
Physico-Chemical Characteristics of Particulate Emissions from Diesel Engines Fuelled with Waste Cooking Oil Derived Biodiesel and Ultra Low Sulphur Diesel

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1. Introduction

A ground breaking invention in 1893 by Rudolf Diesel (Diesel Engine – named after him) made a mark in the world of internal combustion engines; his engine was the first one to prove that fuel could be ignited without a spark. Since this invention, diesel engines have been widely used in various applications such as automobiles, agriculture, ships, electricity generators, construction equipment etc., all over the world. Diesel engines were proved to be very efficient in terms of delivering the required energy levels for their use at very low operating and maintenance costs when compared to gasoline engines. However, diesel engines now pose a serious threat to human health and adversely impact the urban air quality (Sydbom et al., 2001). Diesel engine exhaust contains a host of harmful substances including airborne particulate matter (PM), carbon soot, toxic metals, polycyclic aromatic hydrocarbons (PAHs), nitrogen oxides which induce ozone formation, carbon monoxide, carbon dioxide, volatile organic compounds and other compounds such as formaldehyde and acrolein (EPA, 2002). Of these pollutants, PM from diesel exhaust is of great concern because of a number of reasons: (1) Diesel engines are known to be the largest source of PM from motor vehicles. Two thirds of PM emitted from mobile sources are from diesel vehicles (EPA, 2002); (2) Human exposure to diesel exhaust particles (DEP) is high as these particles are emitted at ground level unlike that of smoke stacks. United States of Environmental Protection Agency (USEPA) reported that 83% of people living in the USA are exposed to concentrated diesel emissions from sources such as highways, heavy industries, construction

sites, bus and truck depots etc (EPA, 1999); (3) The freshly emitted DEP includes ultra fine particles (UFPs, aerodynamic diameter (AED) < 100 nm). These particles can bypass the natural defense of respiratory tract and enter deep into the alveolar region of respiratory system from where they could enter into blood stream (Oberdorster, 2001); (4) The particulate-bound soluble organic compounds such as PAHs, nitro-PAHs and transition metals are considered mutagenic or carcinogenic. PM from diesel exhaust is listed as a "likely Carcinogen," citing cancer risk in the range of one in 1000 to one in 100,000 people for each microgram of annual average exposure (EPA, 2002).

Apart from the health impacts, DEP also has potential environmental impacts. Black carbon or soot from diesels affects cloud cover and is a significant contributor to atmospheric warming (Hansen et al., 2000). In view of these concerns and also to meet the current and future regulation standards imposed by local environmental protection agencies, a large number of researchers have conducted research to reduce the diesel particulate levels by various methods such as introducing new engine designs (Guerrassi and Dupraz 1998; Park, et al., 2004), development of particle trap systems and after-treatment devices (Stamatelos 1997), improving the fuel quality (Kaufmann, et al., 1999). Despite these developments over many decades which improved the emission quality of diesels without any doubt, diesel engines still represent a significant source of PM. Holmen and Ayala (2002) reported that the use of particle trap systems reduces total particle number concentration by 10 to 100 times from diesel exhaust, but also found that the use of particle trap-equipped diesel engines may sometimes result in elevated nanoparticle (diameter < 50 nm) emissions. Also, there is an ongoing debate on whether the diesel engine can be modified and improved continuously down to meet the future regulation standards without economic impact. It is believed that developments on engine design needed to meet upcoming regulations would increase the costs and eventually gasoline vehicles could take the place of diesel vehicles (Pischinger, 1996).

As an alternative strategy to improve emission quality of diesels, the option of replacing diesel or petroleum based fuels by renewable bio-fuels is gaining popularity in recent years. Biodiesel (also known as fatty acid alkyl esters), an alternative fuel derived through transesterification process from vegetable oils or animal fats, has received much attention as a result of renewed interest in renewable energy sources for reducing particulate and greenhouse gas (GHG) emissions from diesel engines. In addition, it also helps in alleviating the depletion of fossil fuel reserves (Pahl, 2008; Janauan and Ellis, 2010). Biodiesel is reported to be carbon neutral because of the lower net carbon dioxide production (Ferella et al., 2010; Gunvachi et al., 2007; Carraretto et al., 2004), making it an important fuel source in the era of climate change. Another main driving force for biodiesel is the lower emissions of PM, CO, hydrocarbon, aromatic and polycyclicaromatic compounds (Xue et al., 2011, Atadashi et al., 2010). In view of these advantages, usage of biodiesel is increasing rapidly. This is reflected in government policies such as partial detaxation, investment in production and research of biodiesel by many countries that include USA, Brazil, European Union, South East Asian and other countries all over the world. With these increased awareness and governmental policies of different countries, annual production of biodiesel nearly tripled globally be-

tween 2000 and 2005. According to National Biodiesel Board (NBB) in USA alone 460 million gallons of biodiesel were sold in 2007, 700 million gallons in 2008, and 802 million gallons in 2011, showing a tremendous raise from 2 million gallons sold in 2000. This move from fossil fuels to bio-fuels as a power source is also caused by the economic consequences due to stringent regulations ((EN-590, 2004) in Europe and (ASTM-D-975, 2006) in USA) imposed on the fuels used in transportation. The notable restriction includes reducing sulfur content in the fuel which increased the investment cost of oil companies and the final fuel price which drive the nations to develop their own reserves indigenously and decrease their dependence on Middle East countries for fuel.

Biodiesel is compatible with conventional petroleum based-diesel and can be completely blended with diesel in any proportion. The chemical composition and several properties of biodiesel make it an attractive option over traditional diesel. Biodiesel has higher cetane number, lubricity, combustion efficiency, biodegradability and lower sulfur and aromatic content (Fazal et al., 2011; Demirbas, 2008). In contrast, there are also unfavorable properties in biodiesel such as being more prone to oxidation, lower heating value, and higher cloud and pour points (Szulczyk and McCarl, 2010). Majority of biodiesel is being produced from soybean, rapeseed, and palm oils. Even though most of the biodiesel feedstock is renewable, competition with food supply has become a serious concern recently because certain feedstocks appear to be edible oils (Januan and Ellis, 2010; Mercer-Blackman et al., 2007). Therefore, alternative feedstocks such as non-edible oils, algae oils, and waste oils have arisen to prominence in recent years. Biodiesel produced from transesterification of waste cooking oil (WCO) is one of the most attractive automotive fuels to be used in place of petroleum diesel because of the added advantages over other types of biodiesel. WCO reuse eliminates the need for disposal, thus alleviating the environment and human health issues associated with waste oil disposal (Giracol et al., 2011). The lower cost of WCO feedstock can also help to make biodiesel competitive in price with conventional diesel (Meng et al., 2008). Many studies have been initiated to investigate the impacts of biodiesel made from several feedstocks including WCO on particulate emissions as compared to diesel fuel (Chung et al., 2008; Lin et al., 2011a; Lapuerta et al., 2008, Turrio-Baldassari et al., 2004; Durbin et al., 2007). An apparent decrease in PM emissions with the biodiesel content can be considered as an almost unanimous trend (Lapuerta et al., 2008). Most of the research on emissions from biodiesel is targeted towards physical properties of PM such as particulate mass, number concentrations and their size distributions. Apparently very little information is available pertaining to the health and environmental impacts of particulate emissions of biodiesel due to paucity of data on their chemical composition.

