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Particulate Morphology and Toxicity of an Alcohol Fuelled HCCI Engine

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ABSTRACT

Homogeneous charge compression ignition (HCCI) engines are attracting attention as next-generation internal combustion engines mainly because of very low NO_x and PM emission potential and excellent thermal efficiency. Particulate emissions from HCCI engines have been usually considered negligible however recent studies suggest that PM number emissions from HCCI engines cannot be neglected.

This study is therefore conducted on a modified four cylinder diesel engine to investigate this aspect of HCCI technology. One cylinder of the engine is modified to operate in HCCI mode for the experiments and port fuel injection technique is used for preparing homogenous charge in this cylinder. Experiments are conducted at 1200 and 2400 rpm engine speeds using gasoline, ethanol, methanol and butanol fuels. A partial flow dilution tunnel was employed to measure the mass of the particulates emitted on a pre-conditioned filter paper. The collected particulate matter (PM) was subjected to chemical analyses in order to assess the amount of Benzene Soluble Organic Fraction (BSOF) and trace metals (marker of toxicity) using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Field emission scanning electron microscope (FE-SEM) was used for particulate morphology investigations at 1000X and 5000X resolution. Trace amount of particulates were observed on the filter paper for the test fuels. The concentration of different trace metals analyzed also showed decreasing trends with increasing engine loads.

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INTRODUCTION

Concerns regarding energy availability and environmental impact of emissions such as oxides of nitrogen (NO_x) and particulates have motivated researchers towards the design of next generation internal combustion engines, which are capable of delivering higher efficiency and lower emissions simultaneously. One possible option to improve the trade-off between efficiency and emissions is HCCI combustion engine. HCCI is known as a combustion concept that combines some of the features of both conventional spark ignition (SI) and compression ignition (CI) combustion concepts. HCCI engine operates on a premixed charge of fuel and oxidizer similar to SI engine and as the CI engine, it runs un-throttled and is auto ignited due to the increased temperature by the compression. The main objective of HCCI combustion concept is to reduce soot and NO_x emissions while maintaining high fuel efficiency at part load conditions. Based on potential of HCCI engines, a large number of studies related to the HCCI combustion have been published during last three decades [1,2,3,4,5].

HCCI engines are inherently fuel flexible and can run on low or high grade fuels as long as the fuel can be heated to the point of auto-ignition [6]. In particular, HCCI engines can run on alcohols [7,8,9]. Alcohols have often been suggested as promising alternative fuels, and they are identified as having the potential to improve air quality, while replacing the gasoline/diesel in the conventional internal combustion engine [8]. Sustainable renewable fuels such as methanol and ethanol, besides aiding the implementation of HCCI combustion, are an alternative option to reduce energy depletion and substitute for fossil fuels. Cleaner combustion and hence, reduced exhaust emissions is another benefit of these oxygenated fuels. Therefore, it is interesting to combine the advantage of HCCI combustion with oxygenated fuels [10]. Oakely et al investigated HCCI combustions on single cylinder engine using methanol and ethanol at raised intake air temperature [11]. They found that in HCCI mode ethanol and methanol operated over a wider range of relative air/fuel ratios and EGR concentrations than gasoline. Xie et al. compared alcohol HCCI combustion including ethanol and methanol and its blend over gasoline combustion and showed that ethanol fuels tended to auto-ignite earlier resulting in higher peak pressure than that of gasoline [12]. Due to lower peak combustion temperature, very little NO_x emission was emitted with pure alcohol fuels. Zhang et al [13] noted that the CAI combustion of pure ethanol could be achieved with a high amount of hot trapped residual gas. Controlled auto-ignition (CAI) combustion of methanol has been used in CI engines using premixed charge and found that methanol reduced dramatically NO_x emission while maintained brake specific fuel consumption similar to a diesel engine in the middle load range [14-15]. They also found that thermal efficiency of methanol was almost the same as that of diesel, under the low load condition. However, most of these studies focused on the attainability of HCCI combustion, emission characteristics and the operating range limits for alcohol fuels.

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 [16-17]. PM can be collected by filtering the engine exhaust. In general, PM collected on a filter paper is usually separated by extraction solvents into two fractions named as soluble organic fraction (SOF) and soot (solid carbon material that cannot be dissolved by organic solvent) [18-19]. SOF is normally adsorbed on to the surface of the soot or condensed onto the filter paper. SOF of PM consists of un-burnt fuel, lubricating oil and their thermally synthesized products [18]. Conventional SI gasoline exhaust particles consist of similar materials and have similar morphology to Diesel particles in compression ignition engines. However gasoline exhaust particles are smaller and composed primarily of volatile materials [20]. Formation of particles in spark ignition gasoline engine is more dependent on engine operating conditions compared to diesel combustion [20]. Kayes et al. investigated PM formation in SI engines and found that total mass and number concentration, as well as number weighted mean and mode particle sizes, were at a minimum near stoichiometric mixture [21]. They also reported that as engine load increases, both, PM mass and total number of particles increases. Conventional gasoline engines are not known for emission of smoke or particulates. Studies conducted to investigate gasoline particulates showed that gasoline engines have higher “mass” exposures (if gas and particle phase are summed), lower total particle mass exposure and almost similar particulate number-size distributions compared to diesel engines [22,23,24].

