



A Comparative Morphological Study of Primary and Aged Particles Emitted from a Biodiesel (B20) vis-à-vis Diesel Fuelled CRDI Engine

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ABSTRACT

A comparative morphological analysis was performed on the exhaust particles emitted from a common rail direct injection (CRDI) sports utility vehicle (SUV) engine for primary and aged particulates. In this study, soot particles were collected from the CRDI engine fuelled with mineral diesel and 20% biodiesel blend (B20). The engine was operated at a constant speed of 1800 rpm for five different loads (0%, 25%, 50%, 75%, 100% rated load) for primary and aged particulate collection. Primary particulate samples were collected on pre-conditioned quartz filter papers from the exhaust stream after partial dilution. For collection of aged particles, the diluted exhaust was passed through a customized photochemical chamber with 2 hour retention time. This allowed photochemical reactions to proceed in presence of ultra-violet light leading to particulate aging in simulated daylight conditions and particulates were collected downstream of the photochemical chamber. Particulate laden filters were observed by scanning electron microscopy (SEM). It was observed that B20 emitted significantly lower primary particulates in comparison to mineral diesel for all the loads. B20 emitted lower particulates at lower load conditions for aged samples. At higher engine loads (75% and 100%), this reduction in aged particulates for B20 compared to mineral diesel was quite significant.

Keywords: Scanning electron microscopy (SEM); Biodiesel; Elemental and organic carbon (EC/OC); Sulphate; Particle morphology.

INTRODUCTION

Atmospheric aerosols are mainly composed of elemental carbon (EC), organic carbon (OC) and inorganic species (Heintzenberg, 1989), whereas diesel particulate matter (DPM) consists mainly of EC, OC, sulphate and trace metals. High temperature and pressure conditions in the combustion chamber during combustion in diesel engine results in formation of numerous organic compounds, which get adsorbed onto the solid carbonaceous core of the particulates. These organic compounds are formed as a result of incomplete combustion in the combustion chamber, and are responsible for grave health concerns. Identification and quantification of these compounds has been quite a challenge so far because it depends on a large number of variables such as type of fuel used, type of lubricating oil used, design of combustion chamber, fuel injection strategies etc.

Diesel particulates can be categorized as primary and aged particles. Primary particles are produced directly by the emission source i.e., diesel engines and aged particles are

formed by condensation of gaseous species present in the diesel exhaust over existing available nuclei as a result of complex photochemical reactions in the atmosphere and subsequent transformations (Gupta *et al.*, 2011). DPM lead to poor visibility and have adverse effects on human health, therefore DPM categorized as “Carcinogenic” (Mansfield *et al.*, 1991). Organic species present in the engine exhaust consists of some highly carcinogenic compounds such as nitro-polyaromatic hydrocarbons (nPAHs) (Ravindra *et al.*, 2008). On the other hand, primary diesel particulates undergo complex chemical transformation in presence of sunlight and oxidizing agents in the atmosphere and may get converted into even more toxic secondary species. When exhaust is released into the atmosphere, dilution ratio reaches around 1000 within a couple of seconds and the temperature of the exhaust drops rapidly (Abdul-Khalek *et al.*, 1999). Due to excessively high saturation condition, particle formation is enhanced by formation of sulphate nuclei, upon which, various organic compounds get condensed. These organic compounds are primarily high boiling point hydrocarbons, which are already present in the engine exhaust (Kittelson, 1998). In order to investigate the primary and aged particulates, sampling of diesel particulates needs to be done carefully. Sampling technique should not affect the particle’s physical and chemical characteristics. Abdul-

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Khalek *et al.* (1999) explained that the particulate characteristics may change with the use of inappropriate dilution technique. Particle number and size distribution are highly dependent on the dilution ratio, dilution temperature, residence time etc.

Researchers have attempted to reduce particulate emissions by using alternative fuels such as biodiesel. In numerous recent studies, it has been shown that biodiesel blends significantly reduce the particulate emissions (Lapuerta *et al.*, 2008; Gangwar *et al.*, 2012). Biodiesel is comprised of various fatty-acid esters, which offer few advantages over mineral diesel such as higher cetane number, higher fuel oxygen content (~11%) (Junget *et al.*, 2006), lower aromatics etc. Aromatics and sulphur contents are nearly absent in biodiesel, which results in relatively lower toxic potential. The oxygen content of biodiesel reduces the calorific value of the fuel, therefore higher volume of fuel is consumed for per unit power production, however the fuel oxygen in biodiesel reduces the calorific value but it improves combustion quality. Agarwal *et al.* (2011) studied physical and chemical aspects of particulate emissions from biodiesel and took SEM images of B100 and B20 particulates and found bigger size grains compared to diesel particulates.