2. Physical characterization of PM emitted from WCOB and ULSD

Conventional regulatory procedure involving dilution tunnel sampling and filter collection proved to be satisfactory for collection of PM from diesel engines a decade ago. However, in the current scenario, the low emission rate (~1mg/km) of PM from modern-era diesel engines places difficulties in sampling through traditional procedures because of their high de-

tection limits. Nor is this traditional method agreeable to recent regulations aimed at in-use emissions monitoring or to the vast variety of off road applications. A workshop was organized by Coordinating Research Council (CRC) in 2002 to discuss possible changes to measurement of DPM, and it is proposed that particle number-based methods potentially allow detection at very low levels with consistency provided formation of nucleation mode particles can be avoided (CRC, 2002). However, it is a difficult task to establish particle number-based standards and a standard methodology for measurement because of the sensitivity in detection, and great variability of nano-sized particles in engine exhaust. The European PMP (Particle measurement Program) and many other organizations including USEPA are working towards improving the methodology for measurement of solid particles to supplement the traditional mass method. A well-designed dilution tunnel satisfying the above requirements and reducing losses is the first step for this purpose.

Typically, DEP are agglomerates of many primary spherical particles of about 15-40 nm diameter. Airborne particles differ in size, composition, solubility and therefore also in their toxicological properties. It is a well-established fact that the current standards on diesel engine emissions not only improved the engine technology but also the fuel quality. These modern day engines emit particles of very low diameter (Su et al., 2004). Most of the particle mass exists in the accumulation mode in the diameter range of 0.1-0.3 μm (Kittelson, 1998). A large part of UFPs go unnoticed when only mass concentration is used as a metric. UFPs contribute a small fraction to the mass concentration of ambient aerosol particles, but may contribute disproportionately to their toxicity because of their high number concentration and surface area, high deposition efficiency in the pulmonary region, and high propensity to penetrate the epithelium (Donaldson et al., 2000).

2.1. Design of dilution tunnel

A dilution tunnel is a closed and controlled chamber where hot exhaust from engines, industrial stacks etc is mixed with dilution gas (usually ambient air) prior to sampling. Dilution sampling was originally used to characterize fine particle emissions from combustion sources because it simulates the rapid cooling and dilution that occurs as exhaust mixes with the atmosphere. Several researchers have developed dilution tunnels over decades for this purpose; one of the popular dilution sampling systems to simulate atmospheric conditions is CALTECH design (Hildemann et al., 1989). However dilution tunnels can also be used to freeze the size distribution by proper design criteria to avoid unwanted nucleation, condensation and coagulation. These dilution tunnels are developed for consistent measurement of particle number concentrations (PNC) from diesel engines.

The design of the sampling and dilution system determines largely what is measured later. Burtscher (2005) suggested in his review paper that the solid nanoparticles from the exhaust are closely related to health impacts and thus solid fractions of the exhaust should be separated from the volatile fraction and be studied for better understanding of health effects. Also, Kittelson (1998) identified that nucleation and coagulation of volatile fraction changes dramatically during dilution and sampling making it difficult to design a standard. Thus, one of the major issues in dilution sampling of engine exhaust is to decrease or eliminate

nucleation processes. Typical dilution tunnels for particulate sampling from engines are designed to meet the following requirements.

- a. To reduce the particle concentration in raw exhaust to a concentration that can be handled by the measurement system;
- b. To reduce the temperatures to an adequate value usually close to ambient temperature;
- c. To control the nucleation/condensation processes;
- d. To reduce the losses of particulate matter during dilution and sampling.

a. Reducing the PM concentration

The PM concentration in raw exhaust varies with engine model, design, applied load and other parameters. A rough estimate of the total number concentrations of diesel engines is in the range of 10^8 – 10^9 cm^{-3} . The present day sampling equipment and monitoring devices are designed to capture/monitor the particles in nanoscale that are abundantly present in today's diesel exhaust. These sampling instruments are highly sensitive, fragile and are reliable. Heavy loading of PM can easily disrupt the configuration, damage crucial systems leading to either inaccurate data, or render the equipment to be useless. So, it is required that the concentrations be brought down well below the instrument's maximum capacity.

b. Reduction in exhaust temperature

A typical temperature of raw exhaust is in the range of 200–400°C, and such high temperatures can damage the charger columns and sensitive electrode plates used for detecting nanoparticles. Also, collection of PM on filter media from hot raw exhaust can alter the chemical composition of PM by inducing chemical reaction between the collected particles and filter media. Current regulation, for example the one used by the USEPA, requires that, PM be collected on filter media after the exhaust has been diluted and cooled to a temperature below 52°C (CFR, 2001).

c. Reduction in nucleation /condensation and coagulation

Engine exhaust contains both gaseous phase and particle phase pollutants. Because of lower volatility and saturation coefficient some organic compounds and other precursor gases such as sulfur dioxide either condense onto the pre-existing particle surface altering their size (diameters), or nucleate to form new particles affecting number concentration. Also, particles can coagulate during dilution changing both the diameter and number of particles. Impact of these processes is very uncertain as they change dramatically during dilution and sampling (Kittelson, 1998) and thus makes comparisons from different sources difficult. It is therefore recommended that the dilution tunnels be designed to minimize or eliminate nucleation, condensation and coagulation (Burtscher, 2005).

d. Reducing losses during sampling

Particles are lost during transfer of exhaust from a tail pipe to sampling instruments and during dilution due to particle – wall interactions. These losses include mechanical losses such as inertial impaction, gravitational settling, electrostatic deposition, and due to diffu-

sion (Kittelson and Johnson 1991). Apart from mechanical losses particles are also lost due to thermophoretic deposition. These losses can impact the particle number concentration and size distribution.

The primary design objective of the dilution tunnel is to make sure that what is released at tail pipe is measured at sampling instruments. In other words, it is designed to minimize/eliminate dilution artifacts, reduce losses, avoid nucleation to preserve the number and size distribution of particles as it is emitted from tail pipe. Before describing the actual design, it is useful to understand the theoretical basis underlying the design. The following sections 2.1.1 and 2.1.2 describe the important mechanisms that play a key role in altering the physical and chemical properties of particles during dilution and the measures taken to prevent such changes. Section 2.1.3 presents actual design of the dilution tunnel.

2.1.1. Nucleation, condensation and coagulation

Concentration of an inert species (C_i) when diluted is given by (Kerminen and Wexler 1995).

$$C_i - C_{i,A} = f(C_{i,E} - C_{i,A}) \quad (1)$$

where, $C_{i,E}$ and $C_{i,A}$ are concentrations in the exhaust and ambient air respectively, and f is dilution factor. Dilution factor simply means when the exhaust dilutes, a small parcel of air contains a certain fraction of the original exhaust and the remaining fraction is ambient air. That fraction of original exhaust in the air parcel is the dilution factor (f).

Temperature of an air parcel also changes in similar manner.