Price et.al [17] suggested that 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 [17]. Kaiser et al. suggested that particulate emissions from the HCCI engines at moderate loads were much lower than conventional CI engines but almost equal to direct injection spark ignition engines [25]. Misztal et al. conducted more detailed study of HCCI particle size distributions using DI-HCCI system by injecting unleaded gasoline directly into the cylinder employing negative valve overlap (NVO) to capture residuals [26]. Other investigation by Misztal et al. examined the role of injection timing in PM formation in the same engine [27]. The DI mode of fuel delivery led to discovery of high sensitivity of PM formation to injection timings. The most advanced timings generally showed the highest PM mass and number emissions even though mixing times were the longest. The authors attributed this to wall wetting effects from impingement of most of the fuel on the piston surfaces. They also noticed that PM emissions were very closely coupled to mixture homogeneity for this type of HCCI engine. 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 [17]. All the facts mentioned above leads to conclusion that the particulate emission from HCCI engines cannot be neglected.

It is important to investigate and characterize the PM from HCCI engines due to adverse health effect and environmental impact. The organic fraction of PMs contain chemical species such as alkanes and alkenes, aldehydes, aliphatic hydrocarbons, PAH and PAH derivatives. Basically organic fraction containing neutral and aromatic fraction of particulate are mutagenic and carcinogenic in nature. Toxic potential of organic faction of PM can be evaluated by benzene soluble organic fraction (BSOF) [28-29]. Main source of organic fraction of PM originates are partially oxidized/ pyrolysed fuel and lubricating oils [30-31]. Study conducted by Kittleson et al. [32] suggested that carbonaceous agglomerates comprise most of the mass from the diesel engines, which is significantly lower in HCCI engines. 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. Recent study conducted by Singh et al. on the characterization of exhaust particulates from diesel fuelled HCCI engine found that toxic potential of the particulate emitted is higher at higher engine load and vice versa [33].

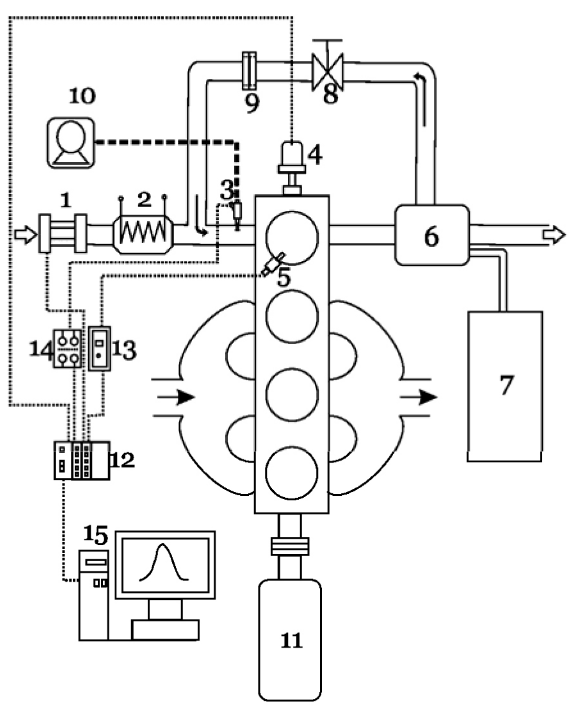
Particulate emission data characterizing toxicity of PM for gasoline and alcohol fuelled HCCI combustion is not available in open literature therefore it is worth investigating the toxicity and morphology of PM emissions from HCCI engines.

