



Characterization of exhaust particulates from diesel fueled homogenous charge compression ignition combustion engine



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ABSTRACT

Engine exhaust particulates undergo different processes in the ambient environment such as agglomeration, coagulation, surface condensation, adsorption, and oxidation before evolving as mature particles. Conventional CI engines emit a significant mass/number of particulates due to heterogeneous combustion. However this problem can be resolved by using an advanced combustion technology named as Homogeneous Charge Compression Ignition (HCCI), which has potential to substantially reduce particulates and NO_x simultaneously and deliver efficiencies comparable to conventional CI combustion. In the present study involving homogeneous mixture of diesel and air, an electrically heated diesel vaporizer was developed. Experiments were performed at different relative air-fuel ratios and EGR levels. Enrichment of the mixture increases the peak in-cylinder temperature, which was effectively controlled by EGR under leaner HCCI conditions. A partial flow dilution tunnel was used to collect particulate samples for trace metal content and Benzene Soluble Organic Fraction (BSOF), which is considered to be a marker of toxicity. This analysis showed that the trace metals detected were comparatively lower in HCCI particles. Trace metal concentration increased with application of EGR in the HCCI engine. BSOF content of the HCCI particulates increased when the mixture becomes leaner as well as with increasing EGR. Physical characterization of particulates was also carried out using engine exhaust particle sizer (EEPS), which measures the particle size-number distribution for the nano-particles in the exhaust. The particles collected on the filter paper were also analyzed for morphology using scanning electron microscopy (SEM).

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1. Introduction

Internal combustion engines are the main workhorses of the modern automotive industry. In last two decades, automotive industry has introduced several different types of vehicles using direct injection technology, which delivers superior engine performance as well as lower emissions. DI (Direct Injection Compression Ignition) and SI (Spark Ignition) engines are two fundamental technologies, which are most widely used in vehicles. Various other technology options such as fuel-cells, gaseous fuels (CNG, LPG etc) and alternative fuels are also available but each one of them have their own pros and cons. Concerns about energy availability and emissions such as oxides of nitrogen (NO_x) and

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particulates have motivated concerted efforts towards the design of next generation internal combustion engines, which are capable of delivering higher efficiency and lower emissions simultaneously. Carbon dioxide, carbon monoxide and unburned hydrocarbons from IC engines contribute to global warming. Apart from this, nitrogen oxides and hydrocarbons react in the atmosphere to form photochemical smog that severely impairs visibility. Due to adverse environmental and health effects of these pollutants, increasingly stringent emission standards in the world are mandated, which require simultaneous reduction of particulate and NOx emissions ([Mose et al., 2001](#); [Ellinger et al., 2001](#)). DI diesel engines generate more particulate matter (PM) emissions than other types of engines. Exhaust PM is the substance other than water, which can be collected by filtering the exhaust ([Colin & Allen, 2001](#); [Heywood, 1988](#)). In general, PM collected on the filter paper is usually separated by an extraction solvent into two fractions ([Colin & Allen, 2001](#); [Heywood, 1988](#); [Tan et al., 2004](#)). One fraction is solid carbon (soot), which cannot be dissolved in an organic solvent. It is harmful for human health and it also influences atmospheric visibility by creating photochemical smog. The other fraction, which can be dissolved by an organic solution, is called soluble organic fraction (SOF). This is normally adsorbed on to the soot surface or condensed onto the filter paper. It primarily consists of un-burnt fuel, lubricating oil and their thermally synthesized products.

HCCI combustion reduces both pollutants (PM and NOx) by compression ignition of homogeneous mixture of fuel and air. It is an advanced combustion concept which has shown excellent potential for simultaneous reduction of NOx and PM, while providing high diesel-like efficiencies. Homogeneous mixture reduces the formation of particulates because of the absence of fuel-rich zones whereas auto-ignition by compression ignition reduces the peak in-cylinder temperature, thus reducing the formation of NOx. In HCCI engines, spontaneous auto-ignition occurs at multiple points throughout the in-cylinder charge. This has been verified by several researchers using optical diagnostic techniques ([Furutani et al., 1993](#); [Iida, 1994](#); [Aoyama et al., 1996](#); [Mancaruso & Vaglieco, 2010](#)). This unique property of HCCI allows the combustion of ultra-lean mixtures, resulting in low bulk as well as local combustion temperatures. This significantly reduces engine-out NOx emissions. Also unlike conventional CI combustion, the combustible charge is well mixed in HCCI and there are no fuel-rich pockets, therefore PM emission is also extremely low.

Initial efforts for HCCI were made on a gasoline-fueled engine by [Onishi et al. \(1979\)](#) with an objective of increasing combustion stability of the two-stroke engines. This technology continues to be strongly pursued even today and is named “Active Thermo-Atmosphere Combustion” (ATAC). After successfully achieving HCCI combustion in gasoline engines, research efforts were directed toward attaining diesel HCCI in the 1990s. Initially, early fuel injection and late fuel injection strategies were attempted for obtaining diesel HCCI however these techniques resulted in poor mixture quality and inferior combustion. Basic problems related to design and operational parameters related to diesel HCCI were evaluated by [Suyin et al. \(2011\)](#). In their experiments, in-cylinder mixture preparation technique was used and various experiments were performed under varying operational condition such as different injection strategies, injection pressures, injection timings, intake air temperatures etc. along with varying design parameters such as piston geometries, compression ratios, swirl etc. It was concluded that the possibility of attaining diesel HCCI combustion exists with various limitations. Main challenge was low volatility of diesel. For resolving this issue, external mixture preparation techniques were developed, in which, fuel was injected inside the intake manifold, and mixed with hot air to provide premixed homogeneous charge. [Ryan and Callahan \(1996\)](#) applied homogeneous mixture preparation technique and used port fuel injection of diesel into the intake air stream. An intake air heater was installed upstream of fuel injector to preheat the air. Engine compression ratios were varied from 7.5–17 along with the recirculation of the exhaust gas. Concept of external mixture formation was further developed by [Gray and Ryan \(1997\)](#) and they identified two key operational issues with this technique. The first issue was the requirement of a high temperature for successfully achieving diesel HCCI combustion and to avoid accumulation of diesel in the intake manifold because of poor vaporization characteristics. The second issue was emissions of very high unburned HC. However, they reported dramatic reduction in emission of NOx. Similar experiments were also conducted by [Maurya and Agarwal \(2009\)](#) using gasoline, various primary alcohols and their blends with gasoline and the external mixture formation technique was successfully implemented for a high compression ratio (16.5) engine. Researchers also explored the possibility of using methods for combustible mixture formation outside of the intake manifold ([Nakagome et al., 1997](#); [Roy & Hiromichi, 2003](#)). [Shawn et al. \(2003\)](#) atomized fuel and mixed with air to prepare a homogeneous mixture in a diesel atomizer. They investigated the effect of various parameters such as EGR, air-fuel ratio, intake air temperature, engine speed on HCCI combustion. They suggested that EGR is the most promising solution that can control the formation of NOx. [Agarwal et al. \(2004\)](#) suggested that EGR is an excellent approach to reduce NOx emission, however it leads to fuel penalty. EGR also affects other important performance and emission parameters such as thermal efficiency, brake specific fuel consumption and smoke. In normal CI combustion, increasing EGR rate leads to higher soot formation and emission. This tends to degrade the lubricating oil due to higher soot contamination and also results in higher engine wear ([Singh et al., 2006a,b](#)). For HCCI combustion, it is observed that at higher engine speeds, advanced injection timings produce relatively lower PM emissions. There seems to be a correlation between the amount of fuel injected, EGR rate, engine speed, and PM emissions ([Misztal et al., 2009](#)). [Singh et al. \(2006a\)](#) investigated the effect of EGR on lubrication oil degradation. Organic fraction of particulate matter originates from partially oxidized/pyrolysed fuel and lubricating oils ([Williams et al., 1987](#); [Agarwal, 2005](#)). The organic fraction of particulates contain chemical species such as alkanes and alkenes, aldehydes, aliphatic hydrocarbons, PAH and PAH derivatives. Basically organic fraction containing neutral and aromatic fraction of particulates are mutagenic and

carcinogenic in nature. Their toxic potential was characterized by benzene soluble organic fraction (BSOF) (Johnson et al., 1994; Cheung et al., 2010).