The effect of engine operating conditions on the particle size and nanostructure was studied by numerous research groups (Zhu *et al.*, 2005; Lapuerta *et al.*, 2007; Lee *et al.*, 2011). Stevenson, 1982 investigated the morphology and crystallography of DPM. It was observed that the degree of crystallinity of carbonaceous DPM increases with particle size and are more crystalline in nature near the centre of the agglomerated particle (Stevenson, 1982). Zhu *et al.* (2005) concluded that most particle size measuring instruments measure the aggregate particle diameters, which are known as aerodynamic and mobility diameters. In reality, most particles have fractal shapes, which can only be observed by direct visualization techniques like SEM (Zhu *et al.*, 2005) or transmission electron microscope (TEM). SEM is also useful for observing the particulate microstructures.

Ruiz *et al.* (2007) designed and fabricated two photochemical chambers in order to generate aged sulphuric acid particles (aged aerosol sampling). They used one of the chambers in the laboratory for aged sulphuric acid particle generation by providing artificial gases; it was observed that the sulphuric acid production increased with the enhanced ozone concentration in the chamber (Ruiz *et al.*, 2007). Other photochemical chamber was used for sampling the diluted exhaust from a coal fired power plant for aged sulphuric

acid particle generation for comparison with the laboratory data (Ruiz *et al.*, 2007). Lu *et al.* (2012) investigated the primary particle size and nano-structure by using TEM for diesel exhaust. It was observed that particulates possessed disorder in size and shape at low loads and high speeds. Lee *et al.* (2002) investigated microstructure, dimensions and fractal geometries of diesel particulate samples using a high resolution TEM. Their study revealed that the primary particulate samples were amorphous and were mainly composed of soluble organic compounds, while particulate sample at higher engine loads were EC enriched, ordered, graphitic structures. To study the primary particle size, fractal dimensions of the particulates and nano-particle characteristics, studies were conducted using SEM/TEM (Ishiguro *et al.*, 1997; Park *et al.*, 2004). Particulates in the diesel exhaust remain one of major concerns in the context of present emission regulations. In-cylinder and after-treatment technologies were developed and they need further improvements in order to reduce particulate emission (Majewski and Khair, 2006), in view of globally emerging emission regulations. Therefore, it is necessary to have complete understanding of the particle formation and its physical and chemical transformations after it comes out of the engine tailpipe, followed by its subsequent aging (photochemical oxidation) in the atmosphere. Keeping this in mind, the present study explored the morphological changes in the primary and aged particulates emitted from a modern diesel engine used in a SUV. Furthermore, the effect of blending biodiesel (B20) with diesel on such particulate emissions is also presented here.

EXPERIMENTAL SETUP

A CRDI diesel engine, typically used in a SUV, was used for the comparative study of diesel and B20 (Tata India; Safari Dicor 3.0 L, Euro III). This four cylinder engine was equipped with a CRDI fuel injection system, which was having a maximum fuel injection pressure of 1600 bar. The engine was turbocharged with intercooling. Engine performance was optimized by an electronic control unit (ECU). An eddy current dynamometer (Dynomerck controls, Pune, India, EC300) was coupled with the engine for loading it. Detailed specifications of the test engine are given in Table 1.

This engine does not use any exhaust gas after-treatment device. Mineral diesel was purchased from a local diesel filling station in Kanpur, India. Karanja biodiesel was

Table 1. Technical specifications of the test engine.

Make/Model	Tata, India/Safari Dicor 3.0 L (BS-III/Euro-III)
Engine type	Water cooled, CRDI, turbocharged, intercooled
No. of cylinder	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 1800–2000 rpm
Compression ratio	17.5
Fuel injection system	CRDI with 1600 bar fuel injection pressure (max.)

prepared in laboratory scale biodiesel pilot plant using Karanja oil as feedstock vegetable oil and methanol, which was also procured locally. Details of the production process are provided in our earlier publication (Agarwal *et al.*, 2009). Hoekman *et al.* (2012) reported that the biodiesel feedstock significantly affects the properties of the biodiesel. Karanja biodiesel blend (B20) was prepared by mixing 20% Karanja biodiesel (V/V) and 80% mineral diesel (V/V).