EXPERIMENTAL SETUP

A four cylinder, four-stroke, water-cooled, naturally aspirated, direct injection diesel engine is modified for conducting proposed investigations. Test engine specifications are given in Table 1. The engine is coupled with an eddy current dynamometer. One of the four cylinders of the engine is modified to operate in HCCI combustion mode, while the other three cylinders operated like an ordinary diesel engine, thus motoring the first cylinder for achieving HCCI combustion. The intake and exhaust manifolds of HCCI cylinder are separated from the remaining three cylinders. Schematic of the experimental setup is shown in Figure 1. The fuel is premixed with air using port fuel injector installed in the intake manifold. Electronic fuel injector has 4 nozzle holes and the fuel is injected in the manifold at 3 bar fuel injection pressure. The quantity of fuel injected in every cycle and injection timings are controlled using Compact-RIO microcontroller (cRIO-9014, National Instruments) and a customized injection driver circuit. Compact-RIO (Reconfigurable Input-Output) combines an embedded real-time processor, a high-performance FPGA (field-programmable gate array), and hot-swappable I/O (input-output) modules. Each I/O module is connected directly to the FPGA, providing low-level customization of timing and I/O signal processing. The FPGA is connected to the embedded real-time processor via a high-speed PCI bus. Compact-RIO is programmed by LabVIEW FPGA and LabVIEW Real-Time module software.

Table1. Test engine specifications.

Make/ Model	Mahindra/ Loadking
No. of cylinders	Four
Displaced volume	652 cc/ cylinder
Stroke/Bore	94/ 94 mm
Connecting Rod Length	158 mm
Compression ratio	17.5:1
Number of Valves	2/ cylinder
Exhaust Valve Open/ Close	56° BBDC/ 5° ATDC
Inlet Valve Open/ Close	10° BTDC/ 18° ABDC



1. Hot-film Air Mass Meter 2. Air Heater 3. Fuel Injector
4. Rotary Shaft Encoder 5. Pressure Transducer
6. Exhaust Plenum 7. Emission Analyzer 8. EGR Valve
9. Orifice 10. Fuel Tank with Pump 11. Dynamometer
12. Compact RIO 13. Charge Amplifier 14. SS-Relay
15. Computer

Figure 1. Schematic of the experimental setup.

The Compact-RIO receives signals from precision shaft encoder (H25D-SS-2160-ABZC, BEI, USA), air mass flow meter (HFM5, Bosch, Germany) and an in-cylinder piezoelectric pressure transducer (6013, Kistler, Switzerland). Compact RIO generates an output pulse to trigger the fuel injector after processing the acquired signals according to the user defined operating conditions. Based on the output pulse, fuel injector injects the required quantity of fuel in the intake manifold, at an appropriate time.

Air supplied to HCCI cylinder is measured by a hot-film air mass flow meter, which precisely measures the actual intake air-mass flow rate. To achieve HCCI combustion with proper combustion phasing of gasoline like fuels, the air-fuel mixture must be preheated to a required temperature before entry into the cylinder. Fresh air entering the engine is preheated using an electric air preheater upstream of the intake manifold. The intake air preheater is controlled by a close loop controller, which maintains constant intake air temperature as defined by the user. The heater controller takes feedback from a thermocouple installed in the intake manifold, immediately upstream of the fuel injector. A thermocouple in conjunction with a digital temperature indicator is used for measuring the intake and exhaust gas temperatures. Provision for EGR (exhaust gas recirculation) is made for the HCCI cylinder so that some exhaust gas can be re-circulated using EGR valve for controlling the combustion phasing.

The in-cylinder pressure is measured using a piezoelectric pressure transducer, which is mounted flush with the cylinder head. To measure the crank angle degree (CAD) position, a precision optical shaft encoder is coupled with the crankshaft using a helical coupling. The in-cylinder pressure history data acquisition and combustion analysis is done using a LabVIEW based program developed for this study.

Particulate samples were collected iso-kinetically using a partial flow dilution tunnel. This tunnel simulates ambient environmental conditions for particulate development/ growth/ agglomeration/ adsorption processes to complete before collection of PM from the exhaust stream. It draws a fraction of exhaust gases from the main exhaust line and mixes it with pre-filtered (porous paper filter with a pore size of 30-60 microns), preheated atmospheric air in a dilution ratio 10:1. The diluted exhaust undergoes complete mixing and particulate formation steps viz. condensation of high boiling point gaseous species on particulate (heterogeneous condensation) along with adsorption, absorption, agglomeration and coagulation. Residence time in dilution tunnel is designed in such a manner that these reactions gets complete before gas reaches to the filter paper/ sampling probe location. Finally, these particulates are collected on a quartz filter paper for further analyses. Particulate samples were collected for 45 minutes on each filter.

To estimate the trace metals in HCCI particulate, USEPA SW-846, 3015 method [34] was used in this study. Sample extraction was carried out using hot plate digestion method.