Diesel exhaust particulates are a complex mixture of hundreds of constituents present in both gaseous and aerosol phases. Due to large surface area of diesel particulate matter, it is an excellent carrier for adsorbed inorganic and organic species. In the gaseous phase, major constituents of diesel exhaust are N_2 , O_2 , CO_2 , CO, water vapour, sulfur compounds, NO_x and low-molecular-weight hydrocarbons. Approximately 90% of PM mass exists in two distinct sub-micron modes: a nuclei-mode (7.5–56 nm); and an accumulation mode (56–1000 nm) (Johnson et al., 1994). These nano-particles have a very large surface area, and may easily become coated with contaminants that include toxic metals (lead, cadmium, arsenic, chromium, zinc), sulfur, and PAHs (Cass et al., 2000). The liquid phase emissions are composed of organic compounds and sulfates. Sulfates and trace metals are important inorganic constituents of diesel particulates. Typically, a four-stroke heavy-duty diesel engine emits trace metals such as silicon, calcium, zinc and phosphorus (Dwivedi et al., 2006; Agarwal et al., 2010). Calcium was found to be a dominant metal in diesel particulates with levels ranging from 0.01 to 0.29% (w/w particulate). Phosphorus, silica and zinc were the next most abundant trace metals detected. Sodium, iron, nickel, barium, chromium and copper were present either in very small concentrations or were below the detection limits. Singh et al. (2006b) discussed the role of lubrication oil in soot deposition and trace metal emissions from a CI engine operated with EGR. Valavanidis et al. (2000) reported that deposition of these trace metals of diesel particulates in the lower airway of the respiratory system could generate hydroxyl radicals and then trigger production of reactive oxygen radicals which could potentially cause acute and chronic lung injuries.

According to Kittelson and Franklin (2010) carbonaceous agglomerates represent most of the mass from the diesel engines; however, it can be significantly reduced by employing HCCI technology. They suggested that about 10% (w/w) of the emitted PM was inorganic which included metals and ash. In HCCI combustion, PM emissions comprise lesser solid carbon accumulation mode particles and more volatile particles in the nuclei mode. The inorganic fraction might be expected to be a larger fraction of the total PM. They described that engine emission depends not only on the level of soot formed during the combustion but also depends upon the level of oxidation after combustion. It was also reported that carbonaceous agglomerates form most of the mass in the diesel engine particles however it can be significantly reduced by employing HCCI combustion.

According to Price and Stone (2007), PM emissions in HCCI combustion are non-negligible. A significant concentration of accumulation mode PM was detected in HCCI combustion therefore it was predicted that PM mass emission would not be negligible. In HCCI mode, brake specific NO_x ($BSNO_x$) emissions reduced by a factor of 5 or higher as compared to conventional SI combustion. The unburned hydrocarbon emissions were 10–20% higher than conventional SI combustion. At the same operating point, the number concentration of PM in the nuclei mode was relatively lower however, it was relatively higher (by a factor of 2–3) in the accumulation mode. The concentration of particulates in the accumulation mode (80–90 nm) lies between 10^5 and 10^6 particles/cm³. The particle concentration in the nuclei mode (10–20 nm) lies between 10^6 and 10^7 particles/cm³. Kaiser et al. (2002) suggested that particulate emissions from the HCCI engines at moderate loads were much lower than conventional CI engines however almost equal to direct injection spark ignition engines (Valavanidis et al., 2000; Price & Stone, 2007). For a constant engine speed, number and size distribution of PM from the HCCI engine varies with several operational parameters such as valve timing, intake air temperature, air-fuel ratio, engine load and EGR rate. Although most researches proved that HCCI engines produce lower PM however considering the large number of fine particles emitted, the particulate emissions from the HCCI engine cannot be neglected. Therefore, this study was aimed at understanding the nano-particulate emissions from a diesel fueled HCCI engine. It also includes the physical and chemical characterization of PM, especially for toxicity and trace metals. Scanning electron microscopy was performed for PM samples collected on the filter papers to understand particulate morphology. This study also includes the performance and emission characterization for the better understanding of the HCCI combustion system and particulate characterization.

2. Experimental setup and methodology

The schematic of the experimental setup is shown in Fig. 1. The experiments were performed using a constant speed, two-cylinder, four-stroke, air-cooled, direct-injection diesel engine (Indec; PH2). The technical specifications of the unmodified test engine are given in Table 1. In this engine, one cylinder was modified to operate in HCCI combustion mode while the second cylinder worked in conventional CI combustion mode. The compression ratio of the HCCI cylinder was not changed and was kept 16.5. The combustion chamber geometry i.e. piston bowl shape was also not changed and it remained hemispherical, as in the original CI engine combustion chamber. Modifications in the intake system and exhaust line are important. In the intake system, provisions were made to mix the charge from the fuel vaporizer, recirculated exhaust and ambient air. Two separate exhaust lines were provided for the two cylinders so that separate exhaust gas samples can be collected for characterization. For fuel supply, a common rail was modified for housing a single injector system. The engine was coupled with a single phase 9 kW, 220 V AC alternator. A load bank of 10 kW capacity with a loading step of 0.5 kW was used for loading the engine alternator system.

Low volatility of diesel was the main obstacle in formation of homogeneous mixture of fuel and air. In the present investigations, homogeneous mixture of fuel and air was prepared using an external mixture formation device called “diesel vaporizer”. The schematic of diesel vaporizer and its mounting on the engine is shown in Fig. 2.

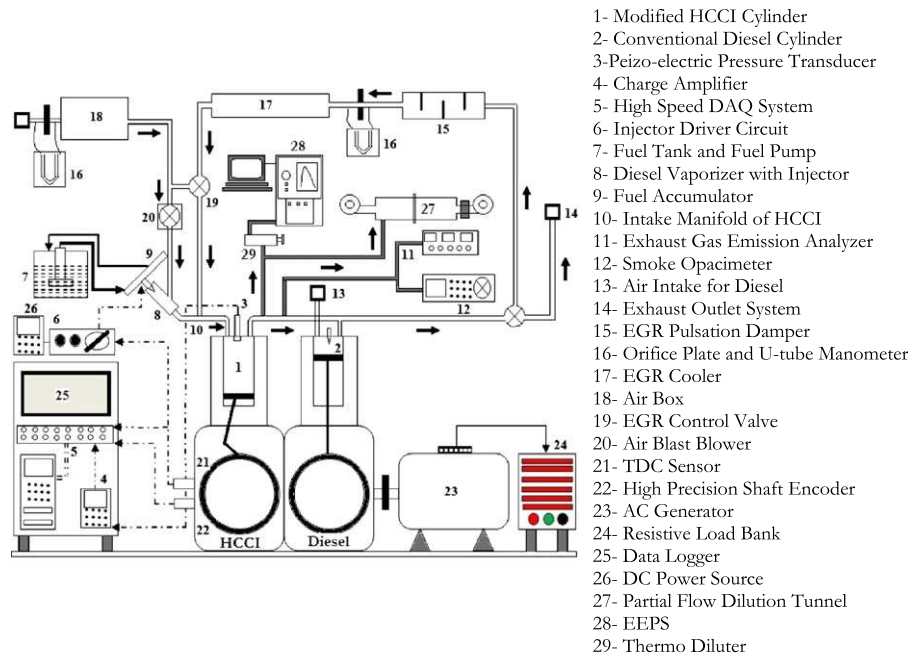


Fig. 1. Schematic of the diesel HCCI experimental setup.

