodiesel.

Fuel Property	Diesel	Biodiesel (B20)
Specific Gravity	0.846	0.848
Kinematic Viscosity (cSt) at 30°C	2.60	3.39
Calorific Value (MJ kg^{-1})	42.21	38.28
Flash Point (°C)	52	79

Table 2
Engine and eddy current dynamometer specifications.

Engine Specifications	
Make/Model	Tata motors, India/Safari Dicor 3.0 L (BS-III/Euro-III)
Engine Type	Water cooled, CRDI, Turbocharged, Intercooled
No. of Cylinders	4, In-line
Bore/Stroke	97/100 mm
Cubic Capacity	2956 cc
Maximum Engine Output	84.5 kW @ 3000 rpm
Maximum Torque	300 Nm at 1600–2000 rpm
Compression Ratio	17.5
Firing Order	1-3-4-2
Fuel Injection System	CRDI with 1600 bar max fuel injection pressure
Timing and Governing	ECU control
Dynamometer Specifications	
Make/Model	Dynomerk, Pune, India/EC-300
Capacity	220 kW at 2500–8000 rpm
Maximum Speed	8000 rpm
Maximum Torque	702 Nm
Direction Of Rotation	Bi-directional
RPM Accuracy	±1 rpm

High fuel injection pressure results in finer atomization of the fuel sprays, which leads to more complete combustion, higher efficiency and lower emissions. The engine is coupled with an eddy current dynamometer for loading the engine at different speeds (Fig. 1). The dynamometer is controlled using a dynamometer controller as well as a computer with a software interface between the dynamometer and the computer. The specifications of the engine and dynamometer used in the experimental setup are given in Table 2.

The schematic of the experimental setup developed for carrying out the engine experiments is given in Fig. 2.

An experimental setup was developed which included a set of different measuring instruments like semi continuous OC/EC analyzer (Semi continuous field v.4, Sunset Laboratory), which measures organic carbon, elemental carbon and total carbon (Bae et al., 2004); Online PAH analyzer (PAS 2000, EcoChem Labs) (Ott and Siegmann, 2006), which measures total particulate bound PAHs for primary as well as secondary aerosols, and emission analyzer (4000 Digas, AVL). A partial flow dilution tunnel was used for dilution of diesel exhaust emissions with ambient air in order to complete the coagulation and condensation processes occurring during the particulate formation. When the diesel engine is operated, carbonaceous soot particles and high boiling point hydrocarbons are emitted from the tailpipe. These hydrocarbons condense on soot (mostly EC) to form PM after being diluted with preheated air inside the partial flow dilution tunnel (Dwivedi et al., 2006). Engine exhaust flows through partial flow dilution tunnel before entering different instrument inlets as shown in the Fig. 2. Experimental setup was developed using pipes, elbows and valves (Swagelok fittings) made of stainless steel (SS, grade 316), in order to ensure minimum contamination during experiment due to the inert nature of SS. Valves were installed at different places to control and distribute required exhaust aerosol flows to the instruments at different times of experiment, for sampling primary aerosols according to the measurement requirements. From the exhaust pipe of engine, small fraction of exhaust gases were passed to partial flow dilution tunnel. Thereafter, preheated and pre-filtered atmospheric air is mixed with this exhaust to attain a specific dilution ratio as specified by EPA (maintained between 10 and 16 in this case). The sample gas is mixed with the ambient air inside the dilution tunnel and they travel together so that mixing and agglomeration processes of particulate formation are completed to a reasonable extent. This diluted gas then passes through the filter assembly, where particulates are filtered out on a preconditioned filter paper. A 4 way valve was put through which undiluted exhaust was passed from one side, on the other side diluted exhaust comes out and from one side ambient air was passed. Finally from the exit line of 4 way valve through pipe, it was passed to Exhaust gas emission analyser. This analyzer measures CO_2, CO, HC, NO, and O_2 in the exhaust gases. The carbon dioxide (CO_2) concentration is measured for undiluted exhaust, ambient air and diluted exhaust for the calculation and verification of dilution ratio using the formulae given below.

$$\text{Dilution ratio } r = \frac{[\text{Undiluted exhaust CO}_2]}{[\text{Diluted exhaust CO}_2 - \text{Ambient air CO}_2]}$$

One exhaust line from the dilution tunnel was taken to the real-time instruments (PAS2000 and OC/EC Analyzer) for measuring the real time measurements of PAHs and elemental, organic and total carbon in the exhaust. The volume of exhaust flow passing through these instruments was controlled by separate two way valves fitted on the pipes going to the instruments.

All the instruments were calibrated and tested individually with ambient air before carrying out the engine experiments. The Semi continuous OC/EC analyzer measures organic carbon, elemental