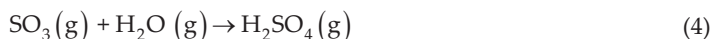
$$T - T_A = f(T_E - T_A) \quad (2)$$

where, T_E and T_A are the exhaust and ambient temperature, respectively.

a. Nucleation

Nucleation and condensation go hand in hand. Nucleation of nanoparticles from the diesel exhaust takes place as the exhaust cools during the dilution process (Abdul-Khalek et al., 1999). When partial pressure is much higher than vapor pressure of nucleating species, they undergo phase transformation. At the same time, due to their low volatility and the existence of large surface area of particles, sulfuric acid and many organic compounds can also condense quickly on the particles. However, Zhang and Wexler (2002) reported that nucleation favors compounds with both low volatility and low-molar volume in the condensed phase. High carbon number organics which usually possess very low vapor pressure, but significantly large condensed-phase molar volume are less likely to be the nucleating species than sulfuric acid (Zhang and Wexler 2004). Although it is still not clear about the nucleation mechanism from SO_2 , it is widely believed that nucleation occurs through binary nucleation of water-sulfuric acid system (Kulmala et al., 1990) or ternary nucleation of Water-

H₂SO₄-NH₃ system (Korhonen et al., 1999). Precursor gas, sulfur dioxide, is oxidized to form trioxide which gets converted to sulfate with water vapor.



The critical value (C_{crit}) for the gas phase concentration of sulfuric acid required for binary nucleation to take place is given by the following formula (Jackervoiron and Mirabel, 1989).

$$C_{crit} = 0.16 \exp(0.1T - 3.5rh - 27.7) \quad (5)$$

where C_{crit} is in $\mu\text{g}/\text{m}^3$, T is Temperature in Kelvin, rh is scaled between 0-1. When the critical ratio $H_2SO_4(\text{g})/C_{crit}$ becomes greater than 1, nucleation (gas-particle conversion) occurs instantaneously, giving birth to fresh nuclei in another log-normal distribution; these are called dilution-induced nuclei mode particles. From eq (5), it is clear that critical concentration is a function of temperature. When the temperature of diluted exhaust is high, the critical concentration required for nucleation tends to increase exponentially. Thus, it is recommended to dilute the hot exhaust with heated air rather than the conventional way of diluting the exhaust with air at ambient temperature. Also, Zhang and Wexler (2004) studied the viability of sulfuric acid induced nucleation and the coupling effect of condensation and nucleation by simulating various cases and reported two important findings: (1) As surface area of combustion induced particles increases, the critical ratio drops and in extreme cases nucleation is totally quenched. This is not to say that supersaturated mixture is not formed, but the sulfuric acid is condensed onto the surface area of particles; (2) Extremely rapid dilution leads to super-saturation of nucleating species and thus nucleation. The possibility of nucleation becomes lower if the dilution is smooth.

b. Condensation

The vapor pressure for volatile compounds is proportional to its temperature. Vapor pressure is related to dilution factor by (Zhang and Wexler 2004)

$$p^0 \alpha \exp\left(-\frac{\Delta H}{R_f T_E}\right) \quad (6)$$

Close to tail pipe, the temperature of exhaust far exceeds the ambient temperature, and therefore equation (2) reduces to $(T \alpha f)$. As a result, a decrease in temperature leads to an exponential decrease in vapor pressures, and the highly super-saturated vapors could make the time scale of condensation very short as 0.1 sec. Another factor important for condensation is particle surface area; by reducing the available particle surface area, condensation can be quenched.

c. Coagulation

Coagulation of particles during dilution occurs either due to turbulent shear, or due to Brownian coagulation. Zhang and Wexler (2004) evaluated coagulation through turbulent shear which has a time scale of $\tau_{ts} = \rho_p / (48 \hat{m}_p \sqrt{\varepsilon_k} / 120v)$ and found that τ_{ts} for turbulent shear is approximately 10^{18} sec, because these tiny particles have such small cross sectional area that shear is insufficient to bring them together. The only mechanism is through Brownian coagulation and it is very insignificant when compared to other mechanisms.

2.1.2. Particle-wall interaction

When the engine exhaust is sampled and passed through dilution tunnel and sampling tubes, particles are lost due to deposition on sampling surfaces. Particles are deposited through several ways which include mechanical (inertial, gravitational, electrostatic, diffusion) and thermal (thermophoretic losses). In their review of variability in particle emission measurements during heavy duty transient tests, Kittelson and Johnson (1991) discussed the impact of exhaust system temperatures on particle measurement and provided recommendations to minimize the effects on aerosol sampling. They calculated losses during the heavy-duty transient test for a typical test facility and found that the majority of particle loss (5%) is due to thermophoresis, whereas inertial, gravitational, electrostatic, and diffusion depositions put together resulted in a loss of 0.2%. Thermophoresis is a physical phenomenon in which particles, subjected to a temperature gradient, move from high- to low temperature zones. A temperature gradient is established during sampling and the dilution between exhaust and the sampling surfaces due to difference in their temperatures. This gradient results in thermophoretic deposition of particles on sampling and dilution system surfaces. Eventually, these deposits are reentrained in the exhaust stream, or cause fouling of sampling surfaces. Reentrainment is unpredictable, and increases variability in mass measurements because of the increase in the number of coarse particles. These particles are not necessarily representative of diesel aerosol and make aerosol size distribution measurements more difficult. To avoid large differences in temperature between lines and exhaust gas, sampling lines should be fully insulated and kept to optimum size to reduce the residence time of exhaust in the sampling lines. Short sampling lines also reduce gravitational and diffusional losses.

2.1.3. Dilution tunnel

Figure 1 shows the schematic of a typical dilution tunnel used for particulate sampling from diesel engines. The engine exhaust was sampled through a sampling probe inserted into the main exhaust stream. The exhaust was then directed into a dilution tunnel, where the hot exhaust was mixed with a stream of pressurized, particle free, dry air in two stages using. In the first stage, the exhaust was transferred into the primary dilution tunnel, where the hot exhaust was mixed with a stream of pressurized particle free dry air preheated to a temperature of close to the temperature of the exhaust, to avoid particle nucleation, condensation, etc. The primary dilution tunnel was also heated to a temperature close to engine exhaust

temperature to avoid thermophoretic deposition of particles onto the walls of the dilution tunnel. In stage 2, some portion of the diluted exhaust from the primary dilution tunnel was transferred to the secondary dilution tunnel. During the primary dilution, vapor pressures of volatile compounds decreased, allowing the secondary dilution with cold dilution air without condensing the volatile components. At this stage, the exhaust was mixed with dilution air at ambient temperature to bring down the temperature of the hot exhaust to ambient temperature for sampling. The completely diluted exhaust was then directed to particle measuring instruments. The dilution ratio was calculated by measuring the CO₂ concentrations in the raw exhaust, dilution air and diluted exhaust.