Table 1

Detailed technical specifications of the test engine.

Engine characteristics	Specifications
Make/model	Indec/PH2 diesel engine
Injection type	Direct injection
Number of cylinders	Two
Bore/stroke	87.3/110 mm
Power output/cylinder	4.85 kW at 1500 rpm
Compression ratio	16.5:1
Displacement per cylinder	659 cc
Fuel injection release pressure	210 kg/cm ² at 1500 rpm
Oil sump capacity	6.8l

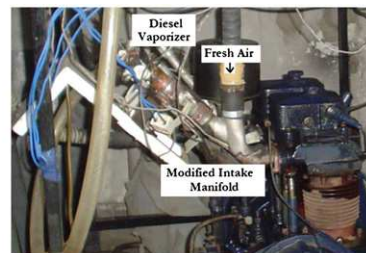
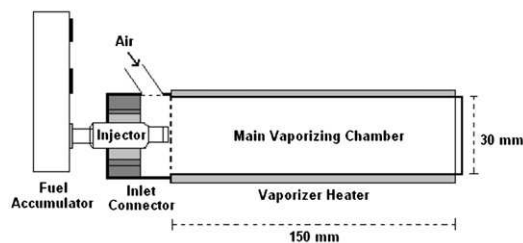


Fig. 2. Schematic of diesel vaporizer and its arrangement on the engine.

The temperature of this vaporizer was controlled by a PID temperature controller. The cut-off temperature for the PID controller was fixed at 160 ± 10 °C. Fuel injector sprayed atomized fuel into an electrically heated vaporizer chamber, where it vaporized and mixed with the incoming air stream to form partially homogeneous fuel-air mixture. Injection parameters such as injection delay, start of injection, fuel quantity etc. were controlled by a customized electronic injector

driver circuit developed (Singh and Agarwal, 2012). For control of HCCI combustion, cooled EGR system was used where exhaust gas fraction was supplied to intake manifold through EGR damper and EGR cooler. For controlling/varying the EGR rate, an EGR control valve was used. The EGR rate was measured by an orifice plate and a U-tube manometer. High speed combustion data acquisition system was used to store and analyze the engine combustion parameters. Data acquisition and combustion analysis program was developed using National Instrument LabVIEW software (V. 8.6). This program allows simultaneous monitoring, processing and recording of various data-sets acquired from the engine. This system acquires in-cylinder pressure signals and few other signals as input, processes the data and delivers engine performance parameters such as IMEP, indicated thermal efficiency and ISFC.

For emission analysis, gaseous species concentration were measured using five gas portable exhaust emission analyzer [AVL; 444]. This instrument measures raw concentrations of NO, HC, CO, O₂, and CO₂. Particulate samples were collected isokinetically using a custom-built partial flow dilution tunnel. This tunnel simulates the ambient environmental conditions for particulate development; growth, agglomeration, and adsorption processes to complete before collecting the PM from the exhaust. It draws a fraction of exhaust gas from the main exhaust line and mixes it with pre-filtered (porous paper filter with a pore size of 30–60 µm), preheated air with a dilution ratio of 10:1. The diluted exhaust undergoes complete mixing and particulate formation steps viz. condensation of gaseous material on particulate nuclei (heterogeneous condensation) along with adsorption, absorption, agglomeration and coagulation. Resident time in dilution tunnel is designed such that these reactions must complete before the sampling probe locations. This residence time is affected by several factors namely flow rate inside the dilution unit, length of the dilution & preheating assembly, flow characteristics (parallel or counter) and nature of mixing inside the dilution unit. For lower residence time, system size should be small so that average time spend by the particles will be low. Finally, these particulate are collected on a quartz filter paper for further analyses.

A part of the filter paper was used to analyze the BSOF of the collected particulate. BSOF mainly consists of organic fraction of fuel and lubricating oil generated pyrolytically and adsorbed during the soot growth process. Filter papers were cut into several small pieces using a plastic scissor and placed into a reagent beaker. Thereafter 20 ml benzene was added and beaker was kept in ultrasonic bath for 20 min. Then the sample was decanted and vacuum filtered through 0.45 µm Millipore filter. The filtrate was collected in a pre-weighed beaker. The procedure was repeated with 10 ml benzene in the same reagent beaker. This pre-weighed beaker was covered with aluminum foil having holes and was kept in oven at 40 °C for 12–18 h until the sample dries. The final weight of the beaker was measured to estimate the total BSOF in the sample (Gangwar et al., 2012).

Engine exhaust particle sizer (TSI; EEPS 3090) spectrometer provides both high temporal and size resolution by using multitude of charge detectors in parallel. This makes EEPS an ideal instrument for measuring engine transients (10 Hz measurement frequency), which measures particle sizes from 5.6 to 560 nm with a size resolution of 16 channels per decade (a total of 32 channels) for measurements, a fraction of engine exhaust is drawn and diluted using rotating disc diluter (Matter Engineering, 379020) to lower the particle concentration to a value within the measurement range of EEPS, which uses computer as a user interface. The results of the experiment are categorized and reported for performance analysis, emission analysis and particulate analysis.

3. Performance analysis

Important performance parameters analyzed in this experiment are indicated thermal efficiency, indicated specific fuel consumption and exhaust gas temperature. Each parameter is described separately in following sections.

3.1. Indicated thermal efficiency

In the experiments, performance of two different cylinders operating in conventional CI and HCCI combustion modes is compared for the indicated thermal efficiency. Fig. 3 shows the indicated thermal efficiency vis-à-vis IMEP, which is analyzed from the in-cylinder pressure data analysis. All other performance parameters are also compared under similar reference conditions (baseline diesel).

Results show that conventional CI combustion delivers slightly higher indicated thermal efficiency as compared to HCCI combustion. Fig. 3 clearly depicts that indicated thermal efficiency decreases with increasing EGR rate. As EGR ratio increases, rate of heat release decreases, resulting in lowering of in-cylinder temperatures (Fig. 5). This lowering of in-cylinder temperature enhances the emission of unburned fuel in the exhaust, which could be noted in Fig. 8. Therefore this also affects indicated thermal efficiency adversely.

3.2. Indicated specific fuel consumption

Fig. 4 shows the variation in indicated specific fuel consumption (ISFC) with respect to IMEP i.e. engine load. As the engine load increases, ISFC decreases because of improved combustion of relatively richer combustible mixture at higher in-cylinder temperatures. Diesel combustion mode shows slightly lower ISFC as compared to HCCI mode. Similar trend is also observed in the indicated thermal efficiency curve (Fig. 3). With increasing EGR rate in HCCI combustion, ISFC increases due to reduced in-cylinder combustion temperatures. This is due to mixture dilution by EGR, which leads to slower combustion.