PARTICULATE SAMPLING SYSTEM

Fuel properties of mineral diesel and B20 were determined using appropriate test procedures and equipments. Table 2 shows the fuel properties for mineral diesel and B20 used in this study. SAE 20W-40 lubricating oil was used. Table 3 shows the specification of the lubricating oil used.

The schematic of the experimental setup used in this study is depicted in Fig. 1. To simulate the environmental conditions, a partial flow dilution tunnel was used for collection of primary exhaust particles from diesel and B20 (Dwivedi *et al.*, 2006; Gangwar *et al.*, 2012). A small portion of exhaust was taken from the engine exhaust stream into the dilution tunnel, which was well mixed with preheated and pre-filtered atmospheric air, in order to get desired dilution ratio, according to EPA guidelines (dilution ratio was maintained at 16) (Baumgard and Kittelson, 1985; Abdul-Khalek *et al.*, 1998). Finally, the particulates were collected on a pre-conditioned 47 mm diameter quartz filter paper. Experiments were performed at a constant engine speed of 1800 rpm at five engine loads using diesel and B20 (Fig. 1). In this study, experiments were conducted at steady state condition only; therefore the results may not be applicable exactly for the transient conditions often encountered with the vehicles on road. In actual road conditions, diesel engines operate in transient conditions and the particulate emission characteristics are quite different. Relatively higher volume of

B20 was burnt in the engine to obtain similar power output for similar operating conditions, because B20 has marginally lower calorific value compared to mineral diesel.

The carbon dioxide (CO₂) concentration was measured for undiluted exhaust, ambient air and diluted exhaust in order to calculate and verify the dilution ratio:

$$\text{Dilution ratio } r = \left[\frac{\text{Undiluted exhaust CO}_2}{\text{Diluted exhaust CO}_2 - \text{Ambient air CO}_2} \right] \quad (1)$$

For aged particulate collection, a photochemical chamber was used (Gupta *et al.*, 2011; Agarwal *et al.*, 2013). Exhaust was diluted with fresh air and was allowed to pass through the photochemical chamber (smog chamber). In the photochemical chamber, particulates get sufficient time to condense, agglomerate and coagulate (Gangwar *et al.*, 2012).

Field Emission Scanning Electron Microscope (FE-SEM)

For morphological investigation, field emission scanning electron microscope facility at IIT Kanpur was used. Particulate samples were collected on quartz filter papers. Sampling duration was kept 15 min for each operating condition. Aged particulates were collected downstream of photochemical chamber with the aid of a PM_{2.5} sampler (Gupta *et al.*, 2011). Samples were collected at 1800 rpm engine speed at five different engine loads (0%, 25%, 50%, 75%, and 100%), fuelled with diesel and B20. Particle laden filters were kept in a desiccator for 24 hours in order to remove the moisture. A small round section was cut from each filter using a 9.5 mm internal diameter punch and these sections were observed in the field emission scanning electron microscope (Carl Zeiss NTS GmbH, Germany; SUPRA 40VP).

RESULTS AND DISCUSSION

The main objective of this work was to perform a comparative morphological study for particulates collected from engine exhaust (diesel and B20) for primary and aged particulate emissions. SEM images were obtained at 5000X magnification. Particulate collection patterns were compared for both the fuels for primary and aged particulates.

Primary Particulates Emission

For primary sampling, particulates were collected directly on to a 47 mm diameter quartz filter paper after diluting the exhaust with clean, pre-conditioned air. There was virtually no significant particulate collection observed on the filter paper at no load condition (Fig. 2). The possible reason for no visual evidence of particulates may be that most of the nuclei mode particulates are formed with very little contribution from EC (Zielinska *et al.*, 2003). Most of the nuclei mode particles were not visible with the magnification used as they may have got trapped deep into the filter fibers and due to dominance of light colored OC, they may not be visible due to poor contrast with the white color filter background.

Table 2. Fuel properties of mineral diesel and B20.

Parameter	Mineral Diesel	Biodiesel blend (B20)
Calorific value (MJ/kg)	43.79	42.73
Viscosity (mm ² /sec.)	2.70	3.11
Density (kg/L)	0.832	0.842
Sulphur content (ppm)	<50 ppm*	~40 ppm**
Cetane number	50*	51.6**

*Bharat Petroleum Corporation Limited. Fuel specifications for High speed diesel-BS IV.

**Nabi *et al.* (2009) and Dhar *et al.* (2013) reported that Karanja biodiesel (B100) has 58 cetane number and 2 ppm sulphur content respectively.