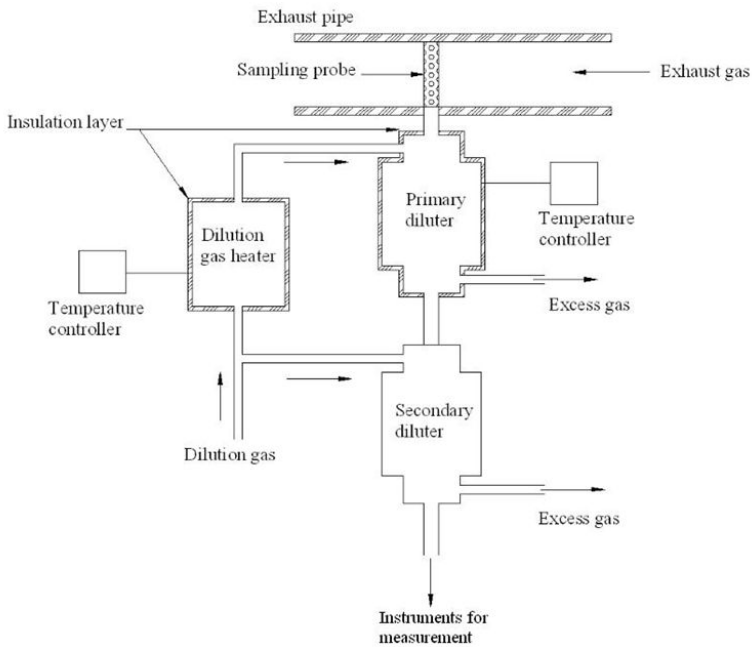


Figure 1. Schematic of a typical dilution tunnel.

A two stage dilution is adopted, firstly to prevent rapid dilution, a dilution is not achieved instantaneously but gradually and secondly, to dilute the exhaust in two different environments to reduce nucleation/condensation. In the primary dilution tunnel, since the exhaust is mixed with pre-heated air, time required for condensation is high comparable to the residence time of the exhaust in dilution tunnel (1~2 sec). In the secondary dilution tunnel, since a small sample from the already diluted exhaust is drawn, the available surface area for condensation is reduced by many times thus condensation is avoided in both stages of dilution.

2.2. Particulate mass concentration

Biodiesel (BD) and blends of ultra low sulfur diesel (ULSD) – BD had a significant effect on particulate emissions. Studies were conducted extensively on PM mass emissions from engine fueled with BD. Although some authors have reported an increase in PM emissions relative to diesel (Durbin et al., 2000; Munack et al., 2001; Alfuso et al., 1993), a large number of studies have confirmed a noticeable decrease in particulate mass while using BD (Lapeurta et al., 2008). However, the reported reductions varied very much depending upon engine conditions, experimental set up, fuel used, engine fuel system and other factors. Several studies reported reductions in the range of around 40 to 50% (Krahl et al., 1996, Lapeurta et al., 2002; Bagley et al., 1998). However, reductions as high as 70 to 90% were also reported by few studies (Canakci and Van Gerpen, 2001; Camden Australia 2005; Kado, 2003; Kalligeros et al., 2003). $PM_{2.5}$ (AED $\leq 2.5 \mu\text{m}$) concentrations for ULSD and WCOB blends were reported by Betha and Balasubramanian, 2011a. They observed that with an increase in percentage of biodiesel in the fuel mixture, particle mass was reduced for B50, and for WCOB (B100) for all loading conditions of engine. For a particular fuel blend, the PM mass increased with load. Lapuerta et al. (2008) reported that many previous studies observed PM reductions in the range of 40-70% when biodiesel was used. The percentage reduction of $PM_{2.5}$ reported by Betha and Balasubramanian, 2011a (~35% at full load) was slightly lower than the range reported by Lapuerta et al. (2008). This is mainly because most of the studies, as reported by Lapuerta et al. (2008) in their review paper, compared biodiesel to conventional low sulfur diesel (sulfur content < 500 ppm) whereas in the study conducted by Betha and Balasubramanian 2011a the comparison of $PM_{2.5}$ emissions was made with ULSD (sulfur content < 15 ppm). The reduction in PM emissions when using BD can be attributed to the following reasons: (1) the absence of aromatics (Knothe et al., 2006), which are considered as soot precursors, in biodiesel reduces the amount of PM formed during combustion; (2) the higher oxygen content in BD tends to enhance the combustion process resulting in lower particulate emissions; and (3) Finally, the presence of unsaturated fatty acids in BD leads to more complete combustion processes. Unsaturated fatty acids have lower boiling points than diesel, and they can evaporate faster in the combustion chamber than diesel (Song and Zhang, 2008). In addition, the higher viscosity and density of BD compared to ULSD can lead to an increase in the injection pressure. Likewise, higher bulk modulus of compressibility of vegetable oils and their methyl esters can lead to advanced injection timing (Boehman et al., 2004) while using BD. As a result, the BD fuel enters the combustion chamber relatively quicker compared to ULSD (Lapuerta et al., (2008). This advancement in combustion process while using BD increases the residence time of soot particles in the combustion chamber, and thus they undergo further oxidation (Cardone et al., 2002) leading to reduction in PM emissions.

2.3. Particle number concentrations and size distributions

New engine designs and emission control devices reduced particulate mass emission drastically allowing the engines to operate below the emission level standards. However, the concerns about UFPs and nanoparticles (AED < 50 nm) which can contribute to human

health effects (Oberdiester et al., 2001, Nel, 2005) significantly raised a serious concern to develop new ambient standards in terms of particle number rather than mass (Burtscher, 2004). Therefore, particulate number concentrations and size distributions are increasingly studied in comparative studies of particulate emissions from diesel and BD (Kittelton, 1998; Lapeurta et al., 2008; Zhu et al., 2010, Di et al., 2009a and 2009b; Di et al., 2008; Burtscher, 2004). In the literature, both an increase and decrease in the total particle number concentrations were reported when using BD. Di et al. (2009b) observed that the total particle number increased 1.5 – 2.5 times when using WCOB compared to diesel depending on the engine load. Similar increments (1.35 – 2.4 times) were observed by them in another study using a direct injection diesel engine. On the other hand, Lapuerta et al. (2007) tested two differently stressed WCOB and observed a reduction (~3 times) in total particle number concentrations (PNC) compared to diesel. Although both of them used WCO in their study, contradictory trends were reported. Studies on other types of BD have also reported contradictory results. A summary of PNC of ULSD and WCOB emissions during different engine operating conditions is provided in Table 1 (Betha et al., 2011a) and their size distributions are shown in Figure 2 (Betha et al., 2011a). In contrast to PM mass emissions, PNC decreased with an increase in load for all the fuels (shown in Table 1). At higher WCOB-ULSD blend ratios, the percentage decrease in PNC with increasing load was relatively small compared to ULSD. For ULSD, total PNC decreased by 26% at full load when compared to idle, or no load conditions whereas, for biodiesel, it decreased by only around 9%.