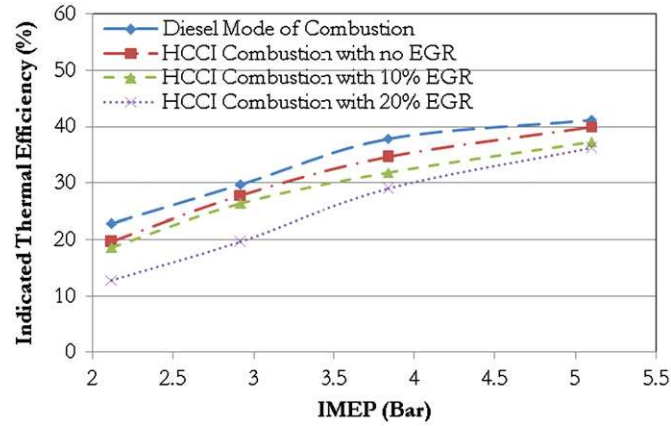


Fig. 3. Indicated thermal efficiency of HCCI combustion at different EGR conditions vis-à-vis conventional CI combustion.

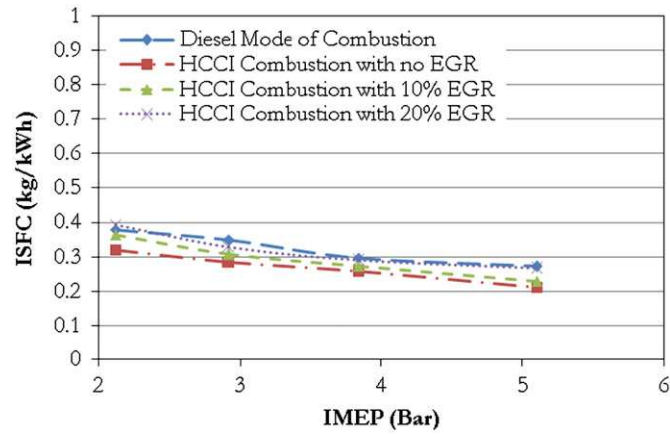


Fig. 4. ISFC of HCCI combustion at different EGR conditions vis-à-vis conventional CI combustion.

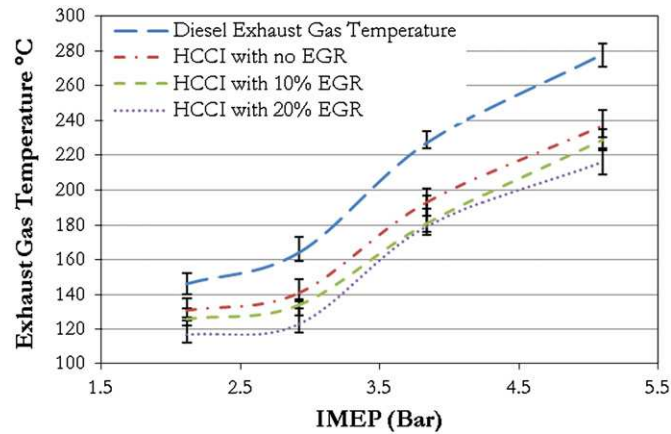


Fig. 5. Exhaust gas temperature of HCCI combustion at different EGR conditions vis-à-vis conventional CI combustion.

3.3. Exhaust gas temperature

Exhaust gas temperature is measured separately in both cylinders working in CI combustion mode as well as HCCI combustion mode. The exhaust gas temperature gives qualitative information about the bulk temperature inside the combustion chamber. Injected fuel quantity, EGR rate and injection timing are important factors affecting exhaust gas temperature.

In HCCI combustion, exhaust gas temperature is significantly lower than conventional CI combustion due to homogeneous mixture combustion and this is one of the main advantages of HCCI combustion as reported by several other researchers (Singh & Agarwal, 2012; Maurya & Agarwal, 2011). Exhaust gas temperature increases with increasing engine load due to formation of richer combustible charge, while it decreases with increasing EGR, which dilutes the charge. At higher EGR conditions, non-reactive inert gases such as CO_2 and water vapor, which have relatively higher heat capacity compared to other constituents of the exhaust gas, absorb the combustion generated heat and reduce the bulk in-cylinder temperature.

4. Emission analysis

Emission of different exhaust gas species (NO_x , HC, and CO) with varying operating conditions such as engine load and EGR vis-à-vis conventional CI combustion is presented in this section. The raw emission data is converted to mass emissions for all the tests using standard SAE protocols. Data presented in this section is therefore reported in terms of mass emissions.

4.1. NO_x Emissions

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the most harmful pollutants emitted by diesel engines and are grouped as NO_x . Usually level of NO in the exhaust gas is higher as compared to NO_2 . High in-cylinder temperature and presence of atmospheric nitrogen in the fresh intake air are the two favorable conditions, which promote NO_x formation. Mainly NO_x formation takes place during post-combustion reactions, when localized temperatures due to heterogeneous combustion exceeds the critical temperature for NO_x formation and molecules of atmospheric oxygen and atmospheric nitrogen start combining.

Mixture quality plays an important role in NO_x formation. A homogeneous mixture burns more uniformly and the localized temperatures are same as bulk temperature, which are invariably lower than the critical temperature required for NO_x chemistry to take place, hence miniscule NO_x formation takes place in HCCI combustion compared to conventional CI combustion. Introduction of EGR gives positive results and further reduces NO_x levels, because of lowering of in-cylinder temperature. Fig. 6 shows large reduction in NO_x emission for HCCI combustion compared to CI combustion, which further reduces by introduction of EGR.

4.2. HC emissions

HC formation takes place largely due to incomplete combustion of fuel. Fig. 7 shows the HC emission from HCCI mode at various EGR conditions vis-à-vis conventional CI combustion. HC emissions in CI combustion mode are significantly lower than HCCI mode. It happens primarily due to incomplete combustion of fuel at lower in-cylinder temperatures and homogeneous combustion of lean mixture. Sizeable amount of homogeneous mixture remains trapped in crevice volumes and in stagnant layers close to cylinder walls, which is emitted without burning during the exhaust stroke in case of HCCI combustion, leading to higher HC and CO emissions. Increasing EGR percentage enhances the HC level due to following two reasons. First is that the recirculation of some unburned HC with EGR leads to reduction in HC emission level. Second is that the reduction in peak in-cylinder combustion temperature leads to increase in HC emissions. Overall effect of increasing EGR on HC emission profile shows increase in mass emission of HC for all loads. At higher IMEP, combustion temperatures are relatively higher, which promotes the re-burning of HC present in the combustion chamber and when the data is converted to mass emission, the BSHC values reduce.

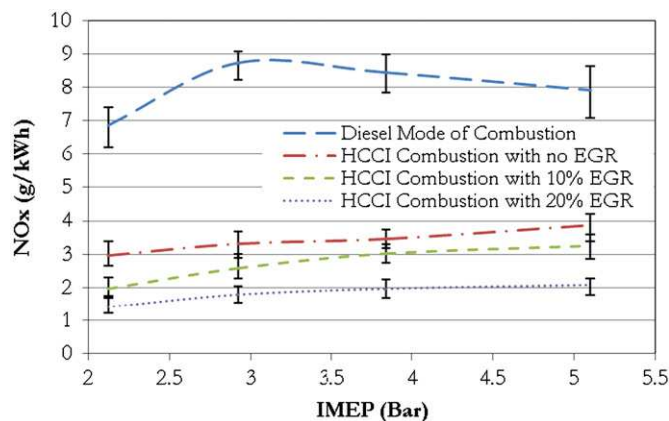


Fig. 6. Oxides of nitrogen in HCCI combustion at different EGR conditions.