Table 3. Lubricating oil properties.

SAE grade	20W40
Kinematic viscosity	110 mm ² /s at 40°C
Viscosity index	128
Density at 15°C	894 kg/m ³
Flash Point Temp.	240°C

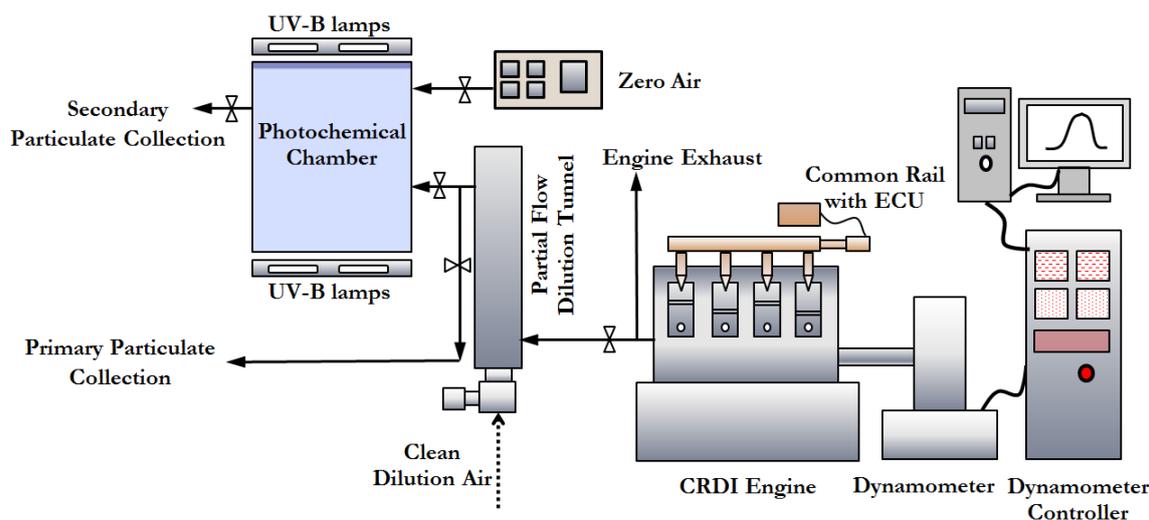


Fig. 1. Schematic of the experimental setup.

With increasing engine load, particulate collection can be observed clearly for both the fuels (diesel and B20) in primary particulates. As the fuel injection quantity increased with increasing engine load, λ (excess air-fuel ratio) decreased, which resulted in higher combustion heat generation, correspondingly leading to higher particulate emissions due to higher degree of heterogeneous combustion. Higher fuel injection quantity led to the increase in number of fuel droplets sprayed in the combustion chamber, which increases the degree of heterogeneity during combustion (Heywood, 1988).

At 25% engine load, flaky particulates were collected. Particulate collection increased with engine load and it reached a maxima at 100% engine load. One important observation was that particulate flakes were relatively dense and bigger in case of 50% load in comparison to lower loads. At 75% and 100% engine loads, particulate collection was so dense that it was difficult to notice the filter fibers, which indicates significantly higher particulate emissions at higher engine loads. Flaky structure near the intermediate engine loads possibly indicates the presence of significant OC and condensed volatile organic materials. However, particulate collection at higher engine load seems more crystalline, which indicated higher EC. Zielinska *et al.* (2003) reported quite high OC content for low engine loads. At lower engine loads, ultrafine particles are emitted, which are mainly composed of OC, whereas at higher engine loads, these particles are mainly composed of EC (Zielinska *et al.*, 2003). Dowling, 1992 reported that fraction of carbonaceous matter in the DPM increases with the increase in engine load and speed. This also suggests presence of higher EC fraction at higher engine loads. Higher in-cylinder temperature at higher engine loads lead to oxidation of majority of OC. EC oxidation is difficult because it requires significantly higher cylinder temperature ($\sim 600^\circ\text{C}$).

As far as fuel is concerned, comparatively higher particulate collection can be observed for diesel than B20 under identical engine operating conditions. A previous study from our group showed that biodiesel blends produced less particulate emissions than diesel (Gangwar *et al.*,

2012). Oxygen content in biodiesel is $\sim 11\%$, which helps in improving combustion thus lowering particulate emissions (Jung *et al.*, 2006). The possibility of oxidation of biodiesel fuel molecules in B20 increases because of the fuel oxygen present in the biodiesel molecules itself. It leads to rapid oxidation of biodiesel fuel molecules therefore oxidation stability of biodiesel remains a serious issue to be dealt with.