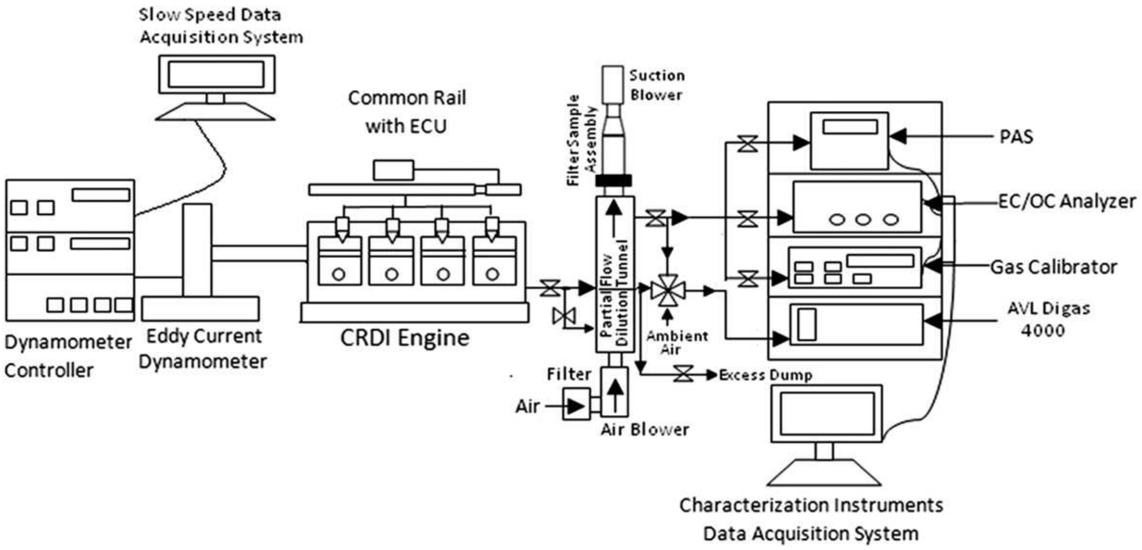


Fig. 2. Schematic of the experimental setup.

carbon and total carbon (Bae et al., 2004). OC/EC instrument provides organic and elemental carbon results, which are comparable to the recognized NIOSH method 5040. Once the sample collection is complete, the oven is purged with helium. This is followed by a stepped-temperature ramp, which increases the oven temperature to 850 °C, thus thermally desorbing OC and pyrolysis products into a manganese dioxide (MnO_2) oxidizing oven. As the carbon fragments flow through the MnO_2 oven, they are quantitatively converted to CO_2. The CO_2 is swept out of the oxidizing oven along with helium stream and measured directly by a self-contained non-dispersive infrared (NDIR) detector system. A second temperature ramp is then initiated in the oxidizing gas stream and then elemental carbon is oxidized off the filter and into the oxidizing oven and measured by NDIR. The EC is then detected in the same manner as the OC (Springer, 1997). Online PAH analyzer (PAS 2000, EcoChem Labs) is a standard real-time monitor for Particle-Bound Polycyclic Aromatic Hydrocarbons (PAHs), which works on the principle of photo ionization of particle-bound PAH. It can range from 0 to 100 pico amp and has sensitivity range of $\sim$0.3–1 g m^{-3} PAH per pico amp. It has response time less than 10 s. PAH analyzer measures total particulate bound PAH content of primary exhaust particulates in the present study. The particulate samples collected on the filter substrate need to be analyzed for detection of elemental trace metals using the Inductively coupled plasma-optical emission spectrometry (ICP-OES) (iCAP DUO 6300 ICP Spectrophotometer, Thermo Fischer Scientific). It is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiations at wavelengths characteristic to a particular element. The intensity of this emission is indicative of the concentration of the particular element present in the particulate sample.

To characterize the emissions from mineral diesel and biodiesel (B20), the engine was operated at loads ranging from 0%, 20%, 40%, 60%, 80% to 100% rated engine load at two constant speeds of 1800 and 2400 rpm. Particulate samples were collected iso-kinetically using a partial flow dilution tunnel. The partial flow dilution tunnel was used to simulate the ambient environment for collecting the exhaust particulates from the engine. This tunnel draws a fraction of exhaust gases from the main exhaust line. Thereafter, pre-filtered and preheated atmospheric air is mixed with this exhaust to attain a specific dilution ratio as specified by EPA, which is maintained between 14 and 16. The diluted exhaust undergoes complete mixing and particulate formation via condensation of gaseous material on tiny nuclei particles (heterogeneous condensation) along with adsorption, absorption and coagulation processes, which are completed to a reasonable extent within the designed residence time inside the dilution tunnel.

For determining the sampling duration for each test, engine experiments were conducted for different time durations and all the particulate samples were collected in triplicate and analysed. Based on the results from the graphical presentation of data, appropriate sampling durations for this study were chosen e.g. for metal analysis of particulate samples, the sampling duration was chosen as 15 min. Similar sampling duration was also recommended by previous studies.

The first step in the sampling procedure was conditioning and preparation of filter papers (Make: Whatman; 47 mm, Tissue-Quartz Filter). Filter papers were first desiccated for 12 h in anhydrate silica gel desiccators and then weighed using a microbalance (CPa2P-F, Sartorius AG). For collecting the particulate sample, pre-weighed, conditioned filter paper was placed in filter holder assembly of the partial flow dilution tunnel. The engine was operated for a predetermined period of time at desired load and speed, and particulates were collected on the filter substrate (Table 3). After completion of the engine experiment, the filter substrate was carefully removed from the filter assembly and kept in the desiccators for 12 h and then weighed again. These filter papers were then further analyzed for total mass of particulates collected, BSOF, and trace elemental metals as per the test plan.

Table 3
Sampling details.

Engine speed (rpm)	Engine load (%)	Sampling duration for Mass/BSOF (min)	Online sampling duration for OC/EC (min)	Online sampling duration for PAHs (min)	Sampling duration for Metals (min)
1800/2400	0	30	7	5	15
1800/2400	20	30	7	5	15
1800/2400	40	30	7	5	15
1800/2400	60	30	7	5	15
1800/2400	80	30	7	5	15
1800/2400	100	30	7	5	15

Note: Particulate samples were collected in triplicate for all the different chemical analyses.