Engine Load (%)	Total particle number concentration(# cm ⁻³)			
	ULSD	B20	B50	B100
0	1.14 x 10 ⁷	1.05 x 10 ⁷	9.57 x 10 ⁶	8.98 x 10 ⁶
30%	9.82 x 10 ⁶	8.99 x 10 ⁶	9.19 x 10 ⁶	8.58 x 10 ⁶
70%	9.00 x 10 ⁶	8.91 x 10 ⁶	8.87 x 10 ⁶	8.40 x 10 ⁶
100%	8.46 x 10 ⁶	8.34 x 10 ⁶	8.31 x 10 ⁶	8.15 x 10 ⁶

Table 1. Total PNC for ULSD and WCOB (B100) blends at various loads (Betha et al., 2011a)

It is expected that in diesel engines, particle counts would increase with an increase in load. However, a decrease in PNC with increasing load was observed in this study. Chung et al. (2008) also observed a reduction in PNC at higher loads in their study using a Yanmar back-up generator similar to the one used in this study. This observed decrease in PNC was probably due to the transfer of particles from nucleation to accumulation or coarser mode at higher loads. It was observed that at higher loads, nucleation mode particles which contribute to a major fraction of total number decreased and accumulation mode particles increased. As a result, there was an overall decrease in total PNC. This shift in particles from the nucleation mode to the accumulation mode was evident from the PSD shown in Figure 2 (Betha et al., 2011a).

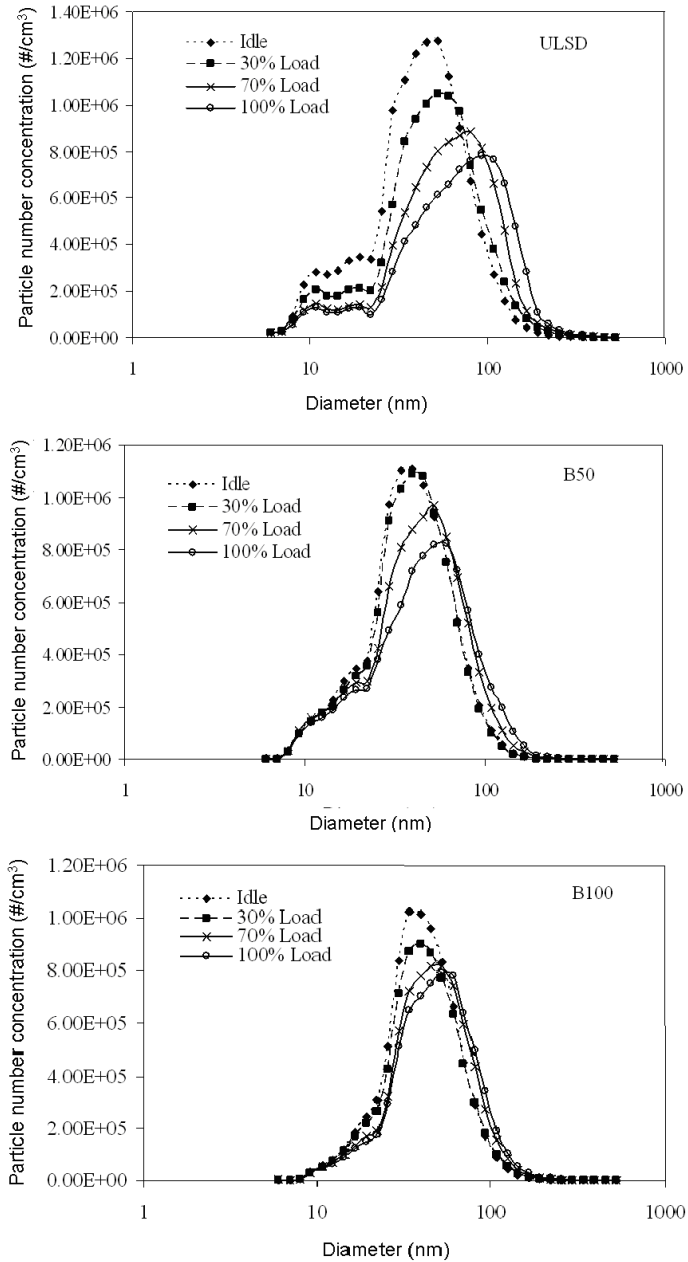


Figure 2. Particle size distributions of emissions at different loads for ULSD, B50, WCOB (B100) (Betha et al., 2011a)

From the PSD shown in Figure 2, it can be observed that with the increase in load, particle peak diameters increased for all fuels. The magnitude of the increase in particle peak diameters at higher loads was greater for the ULSD than the biodiesel. For ULSD, the peak diameter increased from 52.3 nm at idle mode to 93 nm at full load and for biodiesel (B100) peak diameter increased from 34 nm at idle to 52.3 nm at full load. However, in their study on particle emissions from stationary diesel engines, Di et al.(2010) and Zhu et al. (2010) reported an increase in total PNC when engine load was increased. Although there is no definitive explanation for the difference in particle emission trends observed by the above-mentioned studies and trends shown in Figure 2 as well as the study by Chung et al. (2008), a possible reason can be the differences in engine capacities and operating conditions. Both Di et al. (2010) and Zhu et al. (2010) conducted their studies on diesel engines which had much larger capacity and power (~4000 cc and 88 kW). However, the stationary diesel generator used for the the shown results (Table 2 and Figure 2) (296 cc and 4.5 kW) and the one used by Chung et al. (2008) (4.8 kW) have lower capacity and power.

The relative number percentage of nucleation (diameter < 50 nm), accumulation (50-100 nm) and fine particles (diameter > 100 nm) emitted from diesel and biodiesel (B100) fuels at various loads is shown in Figure 3. Biodiesel had relatively a higher fraction of nucleation mode particles ranging from 55% to 70 % at different loads when compared to diesel (35% – 60%). A decrease in the nuclei mode particles (diameter < 50 nm) and an increase in accumulation and fine particles (diameter > 100 nm) were observed with an increase in load for both the fuels. For the stationary engine running with ULSD at full load, nucleation (32%), accumulation (40%) and fine particles (28%) shared almost a similar fraction of particles to the total PNC. However, for BD, nucleation (51%) and accumulation mode particles (43%) were major contributors to the total number concentrations. The fraction of accumulation mode particles increased from 30% during idle mode to 40% at full load in the case of ULSD, and a similar increase was observed for biodiesel as well (from 30% at idle mode to 43% at full load). This observation implies that diesel engines emit more accumulation particles at higher loads. At higher loads, more fuel is injected into the combustion chamber to generate additional torque needed and also the residence time for the particles in the combustion chamber decreases relatively. Therefore, the oxidation of particulate soot tends to be reduced, leading to the release of a large fraction of accumulation and fine particles. In the case of biodiesel, the inherent oxygen in the fuel improves the oxidation of soot. Therefore, the percentage increase of fine particles is relatively less for BD.

3. Chemical properties of particulate emissions

Since diesel engines are one of the most significant air pollutant sources in urban areas (Cass, 1998), chemical composition of diesel exhaust has been widely investigated. The chemical profile of PM plays a crucial role in health and environmental impacts. Variations in the chemical composition of aerosols alter their hygroscopicity and can lead to changes in the cloud-active fraction of the aerosols, or cloud condensation nuclei (CCN) number concentration (Ward et al., 2010). Some carcinogenic and toxic chemical compounds present in DEP when biologically

available can affect human health. Diesel engine emissions consist of a wide range of organic and inorganic compounds in gaseous as well as particulate phases (Bünger et al., 2006). Concentrations of most particle-bound chemical constituents depend on the type of engine, engine load, fuel and lubrication oil properties (Dwivedi et al., 2006). Large surface area of DEP enables adsorption of organics and inorganic compounds from the combustion process and/or the adsorption of additional compounds during transport in the ambient air. DEP consists mainly of elemental carbon (EC) (75%), organic carbon (OC) (19%) and small amounts of sulfates, nitrates (1%) and metals & Elements (4%) (Figure 4) (EPA, 2002a).