Aged Particulate Emissions

It was also observed that the aged particulate collection was wet in nature compared to primary exhaust particulates collected on the filter paper. There were no particulate traces observed at no load condition (Fig. 3). Significant amount of particulates were collected for low and intermediate engine loads (25% and 50% load). Aged particulates were observed bigger in size in comparison to the primary particles collected under similar operating conditions. Gas-to-particle conversion inside the photochemical chamber contributes to this observed significant particle loading of the filter papers. It was observed that the aged particles were relatively denser and larger compared to the primary particles. The possible reason for this phenomenon is the formation of relatively bigger size particles (coagulation and aggregation) followed by adsorption of volatile species on to the PM surface during the photochemical aging process (Agarwal *et al.*, 2013).

For the aged particulate samples collected at 50% engine load, a thick layer of particulates can be observed on the filter paper for mineral diesel. Zhang *et al.* (2008) also reported that soot particles become denser as a result of atmospheric aging process. At 75% and 100% engine load, surprisingly, lower particulate collection on the filter paper was observed, possibly due to loss of aged particulates in the photochemical chamber itself. This might be due to rapid growth of primary particles well above sub-micron sizes (Baumgard and Kittelson, 1985; Singh *et al.*, 2011). At higher engine loads, more fuel quantity is injected into the engine cylinder, which produces higher quantity of water vapor as a combustion product. This water vapor gets condensed in the photochemical chamber due to low