2.2. BSOF analysis procedure

ASTM test method D4600-87 (2001) was used for estimation of BSOF in diesel particulates. This gravimetric method was recommended by National Institute of Occupational Safety and Health (NIOSH), USA to represent the toxic organic compounds present in the particulates collected on filter paper. Filter papers were desiccated for 12 h before and after sampling and initial and final weights were noted. Filter papers were cut into several small pieces using a metal scissor and then placed into a reagent beaker. Thereafter 20 ml of benzene was added to it. These reagent bottles were kept in ultrasonic bath for 20 min. Thereafter sample was decanted and vacuum filtered through 0.45 μm Millipore filter paper. The filtrate was collected in a 100 ml pre-weighed beaker. The procedure was repeated with another 10 ml of benzene in the same reagent beaker. These 100 ml beakers were covered with aluminium foil having holes and were kept in oven at 40 °C for 12–18 h until the sample dried. The initial and final weight of the beaker was measured at room temperatures to estimate the total mass of benzene soluble organic fraction in the sample. In order to check the reference concentration; blank filters were used for benzene extraction as per the same ASTM standard.

2.3. Trace metal analysis procedure

USEPA, MESW-846, 3015A method was used for extracting trace metals from exhaust particulate matter. Sample extraction was carried out using hot plate digestion method. This digestion procedure is used for preparing samples, which are to be analyzed by ICP-OES. One half of the sample laden filter was cut into small pieces using plastic scissors and then put into an inert

Table 4
Average metal presence in blank (tissue-quartz) filter samples.

Metals	Concentration ($mg\ g^{-1}$ filter weight)
Fe	5.73
Ca	2.47
Cr	0.44
Cu	0.23
Mg	1.79
Na	0.33
Pb	0.06
Mn	0.015
B	0.24
Si	0.13

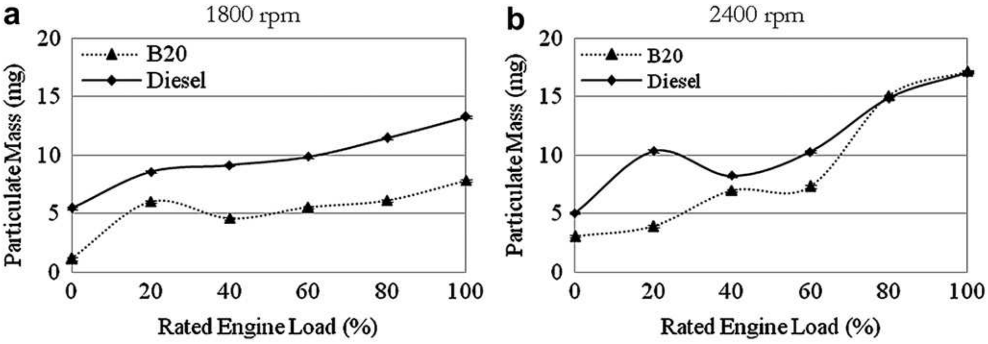


Fig. 3. Comparison of total particulate mass from a CRDI engine.

bottle, in which 15 ml concentrated HNO_3 (High Purity, Merck) was added. The remaining half of the filter paper was taken in similar way into another bottle. Temperature of each sample was raised to 175 °C in less than 5.5 min and maintained at 175 °C for more than 4.5 min. After digestion, the acid from the two vessels was taken together and filtered through 0.22 micron filter paper. The filtrate was measured and diluted 3 times with Milli-Q water and then further stored in inert bottles. Reference was taken as analytical blank filter paper and 30 ml of conc. HNO_3 (High Purity, Merck), 10% of blanks from the same lot of filter papers were used to get a best representative average blank concentration for data correction. By this method, concentrations of trace metals such as Ca, Cu, Cr, Fe, Na, Ni, Pb, Zn, Mn, Mg were analyzed by ICP-OES.

2.4. Quality control and error budget

Various metals were investigated however many of these metals were below detection limit of the instrument and only the metals detected with confidence are presented in this section.

Quality control procedures involved steps like using clear forceps (cleaned with ethanol), while handling the filters each time to avoid contamination; and keeping the filters in sealed glassware in refrigerated environment until the analysis. The data is corrected for blanks and the metals present in particulate collected on the filter paper. 10% analytical blank filters were used for determining metal concentrations using ICP-OES. Table 4 represents average concentration of metals present in the blank filters. Concentration is represented in terms of weight of metal present in blank filter (mg) per gram of the filter paper weight.

All the data presented in this paper have been corrected for blank concentrations. Typical weight of a quartz filter is between 0.14 and 0.15 g, hence contribution of blanks in exhaust particulate samples was miniscule however it has been accounted for in the interest of accuracy of the results.

3. Results and discussion

Samples of particulates from engine operating at various load and speed combinations were collected for soluble organic fraction analysis and metal analysis on filter paper using partial flow dilution tunnel. The exhaust gases were also analysed for total PAHs and EC/OC using online instruments. The two test fuels used in this study were diesel and 20% blend of biodiesel with diesel (B20). In this chapter, these results are discussed and compared.