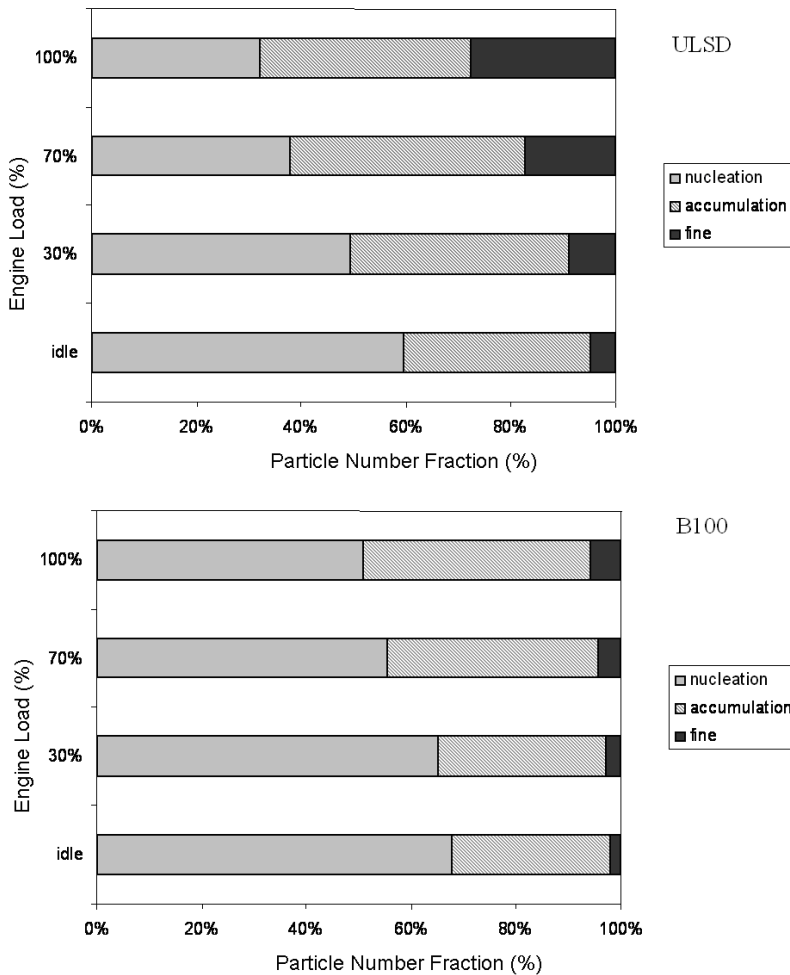


Figure 3. Fractionation of particle emitted from ULSD WCOB (B100) for various loads (Betha et al., 2011a).

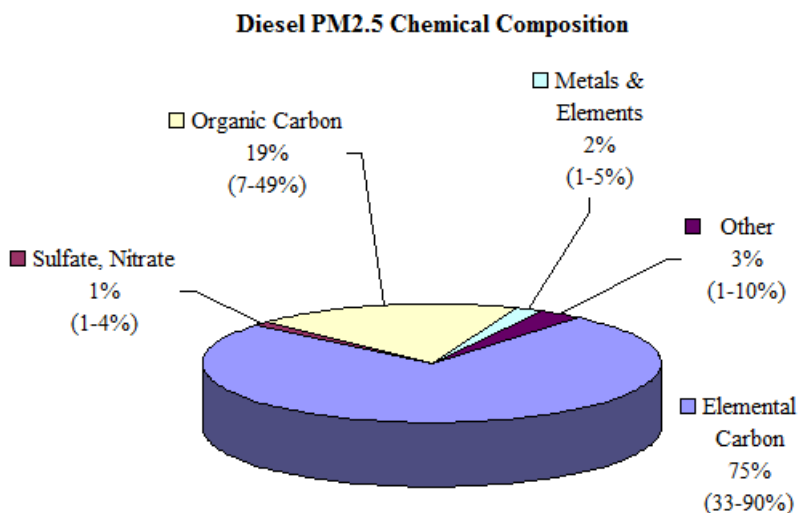


Figure 4. Typical chemical compositions for diesel particulate matter (PM_{2.5}) (EPA, 2002a)

3.1. Particle-bound polycyclic aromatic hydrocarbons (PAHs)

Particulate-bound organic compounds, especially PAHs, are highly carcinogenic. PAHs and their derivatives (nitro-PAHs) together comprise less than 1% of the mass of DEP (EPA, 2002a). The emissions of these compounds are comprehensively studied for diesel engines fuelled with diesel and BD (Jung et al., 2006; Bagley et al., 1998; Correa et al., 2006; Karavalakis et al., 2009; Turro-Baldassari et al., 2004; Zou and Atkinson, 2008; Karavalakis et al., 2010). A majority of studies have found a significant decrease in PAHs emissions with BD compared to that with diesel (Bagley et al., 1998; Correa et al., 2006; Karavalakis et al., 2009). However, a couple of studies have indicated only statistically insignificant reduction in PAHs (Turro-Baldassari et al., 2004; Zou and Atkinson, 2008) when BD is used. The reduction in PAH emission may be attributed to the presence of excess oxygen in BD and the absence of aromatic and polycyclic aromatic compounds in the fuel. One study (Karavalakis et al., 2010) was found in literature reporting higher PAHs emissions when using BD. Karavalakis et al. (2010) tested BD made from soybean oil and used frying oil. They found lower PAH emissions with BD made from soybean oil. However, BD made from used frying oil emitted more PAH compounds compared to those from diesel. They attributed the increase in PAHs to dimers, trimers, polymerization products, and cyclic acids present in the biodiesel made from used frying oil.