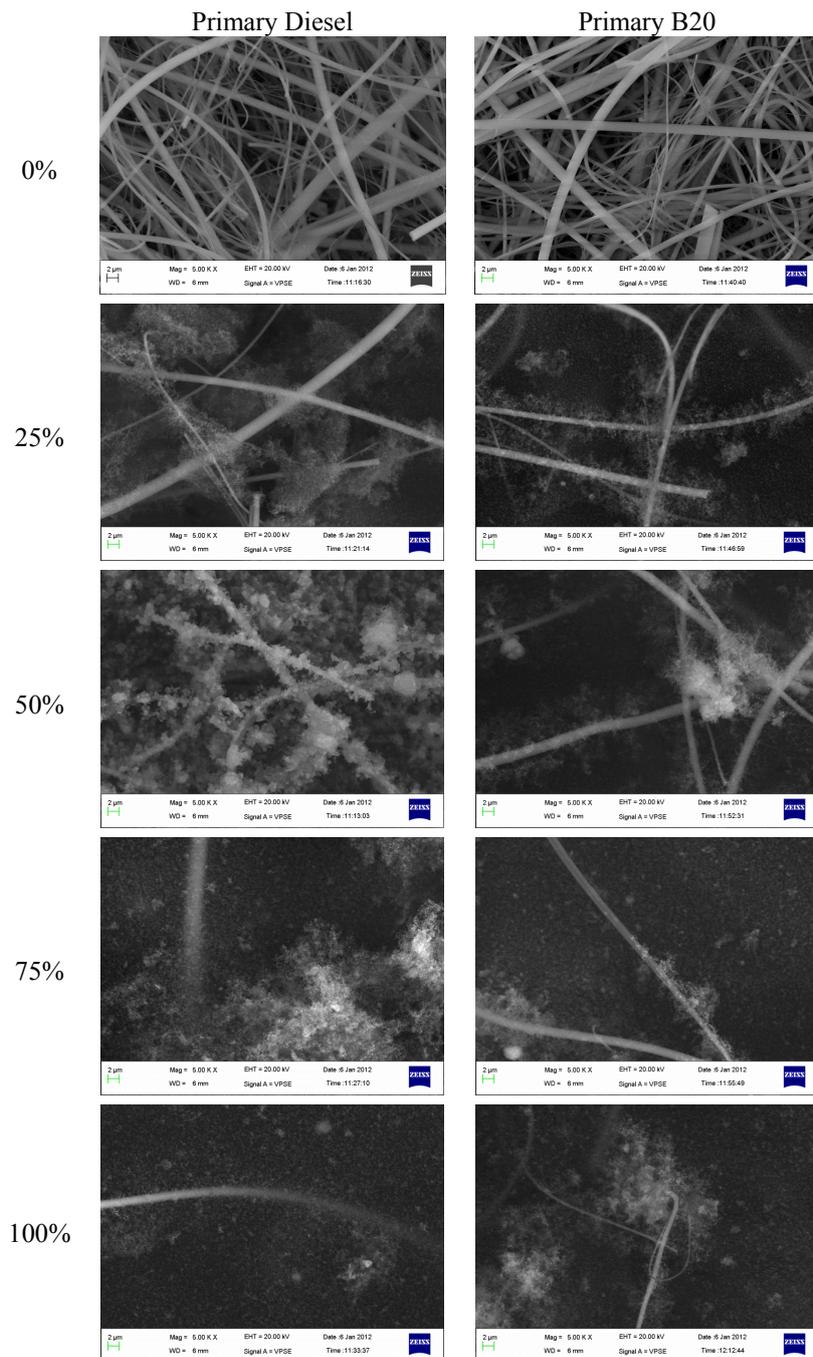


Fig. 2. SEM images for mineral diesel and B20 for primary particulates (5000X magnification).

ambient temperature. Condensation of water vapors to liquid form may lead to faster settling of fully grown water droplets in photochemical chamber, which may also remove several other particles by sweeping mechanism, while settling to the bottom of the photochemical chamber (Singh *et al.*, 2011). Ruiz *et al.* (2007) also reported 21–40% loss for 50–1000 nm size range particles in their photochemical chamber study used for determining the toxicity of coal-fired power plant emissions.

As far as fuels are concerned, comparatively lower particulate collection were observed for B20 compared to mineral diesel for identical conditions. Biodiesel has some

inherent advantages like no aromatics, absence of sulphur content etc. (Jung *et al.*, 2006). Diesel combustion is generally a lean combustion and there is enough oxygen available to burn every fuel droplet in the combustion chamber. However due to the heterogeneous mixing of fuel and air in the combustion chamber, there are localized regions, where fuel-air ratio becomes richer than stoichiometric, leading to incomplete oxidation of fuel molecules due to pyrolysis. This leads to the formation of pyrolyzed compounds, which are primarily soot and unburnt hydrocarbons. In case of biodiesel, oxygen present in the fuel molecule itself helps in combustion in fuel-rich zones and limits the pyrolysis