3.1. Particulate mass emissions

Fig. 3 shows the particulate mass collected on a filter paper from diesel and biodiesel (B20) exhaust from the CRDI engine at constant speeds of 1800 and 2400 rpm for varying load conditions. The sampling of exhaust particulate collected on the filter paper was carried out thrice (30 min each) under identical conditions. The values shown in graph are the average of three readings with the variability depicted in the error bars. The absolute error bars shown in the graph also includes the inherent error introduced due to the overall error associated with the gravimetric measurement.

Fig. 3 shows that the particulate mass increases with increase in engine load for both fuels, biodiesel (B20) and diesel. As the load increases, more fuel undergoes combustion resulting in higher mass of the primary particulate formation in the engine cylinder. However, it is noteworthy that particulate emission is slightly higher in diesel exhaust (13.3 mg @ 1800 rpm and 17.6 mg @

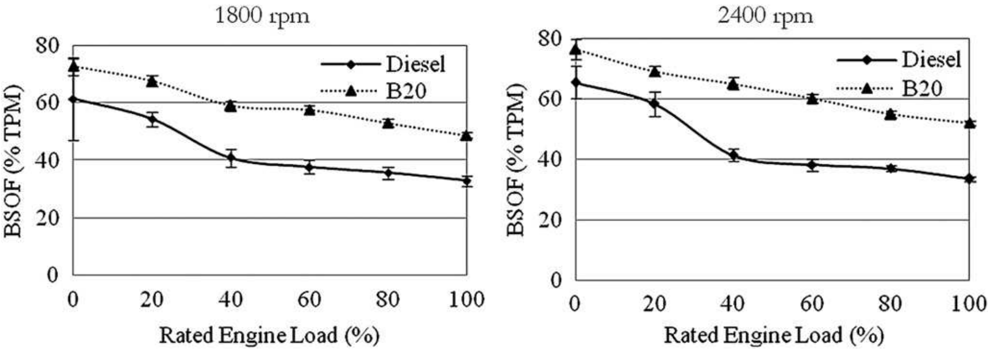


Fig. 4. BSOF of particulates from diesel and biodiesel fuelled CRDI engine.

2400 rpm) at rated load as compared to biodiesel exhaust (7.9 mg @ 1800 rpm and 17.2 mg @ 2400 rpm) at rated load. The reduction in particulate concentration with B20 fuel compared to diesel can be attributed to lower C/H ratio and presence of oxygen atoms in the molecular structure of biodiesel.

3.2. Benzene soluble organic fraction (BSOF) in particulates

The particulates were collected on the filter substrates in triplicate under identical conditions with a sampling duration of 30 min (Table 3). The filter papers were then analyzed for BSOF of