3.2. Particulate-bound elements and trace metals

Studies on particulate-bound metals emitted from BD combustion are not as comprehensive as PAHs, despite a strong correlation between human health risk and particulate-bound

metals (Hu et al., 2008; Verma et al., 2010). Very few studies (Dwivedi et al., 2006; Cheung et al., 2011) were found in literature investigating particulate-bound metals in BD. Dwivedi et al. (2006) conducted a comparative assessment and characterization of particulate-bound trace elemental emissions from diesel and rice bran oil derived BD. Elements such as Cr, Ni, Pb, Cd, Na, Al, Mg, and Fe were investigated. The authors observed that concentration of metals such as Cr, Fe, Al, Zn, Mg increased while others (Pb, Cd, Na, Ni) were reduced with the usage of B20 (20% BD). Cheung et al. (2011) also observed higher concentrations of Fe, Zn, Mg when using BD. However, Cr, Al, Pb, Cd, Na, Ni were lower in BD emission compared to diesel. In both the studies, the particulate-bound elemental concentrations were mainly attributed to the fuel and lubricating oil composition apart from engine wear. Metals and elements that were found higher in fuel were also found higher in the emissions. Since the particulate-bound elements largely depend on fuel quality and composition apart from engine wear, their concentration in the exhaust is expected to vary with feedstock of BD. In another study Betha et al. (2011b) investigated the particulate bound elements from WCOB (B100), ULSD and their blend (B50). They observed that particulate emissions were reduced with the usage of WCOB. However, most of the elements which are known to be toxic such as Zn, Cr, Ni were very high in the WCOB exhaust compared to ULSD. Elements such as As, Co, Al, Mn were found to be in higher levels in ULSD. Elements such as Cr, Cu, Fe, Ba, Zn, Mg, Ni, and K were found in higher concentrations in B100 compared to ULSD. Similar findings were reported by Dwivedi et al. (2006). They found that concentrations of Zn, Fe, and Cr were higher in biodiesel compared to those in diesel. The higher concentrations of elements, especially Cu, Fe, Zn, in B100 used in this study can be attributed to the raw material from which biodiesel was prepared. BD used in this study was derived from WCO generated in restaurants and food courts. The oil has been used for cooking and frying of various food products. Elements such as Cu, Fe, Zn and Mn were found in vegetables, (Kawashima and Soares, 2003) Cu, Fe, and Zn in meat (Lombardi-Boccia et al., 2005) and Cu, Zn and Cd in fish (Atta et al., 1997). These elements might have been released into the oil during cooking and therefore, the concentrations of Fe, Zn, Cu, Mn in BD were found to be significantly high. In addition, these elements can also be leached out from the cooking utensils due to heating (Kuligowski and Halperin, 1992).

4. Estimation of health risk due to particulate emissions

Human health risk assessment was conducted based on the mean concentrations of particulate-bound elements determined through the experimental study. Health risk assessment is especially useful in understanding the health hazard associated with inhalation exposure to PM emitted from B100 compared to that of ULSD. The details and steps involved in health risk assessment are described in detail elsewhere (See and Balasubramanian, 2006). Briefly, it involves four important steps (NRC, 1983) as described below.

Hazard identification – elements which have known toxicity values are considered. Al, Cr, and Mn induce non-carcinogenic effects while As, Cd, Cr, Ni and Co induce carcinogenic health effects.

Exposure assessment –This involves estimation of chronic daily intake (CDI) of these elements calculated from the following equations.

$$CDI(\text{mg kg}^{-1}\text{day}^{-1}) = \frac{\text{Total dose (TD,mg m}^{-3}\text{)} \times \text{inhalation rate (IR, m}^3\text{ day}^{-1}\text{)}}{\text{Body weight (BW,kg)}} \quad (7)$$

$$TD = C \times E \quad (8)$$

where C is concentration of pollutant and E is deposition fraction of particles by size given by (Volckens and Leith, 2003),

$$E = -0.081 + 0.23\ln(D_p)^2 + 0.23 \text{ sqrt}(D_p) \quad (9)$$

where D_p is the diameter of particles. In this study, $PM_{2.5}$ (Aerodynamic diameter $\leq 2.5 \mu\text{m}$) was used i.e. D_p is $2.5 \mu\text{m}$. IR is typically assumed to be $20 \text{ m}^3 \text{ day}^{-1}$ and BW to be 70 kg for adults. As for children, the IR and BW are assumed to be $10 \text{ m}^3 \text{ day}^{-1}$ and 15 kg, respectively.

(3) Dose-response assessment- It is the probability of health effects according to the dose of pollutant of concern. Assuming only inhalation as the major exposure route, the reference dose (RfD, $\text{mg kg}^{-1}, \text{day}^{-1}$) for toxic elements that are non-carcinogenic was calculated from reference concentrations (RfC, mg/m^3) provided by USEPA. Likewise, for carcinogenic elements the inhalation slope factor (SF, $\text{mg}^{-1} \text{ kg day}$) was calculated from inhalation unit risk values (IUR, $\text{mg}^{-1} \text{ m}^3$) provided by USEPA.

(4) Risk characterization or estimation of health risk - was calculated based on the exposure and dose–response assessments. For non-carcinogenic metals, it is indicated by (United States Department of Energy, 1999):

$$\text{Hazard Quotient (HQ)} = \text{CDI}/\text{RfD} \quad (10)$$

For carcinogenic metals, total carcinogenic risk is estimated in terms of excess life time cancer risk (ELCR) given by: (United States Department of Energy, 1999).

$$\text{ELCR} = \text{CDI} \times \text{SF} \quad (11)$$

The human health risk assessment was carried out to quantify the risk associated with the particulate-bound metals emitted from ULSD and WCOB at full load from a stationary engine for illustration.

The pertinent information of the TD and RfD, HQ, inhalation SF and ELCR for adults and children are shown in Tables 2 and 3. The concentrations of metals used for this illustration

are adopted from Betha et al. (2011b) (shown in Table 4) and CDI is calculated using Eqns (7) – (9). The concentrations reported in Betha et al., 2011b represent those emitted from the raw engine exhaust. However, in reality the engine exhaust is diluted by ambient air once it is released to the atmosphere. The dilution factor is typically 1000 times when exhaust is released to the ambient atmosphere on road conditions (Zielinska, 2005). The mean concentrations of elements were divided by 1000 to be used in health risk calculations. The deposition efficiency E for particle with 2.5 μm is nearly 0.70. The CDI is calculated by first estimating the TD of the each element (Tables 2 and 3).

ULSD					
Metals	CDI (mg kg⁻¹ day⁻¹)	RfD (mg kg⁻¹ day⁻¹)	HQ	SF (mg kg⁻¹ day)	ELCR
Non carcinogenic metals					
Al	9.84×10^{-6}	1.43×10^{-3}	6.88×10^{-3}		
Cr	1.22×10^{-6}	2.86×10^{-5}	4.26×10^{-2}		
Mn	9.18×10^{-8}	1.43×10^{-5}	6.42×10^{-3}		
Carcinogenic metals					
As	2.51×10^{-8}			15.1	3.79×10^{-7}
Cd	3.79×10^{-9}			6.3	2.39×10^{-8}
Cr	1.22×10^{-6}			4.2	5.12×10^{-6}
Ni	8.02×10^{-8}			84	6.74×10^{-6}
			$\Sigma=5.59 \times 10^{-2}$		$\Sigma=12.3 \times 10^{-6}$
WCOB					
Metals	CDI (mg kg⁻¹ day⁻¹)	RfD (mg kg⁻¹ day⁻¹)	HQ	SF (mg kg⁻¹ day)	ELCR
Non carcinogenic metals					
Al	6.42×10^{-6}	1.43×10^{-3}	4.49×10^{-3}		
Cr	2.18×10^{-6}	2.86×10^{-5}	7.63×10^{-2}		
Mn	3.85×10^{-8}	1.43×10^{-5}	2.69×10^{-3}		
Carcinogenic metals					
As	9.57×10^{-9}			15.1	1.45×10^{-7}
Cd	2.31×10^{-9}			6.3	1.45×10^{-8}
Cr	2.18×10^{-6}			4.2	9.16×10^{-6}
Ni	8.72×10^{-8}			84	7.33×10^{-6}
			$\Sigma=8.34 \times 10^{-2}$		$\Sigma=16.6 \times 10^{-6}$