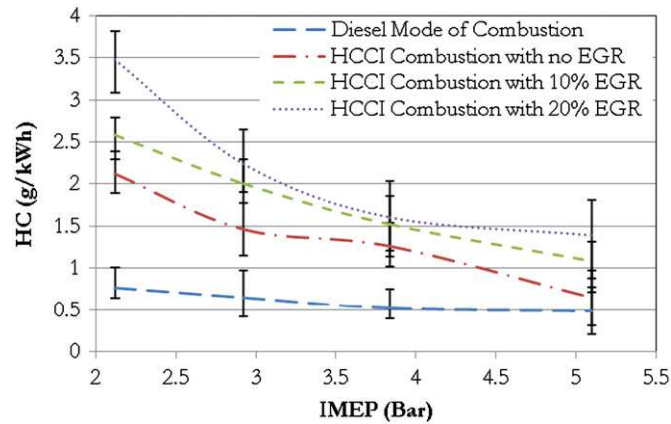


Fig. 7. Unburned hydrocarbons in HCCI combustion at different EGR conditions.

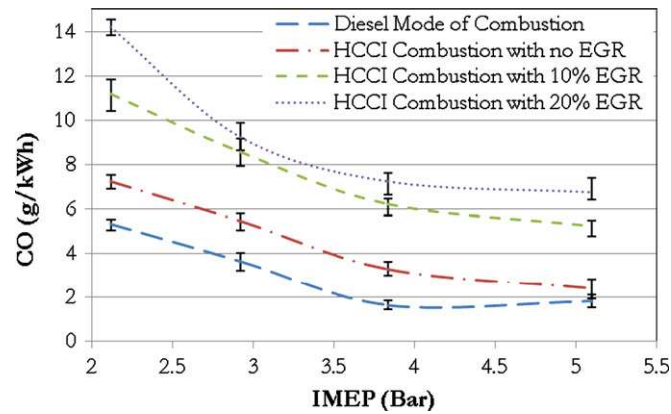


Fig. 8. Carbon monoxide in HCCI combustion at different EGR conditions.

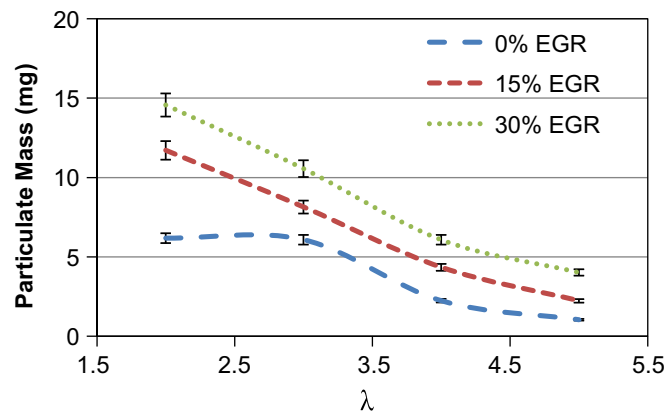


Fig. 9. Particulate mass collected on the filter paper in diesel HCCI mode.

4.3. CO emission

Higher CO emission is one of the major drawbacks of HCCI combustion. CO mass emission for conventional CI and HCCI combustion modes are given in Fig. 8. Similar to HC emissions, major factor, which promotes higher CO formation and emission, is low in-cylinder temperature due to combustion of relatively leaner mixture in HCCI mode. Higher EGR, which is required for combustion control in HCCI mode, further reduces the peak in-cylinder temperature.

At lower peak combustion temperatures, intermediate combustion product CO cannot be fully oxidized in to CO₂. Levels of CO emission decrease with increasing IMEP due to relatively higher combustion temperatures at higher loads. Mass emission of CO in HCCI mode is much higher compared to CI combustion mode. The reason for this behavior is similar to HC emissions, given in the earlier sub-section. It can also be noted from Fig. 8 that by increasing EGR, CO emission increases in HCCI mode.

5. Particulate analysis

The diesel HCCI experiments for particulate analysis were done for varying air-fuel ratio (λ : 2–5) and EGR conditions (0–30%). The PM samples were collected using partial flow dilution tunnel on quartz filters and analyzed for BSOF, trace metals and particulate morphology. The diesel fueled HCCI experiments were done by varying relative air-fuel ratio (λ) and EGR conditions. Particulate number and size distribution were analyzed using EEPS for various engine operating conditions.

5.1. Benzene soluble organic fraction (BSOF)

The exhaust sampling was done for 30 min for assessing the mass of the particles collected on the filter paper under different engine operating conditions and for analyzing the particulates using analytical techniques. The PM mass results are shown in Fig. 9. This figure shows the trend of PM mass collected on the filter paper (mg) with increasing relative air-fuel ratio (λ) for three different EGR conditions. As λ increases, the mixture becomes leaner, i.e. lower fuel quantity is injected and homogeneously combusted, which gives lower PM mass emissions. Fig. 9 shows that PM mass emission increases with increasing EGR. The PM mass is highest for 30% EGR, and lowest for no EGR condition. Use of EGR gives a trade-off between NO_x and PM emission in HCCI mode also because increasing EGR leads to higher specific heat of charge, therefore relatively lower peak in-cylinder temperatures are obtained. As a consequence, increase in EGR leads to lower NO_x emissions and higher PM mass emissions in HCCI mode.

Fig. 10 shows that BSOF increases with increasing λ . At lower λ (i.e. richer fuel-air mixtures), in-cylinder is high enough to burn most of the soluble organic fraction formed. At high λ (i.e. leaner fuel-air mixtures), in-cylinder temperature is relatively lower, resulting in relatively inferior combustion thus producing higher soluble organic species, which will be appearing as BSOF. Experiment also showed that BSOF of particulate increased with the increasing EGR. At higher EGR, the peak in-cylinder temperature is relatively lower compared to no EGR condition, and may not be high enough to burn the fuel completely, leading to higher BSOF. The BSOF of particulates has direct correlation with HC and CO emissions from the engine.

5.2. Trace metals

The amount of trace metals emitted in the exhaust particulate was determined by ICP-OES (Thermo Fischer Scientific; iCAP DUO 6300 ICP Spectrophotometer). Experiments were conducted on the particulate samples collected on the filter paper for determining the trace metals and their variation for varying λ and EGR (Fig. 11). Some of the trace metals detected were below the detection limit of the instrument. Only those elements which were detected with 90% confidence level are reported namely Ni, Pb, Fe, Mn, Si, Cu, and Zn.

Fig. 11 shows that most trace metals follow identical trend with increasing λ , i.e. the trace metal content in the particulate increases with increasing λ . The main reason for this trend is relatively lower in-cylinder temperature for higher λ . At $\lambda \sim 2$, the in-cylinder temperature is quite high and the PM mass is also very high (Fig. 9). Therefore when the trace metal concentration is calculated, it becomes quite low. With increasing λ , lower quantity of fuel is being delivered to the combustion chamber and significantly lower mass of PM is formed (Fig. 9) hence the trace metal emission at higher λ

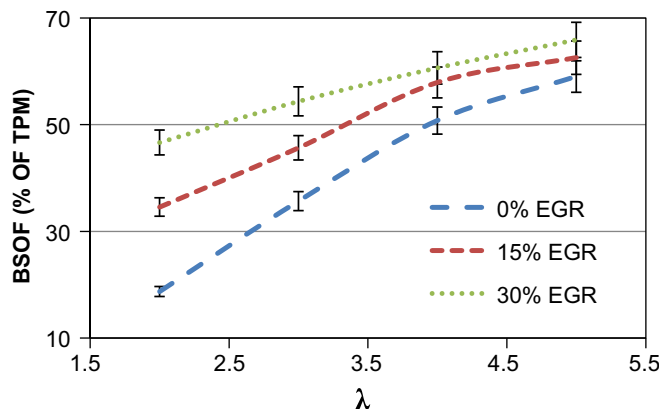


Fig. 10. Variation in BSOF content of HCCI particulates with relative air-fuel ratio (λ).