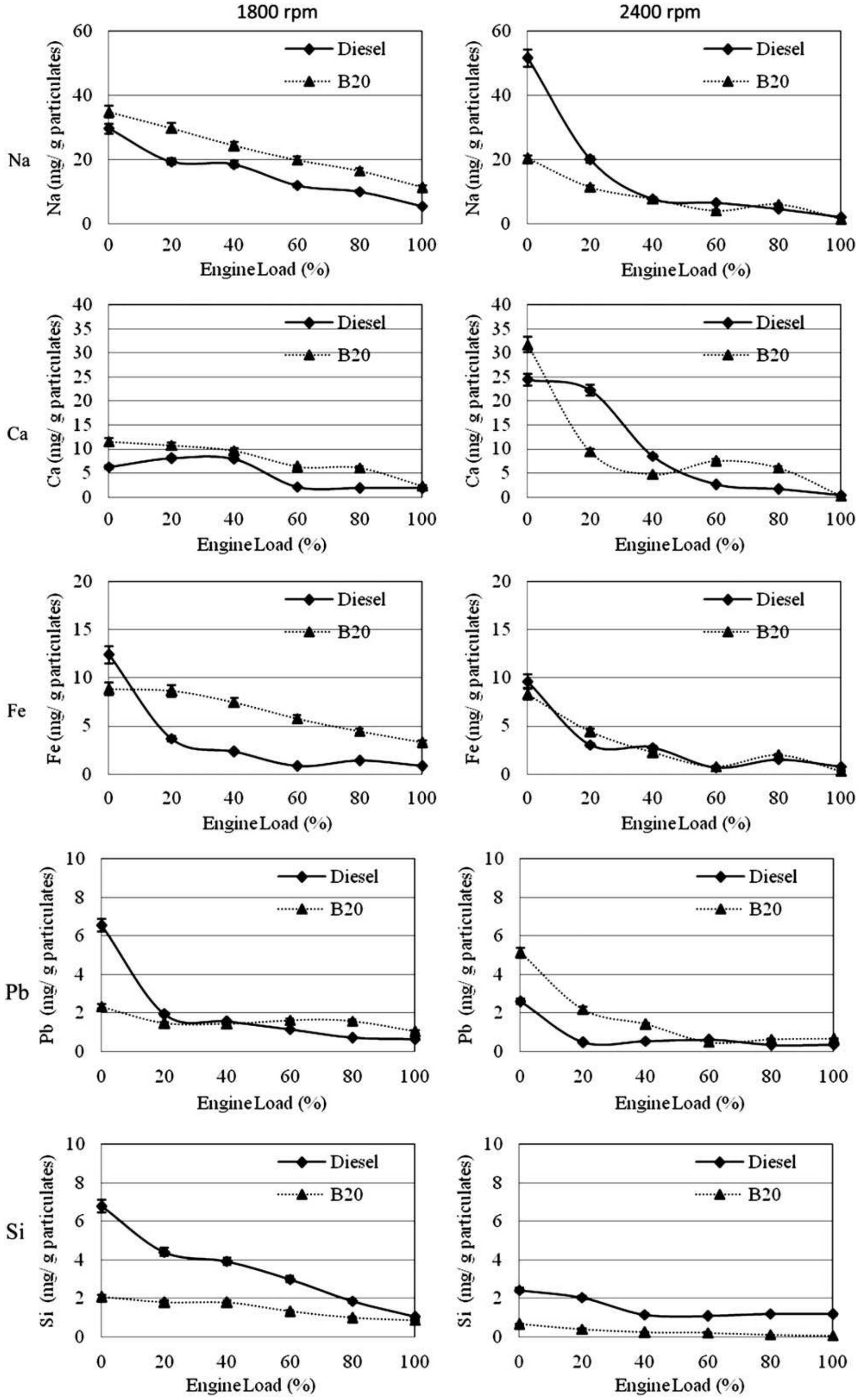


Fig. 5. Comparison of metal content from diesel and biodiesel fuelled CRDI engine.

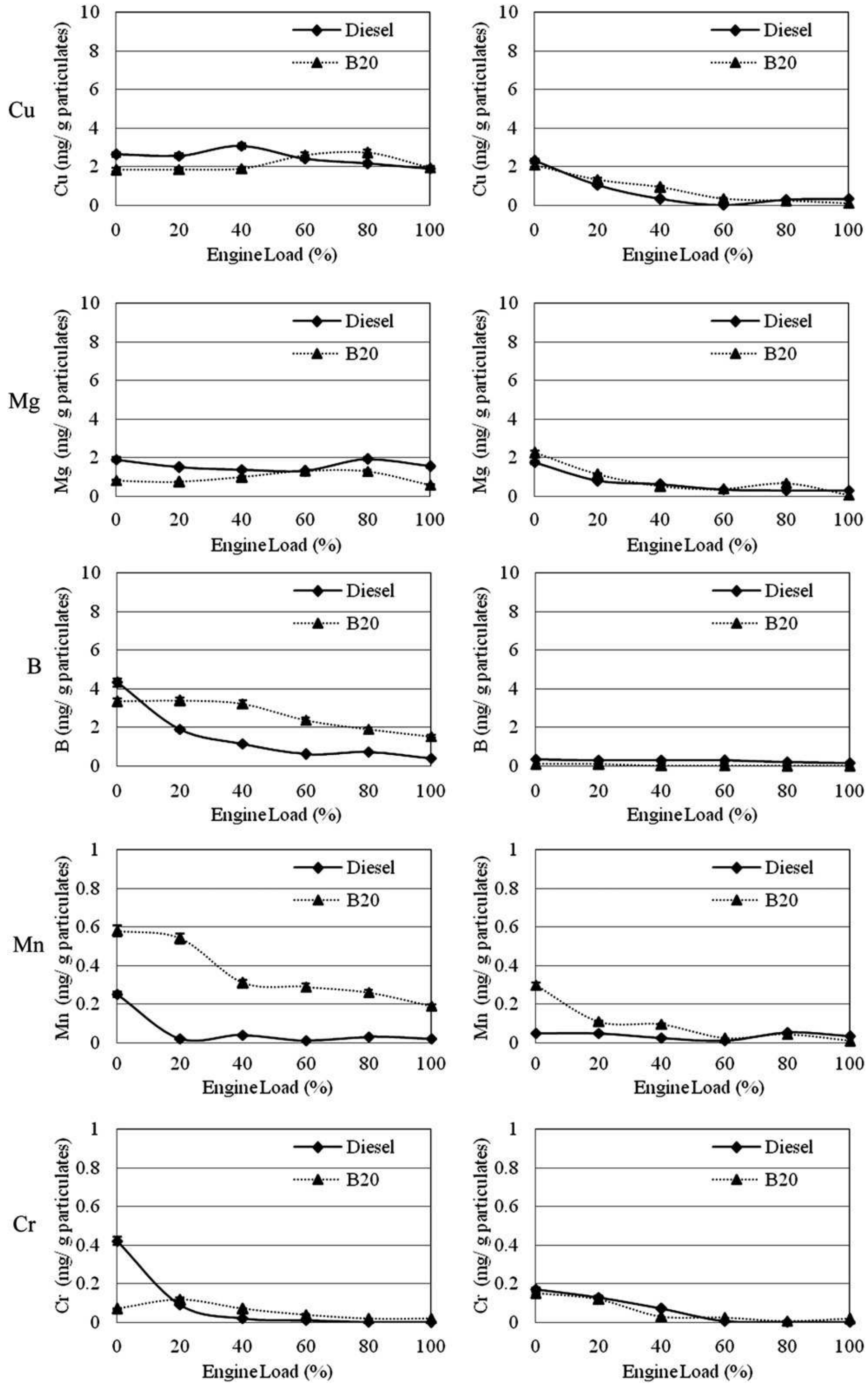


Fig. 5. (*continued*).

diesel and biodiesel exhaust particulates collected at different engine load conditions at 1800 and 2400 rpm respectively (Fig. 4). The values shown in graph are the average of three readings along with the error bars. The data shown in the graph also includes the inherent error, including the errors associated with the gravimetric and chemical analyses methods.