Table 2. Estimation of human health risk in adults due to particulate bound elements from PM_{2.5} emitted from WCOB and ULSD (Betha et al., 2011b)

ULSD					
Metals	CDI (mg kg⁻¹day⁻¹)	RfD (mg kg⁻¹day⁻¹)	HQ	SF (mg kg⁻¹day)	ELCR
Non carcinogenic metals					
Al	2.30 x 10 ⁻⁵	1.43 x 10 ⁻³	1.61 x 10 ⁻²		
Cr	2.85 x 10 ⁻⁶	2.86 x 10 ⁻⁵	9.95 x 10 ⁻²		
Mn	2.14 x 10 ⁻⁷	1.43 x 10 ⁻⁵	1.50 x 10 ⁻²		
Carcinogenic metals					
As	5.85 x 10 ⁻⁸			15.1	8.84 x 10 ⁻⁷
Cd	8.85 x 10 ⁻⁹			6.3	5.58 x 10 ⁻⁸
Cr	2.85 x 10 ⁻⁶			4.2	1.20 x 10 ⁻⁵
Ni	1.87 x 10 ⁻⁷			84	1.57 x 10 ⁻⁵
			$\Sigma = 1.31 \times 10^{-2}$		$\Sigma = 28.6 \times 10^{-6}$
WCOB					
Metals	CDI (mg kg⁻¹day⁻¹)	RfD (mg kg⁻¹day⁻¹)	HQ	SF (mg kg⁻¹day)	ELCR
Non carcinogenic metals					
Al	1.50 x 10 ⁻⁵	1.43 x 10 ⁻³	1.05 x 10 ⁻²		
Cr	5.09 x 10 ⁻⁶	2.86 x 10 ⁻⁵	1.78 x 10 ⁻¹		
Mn	8.98 x 10 ⁻⁸	1.43 x 10 ⁻⁵	6.28 x 10 ⁻³		
Carcinogenic metals					
As	2.23 x 10 ⁻⁸			15.1	3.37 x 10 ⁻⁷
Cd	5.38 x 10 ⁻⁹			6.3	3.39 x 10 ⁻⁸
Cr	5.09 x 10 ⁻⁶			4.2	2.14 x 10 ⁻⁵
Ni	2.04 x 10 ⁻⁷			84	1.71 x 10 ⁻⁵
			$\Sigma = 1.95 \times 10^{-1}$		$\Sigma = 38.8 \times 10^{-6}$

Table 3. Estimation of human health risk in children due to particulate bound elements from PM_{2.5} emitted from WCOB and ULSD (Betha et al., 2011b)

As shown in Tables 2 and 3, the levels of non-carcinogenic risk (total HQ) were estimated to be 0.06 for ULSD and 0.08 for WCOB and carcinogenic risk (total ELCR) to be 12.3 x 10⁻⁶ for ULSD and 16.6 x 10⁻⁶ for WCOB for adults. In the case of children, non-carcinogenic and carcinogenic risks for both the fuels are higher than those in adults. Total HQ was estimated to be 0.13 for ULSD and 0.2 for B100, while total ELCR was 28.6 x 10⁻⁶ for ULSD and 38.8 x 10⁻⁶ for WCOB. It implies that 28 to 29 children or 12 to 13 adults in a million can get cancer after exposure to the toxic trace metals in PM_{2.5} emitted from the combustion of ULSD. In the case of biodiesel, it is even higher, 38 to 39 children or 16 to 17 adults out of a million can get cancer after exposure to PM_{2.5} by B100 fuel.

Element	ULSD (mg/m ³)	WCOB(mg/m ³)
Al	147.6	96.3
Mn	1.4	0.6
Cr	18.3	32.7
Ni	1.2	1.3
Cd	0.06	0.03
As	0.4	0.14

Table 4. Concentration of particulate bound elements in raw exhaust of a stationary engine

From the results it can be deduced that the non-carcinogenic risk indicated by HQ was higher for WCOB compared to ULSD for both groups of people. However, for both ULSD and WCOB, the total HQ was very low for adults compared to children and for both the groups total HQ was below acceptable levels, (Acceptable levels for total HQ =1). On the other hand carcinogenic risk indicated by ELCR was found to be much higher than the acceptable limit for both groups and for both fuels (i.e., 1 in a million) and that ELCR for WCOB was greater than ULSD. From the risk assessment results made in this study, it appears that exposure to PM_{2.5} emitted from biodiesel poses higher risk when compared to PM_{2.5} emitted from ULSD. However, it is to be noted that in this study the carcinogenic risk due to particulate bound elements was used as a measure to evaluate the total carcinogenic risk. A more comprehensive and extensive research needs to be done to evaluate the complete risk assessment including many other carcinogenic compounds such as PAHs and nitro-PAHs. Studies have shown that PAH emissions from biodiesel are very much lower compared to diesel (Jalava et al., 2010; Karavalakis et al., 2011; Lin et al., 2011; Turrio-Baldassarri et al., 2004). Therefore, the total carcinogenic risk of WCOB exhaust particles might be actually lower than ULSD.

In the case of PAHs the the risk assessment for PAHs that are probable and possible human carcinogens were calculated using potency equivalency factor (PEF) relative to BaP and the CDI calculated from Eq (7). Table 5 shows the PAHs with know PEFs (Collins et al., 1998).

PAH	Group	PEF
Benz(a)anthracene, BaA	2A	0.1
Benz(a)pyrene, BaP	2A	1
Benzo(b)fluoranthene, BbF	2B	0.1
Benzo(k)fluoranthene, BkF	2B	0.01
Indeno(1,2,3-cd)pyrene, Ind	2B	0.1

2A: Probable Human Carcinogen 2B: Possible Human Carcinogen

Table 5. Classification of PAHs by IARC and Potency equivalency factor (PEF)

Carcinogenic risk due to individual PAHs is calculated as product of CDI and PEF. The total carcinogenic risk is the summation of individual risk.

5. Summary

Particle. physical and chemical properties play a key role in determining the health effects associated with PM emissions. Smaller particles can penetrate deep inside the alveolar regions of lungs. Bio-available particulate-bound compounds pose serious health problems. WCOB had lower PNC compared to that of ULSD. However, WCOB had a higher fraction of nucleation mode particles relative to that of ULSD, and therefore, a large fraction of PM emitted from WCOB can deposit in respiratory system compared to DPM. Unlike other types of biodiesel WCOB has higher metal concentrations both in the fuel as well as particulate emissions because of the nature of feedstock. Metals are leached into the oil during cooking and also from cooking utensils. Health risk inhalation of PM was calculated by assessing the CDI estimated using the concentration of particulate-bound compounds and the deposition efficiency of PM in human body, which indicates that WCOB has higher health risk compared to ULSD in terms of particulate bound elements. However, when PAHs are also taken into consideration it can either increase or decrease the relative health risk of WCOB particles depending on the PAHs emission concentrations from both the fuels.

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