This digestion procedure is used for preparing samples, which are to be analyzed using ICP-OES. A 16 mm diameter punch was used to cut small portion of sampled filter papers for trace metal analysis. This portion of filter paper was cut into small pieces using plastic scissors and then put into an inert bottle, in which 15 ml of concentrated HNO3 was added. Temperature of sample was raised to 175°C in less than 5.5 min and maintained at 175°C for more than 4.5 min. After digestion, the acid from the vessel is filtered through 0.22 micron filter paper. The filtrate was measured and diluted 3 times with Mili-Q water and then further stored in inert bottles. Reference was taken for analytical blank filter papers and 30 ml of conc. HNO3 (High Purity, Merck) 10% blanks from the same lot of filter papers were used to get a best representative average blank concentration for data correction. By this method, concentrations of trace metals such as Ca, Cu, Cr, Fe, B, Zn, Mn, Mg were analyzed by ICP-OES.

ASTM test method D4600-87 [35] was used for estimation of BSOF in diesel particulates. This gravimetric method was recommended by National Institute of Occupational Safety and Health (NIOSH), USA to represent the toxic organic compounds present in the particulates collected on filter paper. Filter papers were cut into several small pieces using a plastic scissor and then placed into a reagent beaker. Thereafter 20 ml of benzene was added to it. These reagent bottles were kept in ultrasonic bath for 20 minutes. Thereafter sample was decanted and vacuum filtered through 0.45 μm Millipore filter paper. The filtrate was collected in a pre-weighed beaker. The procedure was repeated with 10 ml benzene in the same reagent beaker. The solvent was evaporated in a preheated vacuum oven at 40°C. The final weight of the beaker was measured to estimate the total BSOF in the sample. In order to check the reference concentration, blank filters were used for benzene extraction as per the same ASTM standard.

RESULTS AND DISCUSSION

In this section, the experimental results of HCCI combustion particulate emissions for different engine operating conditions are presented using gasoline, ethanol methanol and butanol as fuel. Experiments were conducted for different relative air fuel ratio at various inlet air temperatures (T_i) for all the fuel. The HCCI operating range obtained for all test fuels are shown in Figure 2. The HCCI operating region is determined by operating limits of high and low load boundaries, which are defined by engine knock and combustion stability. The maximum load in HCCI is often limited by fast combustion rate, where the combustion induced noise becomes a major factor. The Ringing Intensity (RI) compares the pressure rise rate to peak in-cylinder pressure and engine speed, therefore gives a good indication of combustion noise [36-37]. In this study, RI has been used as a criterion to define high load limit. Fluctuation of the indicated mean effective pressure (IMEP) is used as a measure of combustion stability and expressed as COV_{IMEP}. The Coefficient of Variation (COV) of IMEP is calculated by using data of 2000 consecutive engine cycles and used to define the low load HCCI limit (misfire boundary).

In this study acceptable higher and lower boundary value is taken as RI< 6 MW/m^2 and COV_{IMEP} < 3.5%. This value is taken from published literature for similar displacement engines [36-37]. HCCI operating range found for all test fuels using this criterion is presented in figure 2.

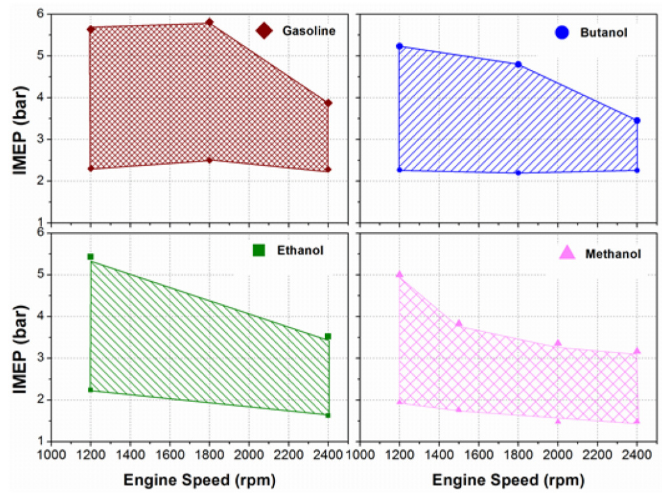


Figure 2. HCCI Operating range for gasoline, butanol, ethanol and methanol.

It is can be noticed from figure 2 that operating region of gasoline is larger as compared to other test fuels. Maximum IMEP found using gasoline was 5.6, 5.8 and 3.9 bar at 1200, 1800 and 2400 rpm respectively. Butanol, ethanol and methanol had maximum IMEP at 1200 rpm and IMEP values were 5.2, 5.4 and 5.0 bar respectively.