Fig. 4 shows that BSOF content of the particulates collected on the filter paper from biodiesel is higher than that of mineral diesel. At no load condition, quality of combustion is relatively inferior and the amount of unburned fuel coming out in the engine exhaust is high therefore the SOF is quite high. SOF of the particulate matter mainly consists of organic portion of fuel itself and pyrolytically

Table 5
Metals concentration in exhaust particulates.

Metals (mg g^{-1} particulate)	No Load				Full Load			
	1800 rpm		2400 rpm		1800 rpm		2400 rpm	
	DE (range)	B20	DE	B20	DE	B20	DE	B20
Na	29.4–29.8	34.6–35.0	51.55–51.59	20.25–20.29	5.50–5.54	11.0–11.4	1.91–1.95	1.37–1.41
Ca	6.22–6.26	11.60–11.64	24.44–24.48	31.70–31.74	1.80–1.84	2.27–2.31	0.39–0.43	0.22–0.26
Fe	12.40–12.44	8.81–8.85	9.62–9.66	8.27–8.31	0.82–0.86	3.26–3.30	0.74–0.78	0.32–0.36
Pb	6.51–6.55	2.31–2.35	2.57–2.61	5.11–5.15	0.61–0.65	1.00–1.04	0.33–0.37	0.61–0.65
Si	6.75–6.79	2.04–2.08	2.40–2.44	0.63–0.67	1.01–1.05	0.84–0.88	1.14–1.18	0.04–0.08
Cu	2.60–2.64	1.81–1.85	2.13–2.17	2.07–2.11	1.89–1.93	1.93–1.97	0.31–0.35	0.11–0.13
Mg	1.89–1.93	0.81–0.85	1.74–1.78	2.23–2.27	1.52–1.56	0.57–0.61	0.27–0.31	0.04–0.08
B	4.30–4.34	3.31–3.35	0.32–0.36	0.07–0.11	0.37–0.41	1.50–1.54	0.14–0.18	0.01–0.03
Mn	0.23–0.27	0.56–0.60	0.057–0.061	0.27–0.31	0.01–0.03	0.17–0.21	0.01–0.05	0.01–0.03
Cr	0.40–0.44	0.05–0.09	0.15–0.19	0.13–0.17	0	0.01–0.03	0.01–0.03	0.01–0.03

generated organic products formed during the process of soot formation. As the load increases, SOF of particulate matter decreases. At higher engine loads, combustion efficiency is relatively better hence amount of unburned fuel decreases leading to lower amount of soluble organic fraction. Fig. 4b also showed similar trend as Fig. 4a however the BSOF content at 2400 rpm at higher speed was higher than that of 1800 rpm. Since the time available for combustion is lower at higher engine speed, which may be the possible reason for relatively higher BSOF of particulates at higher engine speed. The main point to be noticed here is that the BSOF content of particulates from biodiesel engine is higher than that of mineral diesel, indicating possibly higher toxicity potential of biodiesel particulates. This needs to be further investigated and verified by animal exposure studies, before going for large scale implementation of biodiesel program. Similar results were also presented in another earlier study from our research group (Dwivedi et al., 2006).

3.3. Trace metals in exhaust particulates

A detailed experimental study was carried out to study the effects of variation in engine load on the concentration of metals in particulate coming out of engine exhaust, when the speed of engine is kept constant at 1800 and 2400 rpm.

Fig. 5 shows the trace metal content of the particulate collected on the filter paper for 15 min from diesel and biodiesel (B20) exhaust from CRDI engine at varying load conditions at two engine speeds of 1800 and 2400 rpm respectively. The sampling of exhaust particulate collected on the filter paper was conducted in triplicate for each engine load and speed condition. The values shown in the graph are the average of three readings along with the method detection limit (MDL) and standard deviation for each metal measured during the analysis by ICP-OES. Various metals were investigated however many of the metals were below detection limit of the instrument. Experimental data showed that concentrations of Ca, Fe, Cu, Mg, Na, Pb, B and Si were much higher than those of Cr and Mn (Table 5).

Fig. 5 shows comparison in metal concentrations from diesel and biodiesel fuelled CRDI engine at two constant speeds of 1800 rpm and 2400 rpm respectively.

All the graphs for detection of metal content in diesel and biodiesel exhaust showed more or less same trend with increasing loads but Na concentration in particulates is very high compared to any other metal. The possible reason for higher concentration of Na from biodiesel may be addition of NaOH (catalyst) during the process of biodiesel production by transesterification process. All the metal concentration results presented reflect that as load increases, the trace metal content in particulates gradually decreases. This can be explained by the fact that at higher engine loads, combustion takes place at relatively higher temperature; leading to improved thermal efficiency. Brake specific fuel consumption of diesel engine decreases with increasing load/speed and this is reflected in reduced emission of metals with increasing engine load. Three metals silicon, cooper and magnesium are present in higher concentration in the particulate collected from DE compared to BDE. Other metals such as sodium, calcium, iron, lead, manganese and chromium are found in higher concentration in the particulate collected from BDE compared to DE. This can be attributed to the fact that these all metals might be in higher concentration in the fuel itself.