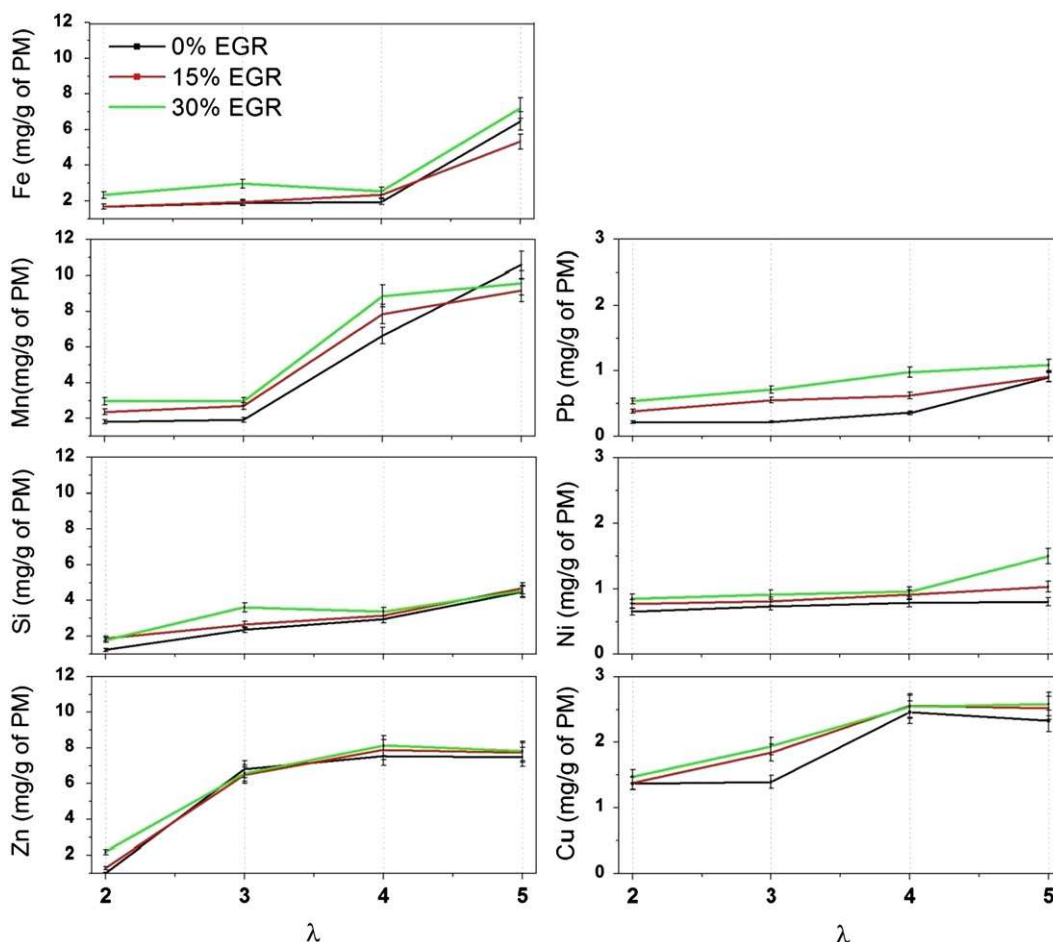


Fig. 11. Trace metals in HCCI particulates (mg/g_{Particulates}) for various air-fuel ratios and EGR conditions.

becomes relatively higher. Trace metals in the engine particulate are contributed by the metals in the fuel, lubricating oil, ambient dust and engine wear. Trace metals concentration shows a slightly increasing trend with application of EGR and is found to be slightly higher at 30% EGR because of relatively lower in-cylinder temperatures.

Fig. 11 shows an increasing trend of iron in the PM with increasing λ . Iron originates primarily from engine wear. When the mixture is relatively richer, higher PM mass is generated, thereby reducing the iron concentration in the particulates. Among the trace metals detected, nickel and lead are detected in lowest concentrations for all engine operating conditions. Nickel is used as an additive in the lubricating oil in very small concentration as Nickel ethoxy-ethylxanthate to improve the lubrication quality. Upon combustion, these compounds dissociate to release nickel, which is seen in exhaust and may cause various harmful health issues. Copper originates from lubricating oil and wear of engine components. The copper concentration in particulate increases with increasing λ (Fig. 11). Zinc containing compound zinc di-alkyl-di-thio-phosphate (ZDDP) is a commonly used additive in the lubricating oils and greases. When the lubricating oil gets heated above 100 °C, ZDDP undergoes thermo-oxidative decomposition in presence of oxygen to form zinc poly phosphate. Zinc poly phosphate reacts with iron oxide in the combustion chamber to produce ZnO. In high temperature environment, ZnO undergoes redox reaction to form Zinc and is emitted as trace metal fraction of the particulate. When the mixture becomes leaner, ZDDP comes in contact with higher amount of oxygen and the above process takes place. Silicon enters the lubricating oil from ambient dust, which is rich in silica. Silicon concentration in the particulate increases with increasing λ and increasing EGR (Fig. 11). Among all trace metals in the particulate, Mn shows highest concentration. Mn compounds are added to the fuel as fuel additives.

More rigorous experimental matrix to compare the toxicity of metals is required to be carried out, for instance in-vitro toxicity test using collected engine exhaust particles. Such facilities and supporting infrastructure to carry out toxicological studies are not available with the authors therefore the present investigation is limited to finding out overall concentration of these metals in the exhaust from the HCCI engine. These metals are bound to particulates in the size range of nm, which have been shown to easily cross the alveolar membrane of the respiratory system and can easily enter into the blood stream, which practically means that whole of the nano-particle is bio-available regardless of their solubility.

5.3. Particulate number and size distribution

Number and size distribution of particulate emitted were measured using engine exhaust particle size (EPPS) spectrophotometer. The number size distribution is shown on a log–log scale in Fig. 12 for various engine operating conditions. This figure shows relatively higher number concentration of particulates at lower λ and vice-versa. This happens because of combustion of higher fuel quantity inside the combustion chamber leading to higher PM mass formation (Fig. 9) and also seen in number concentration graph (Fig. 12). PM number peak shifts towards right with increasing EGR for all values of λ . The maximum number concentration of PM ranges from 5.4×10^7 to 1.08×10^8 for $\lambda=2$ and 9.2×10^6 to 3×10^7 for $\lambda=5$. Most of the particles are in size range of 50–100 nm (between the nano-particle and ultra-fine range) for $\lambda=2$, which seems to be solely the property of HCCI engine. It is above 100 nm for conventional CI engine combustion. For leaner mixtures, PM size peak goes beyond 100 nm. The number concentration of PM may range from 10^8 to 10^9 in case of conventional CI engine (Agarwal et al., 2011), whereas it is in the range of 10^6 – 10^8 for HCCI engines. This shows an order of magnitude lower emission of PM of smaller size from HCCI engine hence putting it in advantageous position among various internal combustion engine technologies.