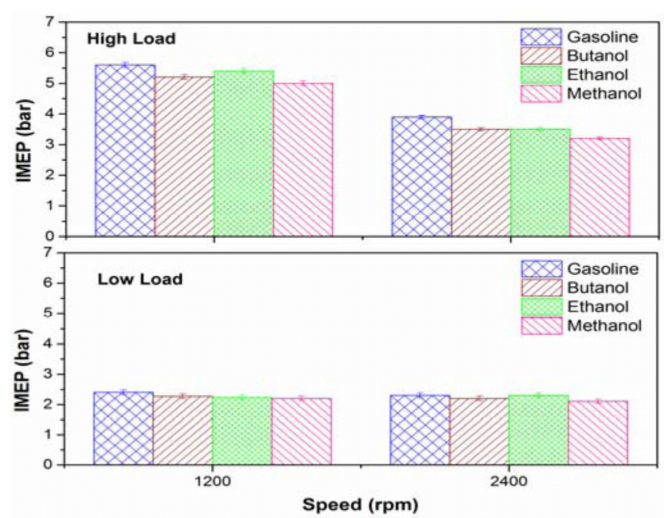


Figure 3. Variation of IMEP (engine load) during particulate sampling for gasoline, butanol, ethanol and methanol.

Particulate collection is done for four test fuels at two engine speeds of 1200 and 2400 rpm. At each engine speed, particulate collection is done for two engine loads (high and low) for each test fuels in HCCI operating range. Figure 3 shows the variation of IMEP with engine speed, at which particulate samples are collected for each test fuel.

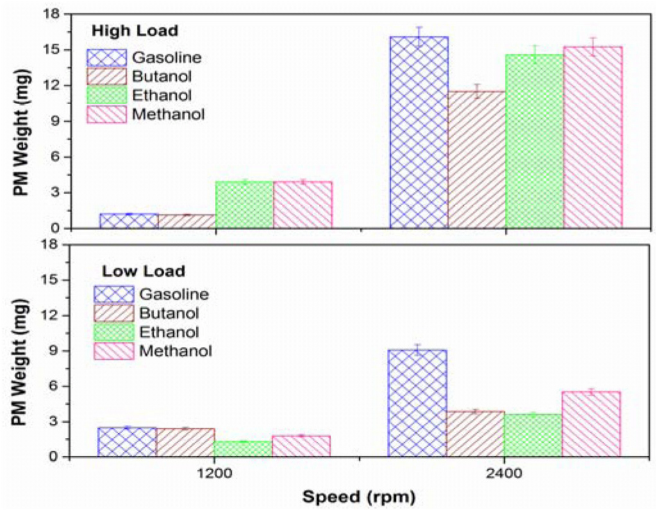


Figure 4. Collected particulate mass at different engine operating conditions for gasoline, butanol, ethanol and methanol.

Figure 4 shows the collected particulate mass on filter paper at different engine operating conditions in 45 minutes sampling duration for gasoline, butanol, ethanol and methanol. Figure shows that the particulate mass increases with increase in engine load and speed for all test fuels (except gasoline and butanol at 1200 rpm in high load). Physical properties of butanol are more closer to gasoline as compared to ethanol and methanol, which leads to similar trend at 1200 rpm. As the load increases, more fuel undergoes combustion resulting in higher particulate formation.

Benzene Soluble Organic Fraction

BSOF has been taken as indicator of organic fraction of particulate which represents the toxic compounds. Soluble organic fraction (SOF) of the particulate matter mainly consists of organic portion of fuel itself and pyrolytically generated organic products formed during the process of soot formation. Figure 5 shows the Variation in BSOF content of HCCI particulates for gasoline, butanol, ethanol and methanol. It can be noticed from figure 5 that BSOF is lower in high load compared to low load conditions at both engine speed for all the test fuels. At higher engine load temperature inside the combustion chamber is high, which burn the soluble organic species formed in cylinder. At lower load, temperature encountered inside the combustion chamber would be relatively lower, resulting in relatively inferior combustion hence produce higher soluble organic species, which will be seen in BSOF. Operating conditions which increase the fraction of the fuel and lubricating oil that remains unburned or partially burned; will increase the BSOF of the particulate.

HCCI combustion is often considered as low temperature combustion, as bulk temperature inside combustion chamber is lower as compared to conventional SI or CI combustion. Therefore, level of total unburned hydrocarbon (THC) emission from HCCI engines are higher over the entire operating range compared to typical CI combustion engines [38].