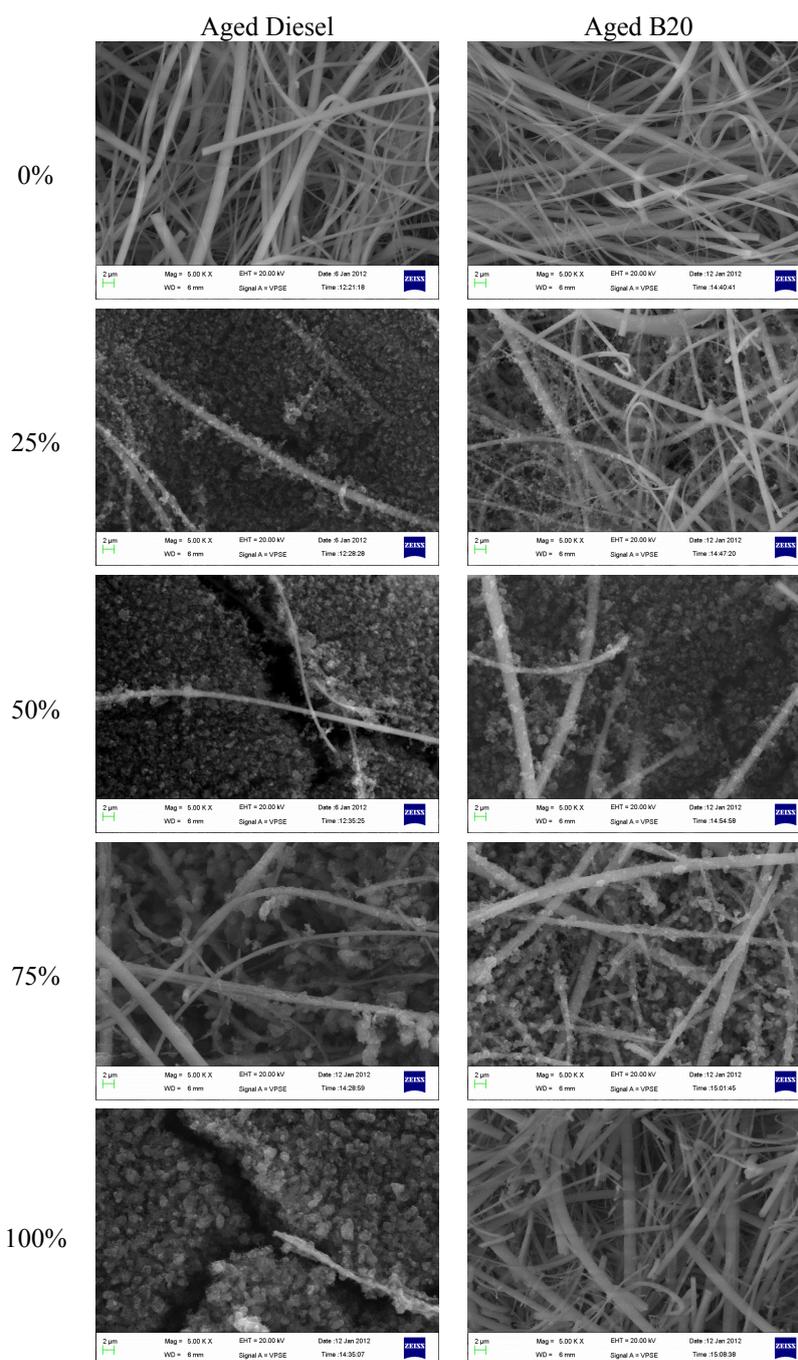


Fig. 3. SEM images for mineral diesel and B20 for aged particulates (5000X magnification).

process. Also, sulphur leads to sulphate (which acts as nuclei for particle growth) formation, which is almost absent in biodiesel. Therefore, B20 leads to formation of lower amount of aged particulates.

In a previous study (Fig. 4) performed in our group by Agarwal *et al.* (2013), it was observed that the EC and OC emissions were lower at low engine loads, which increased with increasing engine load. However, OC reduced at higher engine loads for mineral diesel. These results are in good agreement with the SEM images obtained for primary and aged particulates.

Thick, black and dense particulates observed in SEM

images at higher engine loads indicate higher EC content in mineral diesel exhaust. Also, as noticed from Fig. 4, for both, primary as well as aged particulates, OC content remained fairly constant for B20 whereas it steadily decreased with increasing engine load for mineral diesel. This may very well result in different density as well as morphology of the resultant soot particles.

Fig. 5 shows EC/OC ratio for various engine loads for primary and aged particulates fuelled with diesel and B20. EC/OC ratio increased with engine load for primary and aged particulates, when fuelled with mineral diesel (Fig. 5). In case of B20, it became almost flat near 50% engine

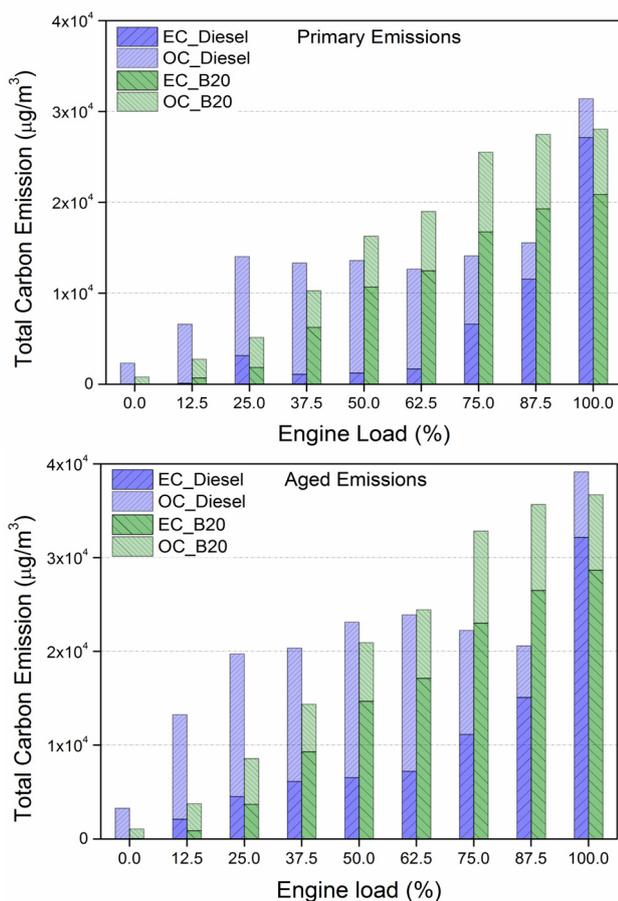


Fig. 4. EC and OC content in diesel and B20 exhaust for primary and aged particulates (data taken from Agarwal *et al.*, 2013).