5.4. Particle surface area and size distribution

Fig. 13 shows the surface area distribution of particles emitted from diesel fueled HCCI engine. Total surface area of particulate emitted by the engine helps in estimating relative particulate toxicity. As the surface area of the particulates increase, it absorbs higher quantity of harmful organic species such as PAHs and N-PAHs. Higher the surface area of particulates, more harmful they will be to human health upon exposure (Karavalakis et al., 2010). The surface area calculations are however done assuming the particles to be spheres, which is not the case with diesel engine exhaust particulate. Fuchs surface area measurement will be a more precise measurement here. Therefore for the results discussed below, it is assumed that the exhaust particles are spherical. Fig. 13 shows the surface area-size distribution of particulates per cc of exhaust increases with increasing EGR. Among all engine test conditions, the surface area of particulates is highest for 30% EGR and lowest for no EGR condition.

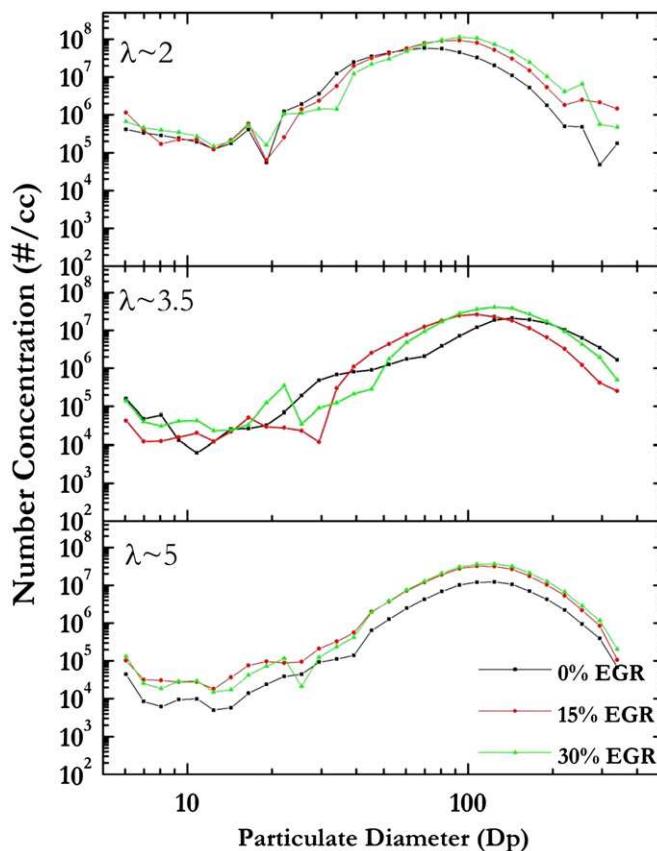


Fig. 12. Number concentration of particles for various air-fuel ratios and EGR rate in diesel HCCI engine.

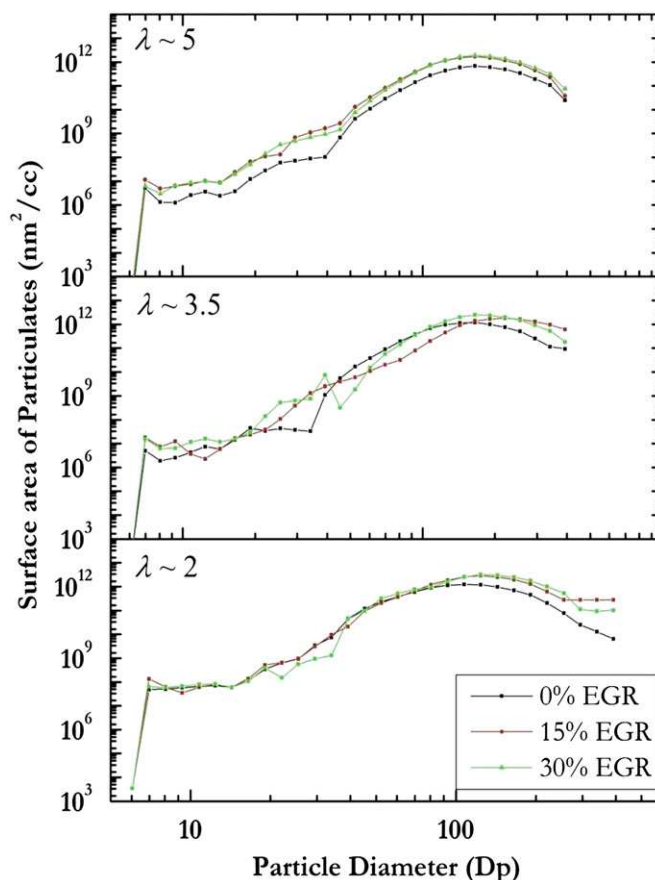


Fig. 13. Surface area and size distribution for particulates at various air-fuel ratios and EGR rates in diesel HCCI engine.

Results show that surface area decreases with increasing λ therefore toxicity of PM is relatively lower for engine operating with ultra-lean air-fuel mixtures in HCCI mode. The surface area is highest ($3.3 \times 10^{12} \text{ nm}^2/\text{cc}$ of exhaust) at $\lambda \sim 2$ and 30% EGR in HCCI mode. The surface area is lowest ($6.5 \times 10^{11} \text{ nm}^2/\text{cc}$ of exhaust) when the engine is operating at $\lambda \sim 5$ and no EGR in HCCI mode.

5.5. Particle mass and size distribution

The Fig. 14 shows the PM mass emission from the engine ($\mu\text{g}/\text{m}^3$ of exhaust gas). Results show an increasing trend of particle mass distribution with increasing EGR (similar to Fig. 9). As the mixture becomes leaner, peak in the graph moves towards larger size accumulation mode particles, which also shows higher soluble organic fraction (Fig. 10). With increasing EGR, the peak of the curve moves further towards right.

Particulate mass emission distribution from the engine varies from 15,000 to 40,000 $\mu\text{g}/\text{m}^3$. Lowest PM mass emission distribution is seen for very lean mixtures ($\lambda=5$) and highest for relatively richer mixture ($\lambda \sim 2$), which validates the results of Fig. 9.

5.6. Scanning electron microscopy

SEM images were taken for the samples collected on the filter paper (30 min sampling duration) from the partial-flow dilution tunnel for varying λ and EGR. The samples were magnified by 1200X. It can be seen from the SEM images that very fine layer of particulate agglomerates are accumulated on the filter paper fibers at no EGR condition. When EGR increases, the particle number also increases significantly. Fig. 15 shows that the PM accumulated in the filter paper fibers at $\lambda \sim 5$ is significantly lower than that accumulated with $\lambda \sim 2$. This is because more amount of fuel is combusted, when the mixture is relatively richer (fuel consumption rate was measured as 1.12 kg/h) and very low fuel quantity is combusted when the mixture is leaner (fuel consumption rate was measured as 0.76 kg/h) in HCCI mode. It is also be noted that the particle size becomes larger with increasing λ . These results are in line with results given in Figs. 9–12.