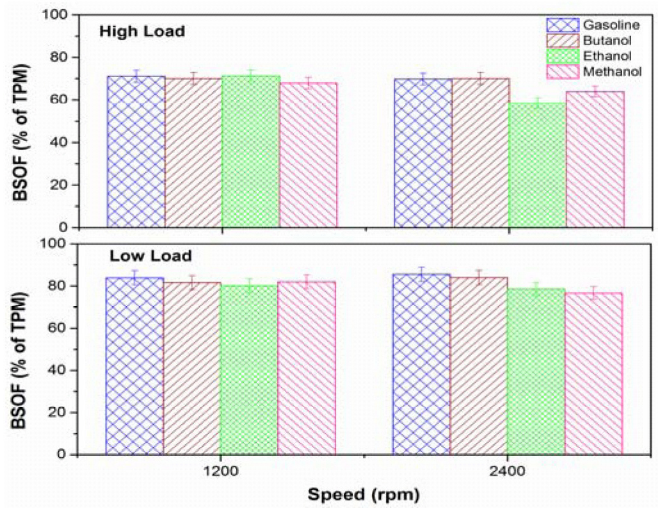


Figure 5. Variation in BSOF content of HCCI particulates for gasoline, butanol, ethanol and methanol.

Higher THC emission may lead to higher BSOF in HCCI engine over entire operating range (Figure 5). Kittleson et al. also suggested that PM emissions have more volatile particles in the nuclei mode [32]. Higher BSOF in diesel HCCI combustion is also reported [33]. The main point to be noticed here is that the BSOF content of particulates from HCCI engine is higher indicating possibly higher toxicity potential of HCCI particulates. Fuel such as methanol is toxic and increased level of soluble organic fraction may be hazardous by utilization of such fuel in HCCI engines. However in order to clearly establish the organic toxicity of HCCI particulates, more investigations are required to characterize the specific organic species emitted in the engine exhaust.

Trace Metals

An experimental investigation was carried out to study the effects in variation of engine operating conditions on the concentration of trace metals in the particulate emitted in a HCCI engine exhaust using different gasoline-like fuels. Various trace metals were investigated however many of these metals were below detection limit of the instrument therefore only the metals detected with reasonable confidence are reported and discussed in this section. Figures 6, 7, 8, 9 show comparison of trace metal concentrations from gasoline and alcohol fuelled HCCI engine at two engine speeds (1200 rpm and 2400 rpm respectively). Engine loads at which particulate samples were collected are shown in Figure 3. It is observed from the experimental data (Figure 6, 7, 8, 9) that concentrations of B, Ca, Fe, Cu, Mg and Zn were higher than those of Cr and Mn for all test conditions.

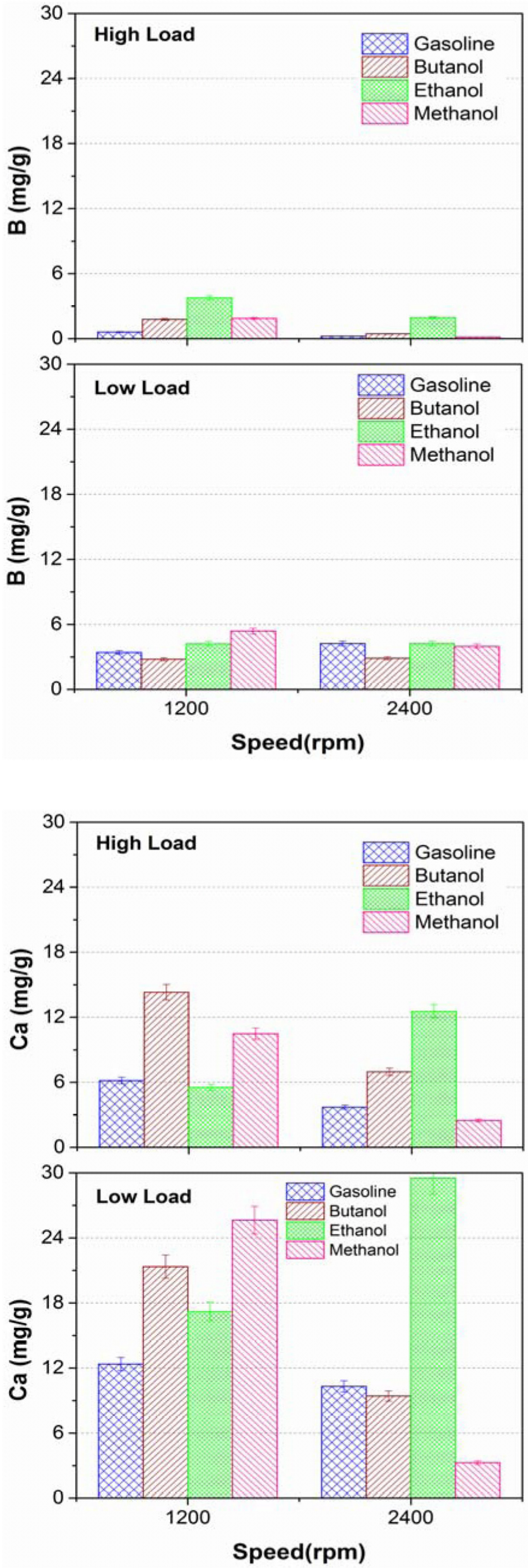


Figure 6. Concentration of B and Ca present in particulates for all test fuels.