3.4. Concentration of particulate bound PAH's

Fig. 6 shows the time-averaged PAH concentrations present in the diesel and biodiesel (B20) exhaust particulates from CRDI engine at 1800 and 2400 rpm respectively. Each data point shown in the graph

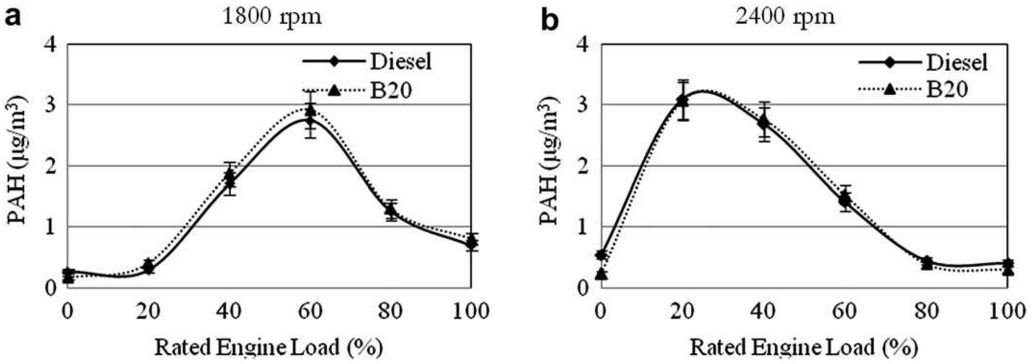


Fig. 6. Particle-bound PAH's from diesel and biodiesel fuelled engine.

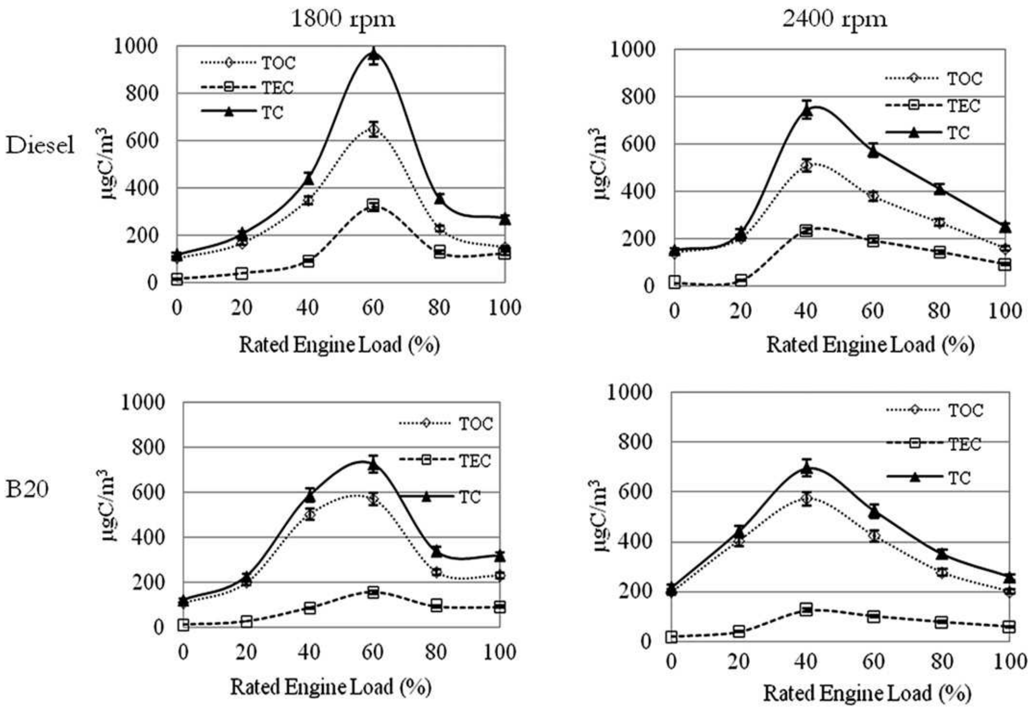


Fig. 7. OC, EC and TC in particulates from CRDI engine.

is an average of three readings along with the error bars, which reflects the maximum possible error asociated with the PAS 2000 (i.e. 1 ng m^{-3}). The online sampling of particulate bound PAH's was conducted for 5 min for each observation under identical conditions.

The PAHs concentration is low at no load condition possibly due to lower combustion temperatures that prevent extensive pyrolysis and cyclization resulting in lower PAH formation. It can be observed from Fig. 6 that the peak concentrations for PAHs are attained at 60% load for 1800 rpm and at 20% load for 2400 rpm indicating that at these engine load, high enough combustion temperatures are attained which favour formation of highest amount of PAHs. As the engine load increases further, the combustion takes place at even higher temperature resulting in reburning of cyclic and organic species and therefore relatively lesser amounts of OC gets produced. Since, OC are important precursors for PAHs, this causes further reduction in overall production of PAHs in the engine exhaust. Another possibility for relatively lower PAHs at higher engine loads could be the migration of particle-bound PAHs to the gas phase, and lesser PAH condensation due to increasing overall combustion temperatures and exhaust gas temperatures.

PAH results are shown in Fig. 6, which show almost similar trends for both diesel and B20 exhaust, with a slightly higher PAH emission from B20. The possible reason for this minor difference is presence of 80% mineral diesel in the B20 blend. The minor difference observed is because of biodiesel component of B20. The trend in the figure indicates that this difference will definitely be more pronounced, if the test fuel was 100% biodiesel.