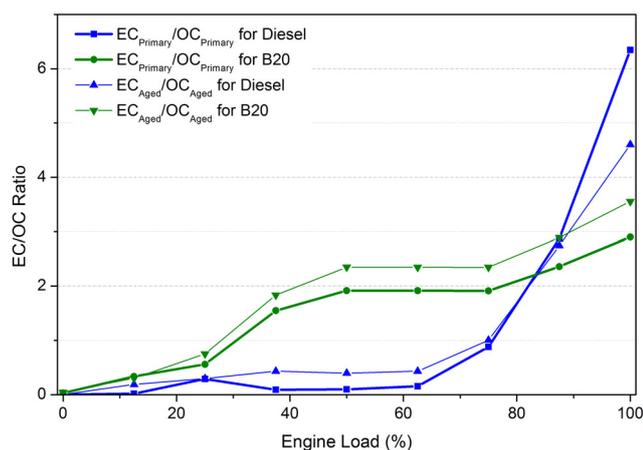


Fig. 5. EC/OC ratio determination for primary and aged particulates (data taken from Agarwal *et al.*, 2013).

load and again increased slightly towards 100% load. It indicates that higher amount of EC is present in mineral diesel and B20 particulates at higher engine loads. One of the important observations was that EC/OC ratio was significantly higher near intermediate loads, when engine

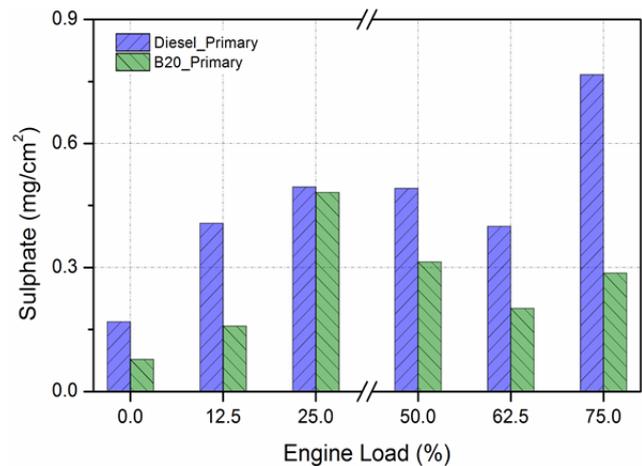


Fig. 6. Sulphate determination in primary diesel and B20 particulates (expressed in terms of PM mass collected per unit filter surface area).

was fuelled with B20 (In comparison to EC/OC for mineral diesel). It indicates higher OC contribution in the primary as well as aged diesel particulates. The collection pattern in the SEM images (Fig. 2 and Fig. 3) showed significantly lower particulate collection for B20 compared to diesel particulates (both, primary and aged). Also, mineral diesel particulates were found to be denser and flaky, which was probably due to higher concentration of OC.

Sulphate in Primary Diesel and B20 Particulate

Diesel particulates consist of sulphates, which lead to higher number concentration of emitted particles in engine exhaust. Sulphate content was determined in the primary particulates of diesel and B20 by using Ion Chromatography (Fig. 6). The details about the sample preparation and sulphate determination methodology are provided in Chakraborty and Gupta, 2010. It can be noticed that the variation in sulphate content in particulates was not consistent but it showed an increasing trend with increasing engine load. Sulphate formation was higher for intermediate and higher engine loads in the tested load range (0–75% load) due to higher fuel quantity burnt. Sulphates significantly contribute to increasing number of nuclei-mode particulate formation (Henket *et al.*, 1992; Majewski and Khair, 2006).

CONCLUSIONS

In primary emissions, particulate collection increased with increasing engine load, which transformed into highly crystalline format higher engine load, indicating higher EC fraction of the particulates. OC contribution to the particulate reduced with increasing engine load because of enhanced oxidation of OC at higher in-cylinder temperatures. Adsorption of organic compounds, and condensation of volatiles at low cylinder temperature resulted in comparatively wetter aged particulate collection. Negligible sulphur content and higher oxygen content in biodiesel led to superior combustion and lower particulate formation for B20 for both, primary as well as aged emissions. It was observed

that particulate collection on filter substrates was relatively significantly lower for aged particulates for B20 at 75% and 100% engine loads. It indicated excessive loss of particulates in the photo-chemical chamber itself during photochemical aging and rapid hygroscopic growth.

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