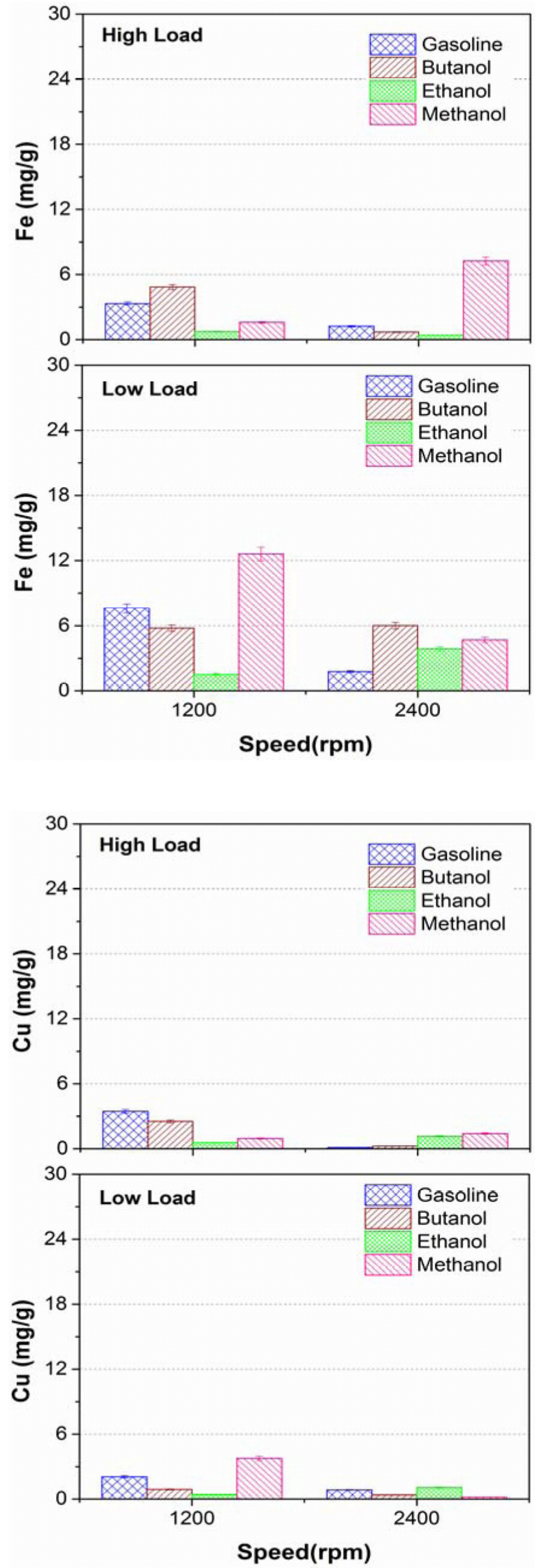


Figure 7. Concentration of Fe and Cu present in particulates for all test fuels.