3.5. Elemental, organic and total carbon in particulates

Fig. 7 shows the time-averaged concentration of elemental carbon (EC), organic carbon (OC) and total carbon (TC) in diesel and B20 exhaust particulates at 1800 rpm and 2400 rpm respectively for varying loads. The sample collection time was 7 min each for different engine loads. The error bars in the plot depict the maximum possible error associated with this measuring technique (0.5 µgC m^{-3}). As it can be seen from the figure, the OC, EC and TC concentration is low at no load condition possibly due to lower combustion temperatures that prevent extensive pyrolysis resulting in lower organic carbon formation. The peak concentrations are

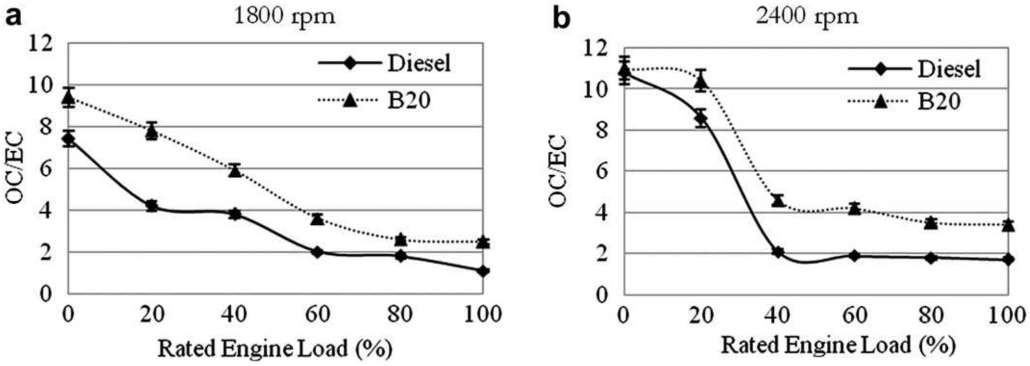


Fig. 8. Comparison of OC/EC ratio from a CRDI engine.

visible at 60% load indicating that at this temperature, high enough combustion temperatures are attained, which favour formation of highest EC and OC. As the engine load increases further, the combustion takes place at even higher temperature resulting in relatively lesser amounts of OC being produced thus lower total carbon emission from the engine.

The only difference at 2400 rpm is that at higher engine speed, the peak shifts towards lower load i.e. at 40%. This means that at higher speeds, favourable temperatures for carbon formation are attained earlier, which favours formation of highest amount of EC and OC.

Fig. 8 shows comparison of OC/EC ratio from diesel and biodiesel fuelled CRDI engine at 1800 rpm and 2400 rpm respectively and it is visible that OC/EC ratio decreases with increase in engine load. This is because of the possibility that at higher temperatures, the amount of OC (organic species produced as a result of fuel pyrolysis) produced decreases or reburns after getting produced. This also suggests that with increasing engine load, the toxic potential of particulates actually decreases, contrary to the prevailing perceptions.

4. Conclusions

Parametric investigations were carried out on a modern automotive CRDI diesel engine operated at different loads at two specific engine speeds (1800 and 2400 rpm), employing diesel and 20% biodiesel blends (B20) produced from Karanja oil. The particulate were collected and analyzed for mass, benzene soluble organic fraction (BSOF), EC and OC, particle-bound PAHs content and trace metal constituents. Biodiesel blend (B20) showed superior engine performance in reducing particulate mass emission at all engine operating conditions compared to diesel. This may be due to lower sulphur and aromatic content of biodiesel. This was followed by chemical analysis of the particulates collected on the filter paper substrate for BSOF. BSOF results showed decrease in its level with increasing engine load for both diesel and biodiesel. For B20, the BSOF content of particulates was found to be higher than that of mineral diesel. This may be primarily because of relatively lower volatility of constituents of biodiesel, indicating possibly higher toxic potential of biodiesel particulates. This was further confirmed by real-time OC measurements which were significantly higher for B20 when compared with those from diesel. The real-time OC/EC graph shows that with increase in engine load, the ratio of OC to EC decreases. At higher temperatures, the amount of OC (organic species produced as a result of fuel pyrolysis) produced decreases or reburns more effectively after getting produced. This also suggests that with increasing engine load, the toxic potential of particulates actually decreases due to lesser OC components. It is observed from the results presented in this study that the PAHs concentration is low at no load condition which increases to a peak concentration for 60% rated load at 1800 rpm and 20% rated load at 2400 rpm and then comes down with further increase in engine load. The possible reason for this can be lower combustion temperatures attained at idle load that prevent extensive pyrolysis and cyclization resulting in lower PAH formation, and in contrast high enough combustion temperatures are attained at 60% load at 1800 rpm and 20% load at 2400 rpm which favours formation of highest amount of PAHs. As the engine load increases further, the combustion takes place at even higher temperatures resulting in relatively lesser OC being produced as most of it gets effectively burnt inside the cylinder. Since, OC are important precursors for PAHs, this causes further reduction in overall PAHs. At higher in-cylinder combustion temperatures, there is a strong possibility of reburning of the PAHs formed therefore lower PAHs emission from the engine tailpipe is observed at higher engine loads. Another possibility for relatively lower PAHs at higher engine loads could be the migration of particle-bound PAHs to the gas phase, and lesser PAH condensation due to increasing overall combustion temperatures and exhaust gas temperatures. The particulates collected from diesel and biodiesel exhaust were analyzed for their elemental composition focusing on trace metals. The concentration of the metals analyzed showed a decreasing trend with increasing engine load for all metals. In summary, inspite of having lower mass emission of particulates, the BSOF and trace metal content of particulates from biodiesel engine is relatively higher than that of mineral diesel, indicating possibly higher toxicity potential of biodiesel particulates. This needs to be further investigated and verified by animal exposure studies, before going for large scale implementation of biodiesel program around the world.

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