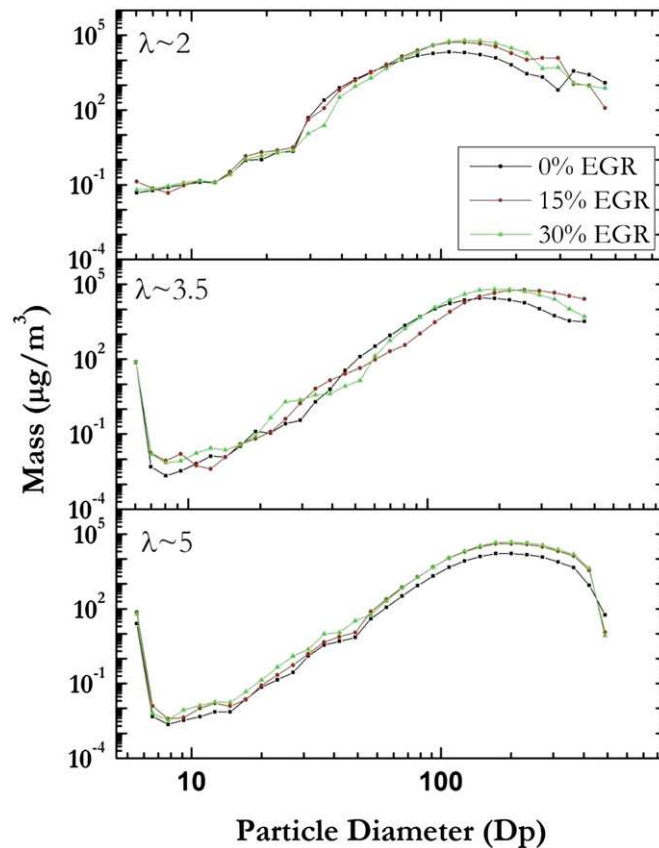


Fig. 14. Particulate mass and size distribution for various air-fuel ratios and EGR rates in diesel HCCI engine.

6. Conclusions

Present study explores the potential of diesel HCCI combustion using fuel vaporizer technology in a constant speed decentralized power generating engine. HCCI combustion delivered comparable engine performance characteristics vis-a-vis conventional CI engine. Indicated thermal efficiency of diesel HCCI was slightly lower than conventional CI combustion, which was offset by its superior emission characteristics. Indicated specific fuel consumption was slightly higher in case of HCCI combustion as compared to conventional CI combustion. Mass emissions of most harmful polluting species in HCCI combustion mode were observed to be significantly better than conventional CI combustion mode. NO_x and PM emissions were simultaneously reduced in HCCI combustion mode. Reduction in NO_x was due to lower peak in-cylinder temperature (local and global) because HCCI combustion takes place in significantly leaner, homogeneous fuel-air mixture. HC and CO emissions were however found to be higher in HCCI combustion mode as compared to conventional CI combustion mode. It was mainly due to lower in-cylinder temperatures and trapping of homogeneous air-fuel mixture in crevice volumes and dead volumes within the combustion chamber. Particulate emissions from the HCCI engine largely depend on the EGR rate and relative air-fuel ratio (λ). When the air-fuel mixture becomes leaner (increasing λ), the PM mass emission decreases from diesel HCCI engine. With increasing EGR, the PM mass emission increases. PM mass and surface area-size distribution were found using EEPs. Most of the diesel HCCI exhaust particles were ultra-fine particles. The particle number concentration tends to increase with increase in EGR rate. Increase in number of particles in accumulation mode is due to higher BSOF of particulate, which increases with increase in EGR and λ . The PM was also analyzed chemically in order to understand their toxic potential and selection of appropriate particulate control technology. The BSOF of PM increases with increasing EGR and λ for diesel HCCI. The particulate samples were analyzed for trace metals (Ni, Pb, Fe, Mn, Si, Cu, Zn). Most of the trace metals were relatively higher when EGR was applied. SEM images show that the PM deposited on the filter paper decreases with increase in λ and increases with increasing EGR and vice versa.

In summary, the diesel HCCI leads to lower particulate emissions and the toxic potential of the particulate emitted is relatively higher at higher engine loads and vice versa.

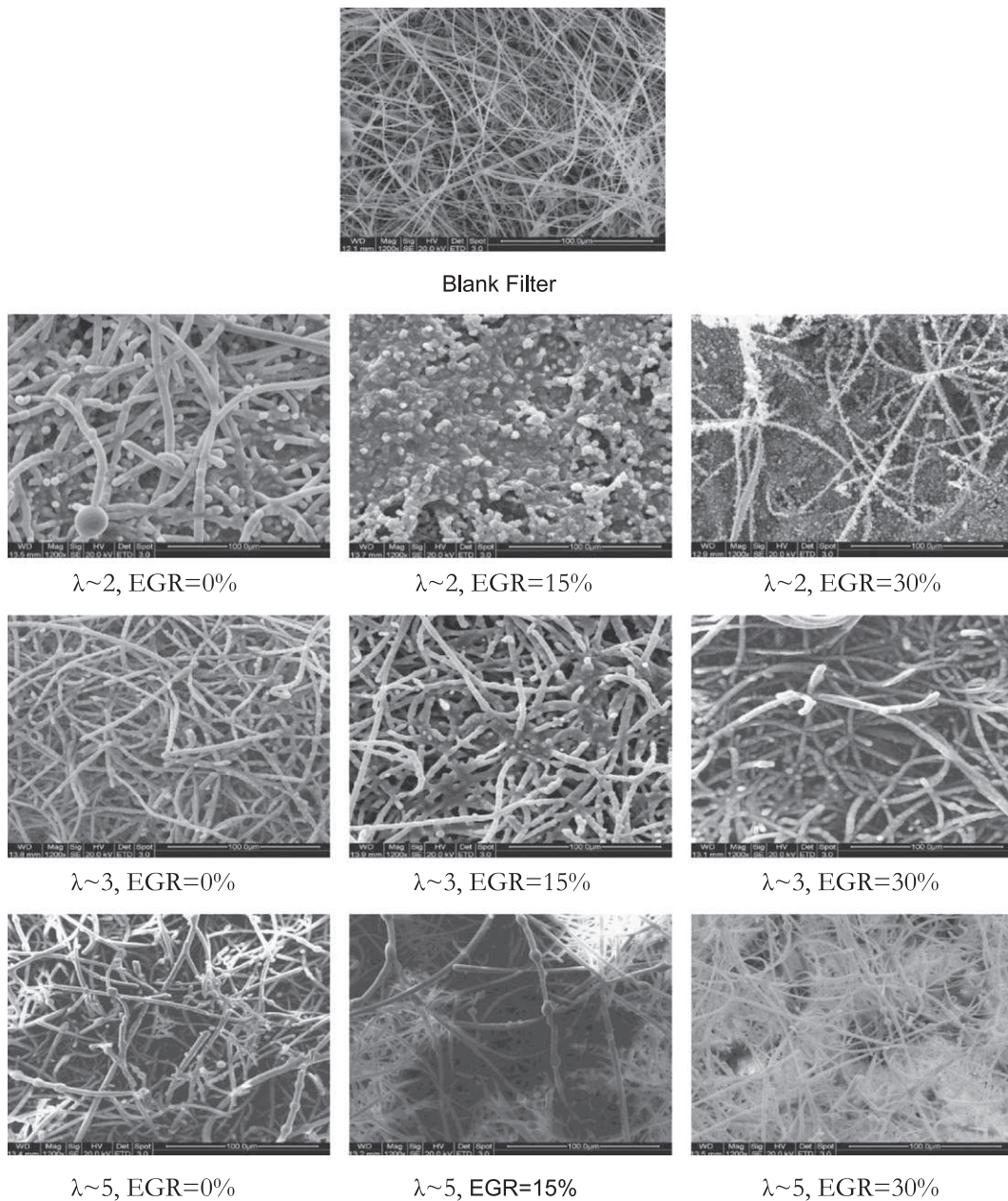


Fig. 15. SEM analysis of HCCI particulate laden filters.

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