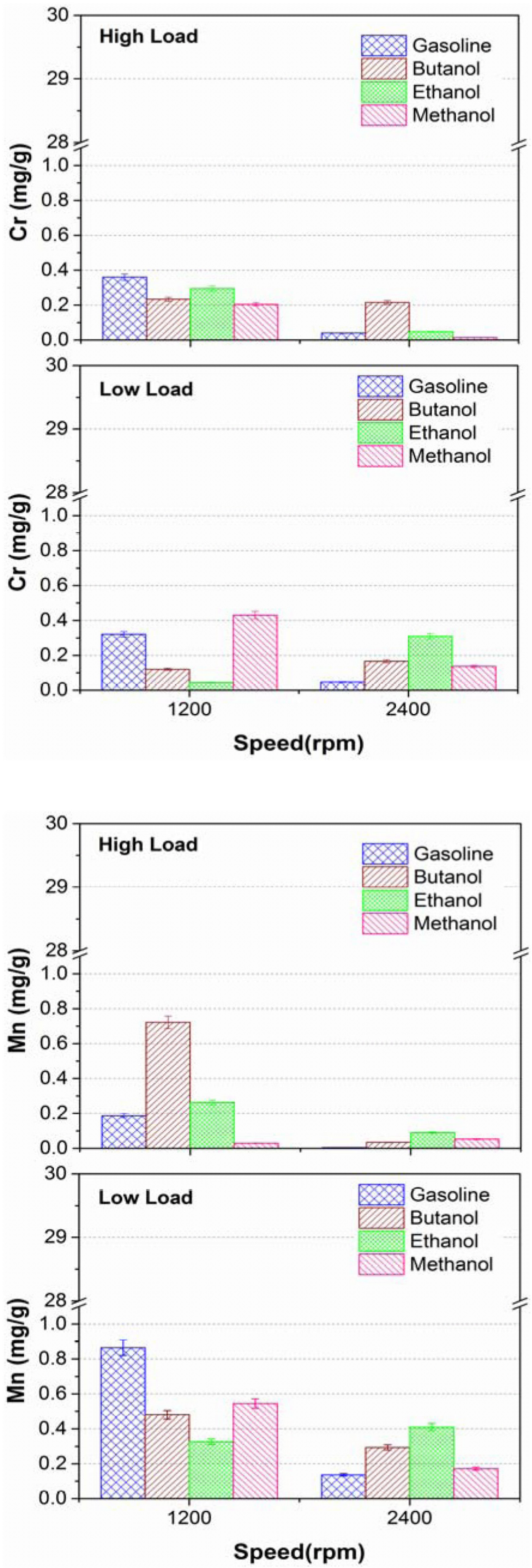


Figure 8. Concentration of Cr and Mn present in particulates for all test fuels.

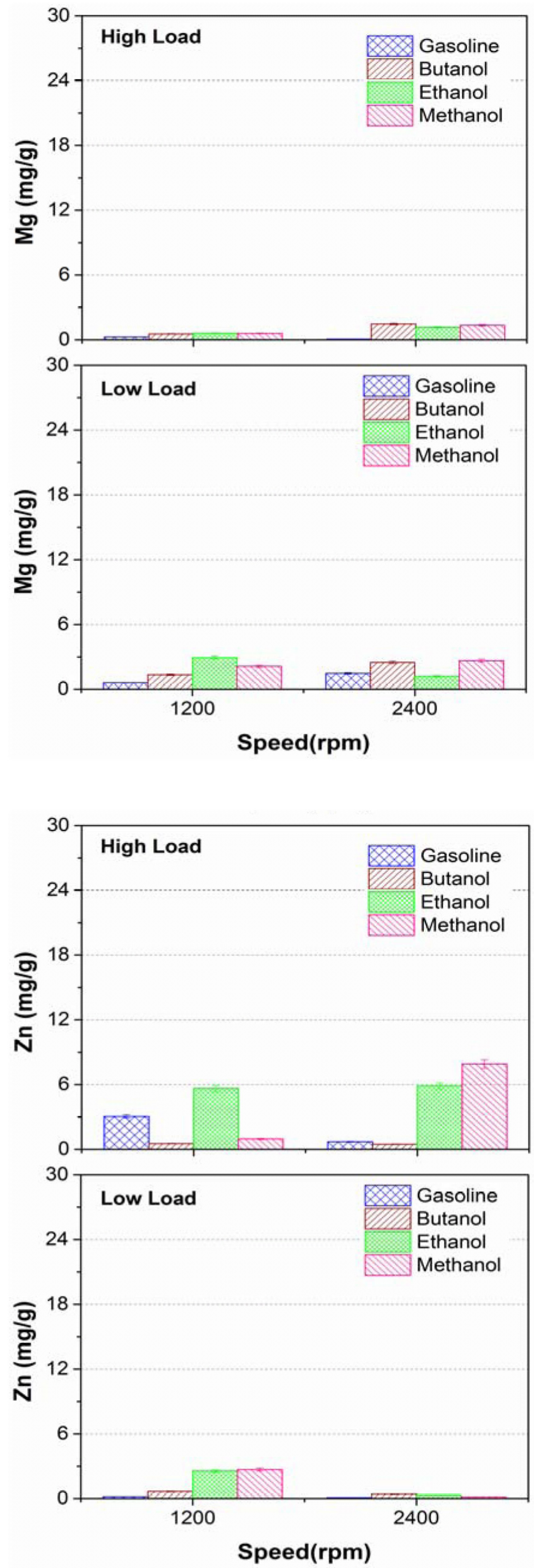


Figure 9. Concentration of Mg and Zn present in particulates for all test fuels.

It can be observed that specific concentration of trace metals decreases with engine load for the test conditions. Similar trend is also observed for metal concentration in diesel and biodiesel exhaust in CI engines [39-40]. This observation can be explained by the fact that at higher engine loads, combustion takes place at relatively higher temperature; leading to improved thermal efficiency and indicated specific energy consumption decreases with increasing load in HCCI engine [38] and this is reflected in reduced emission of metals with increasing engine load. Trace metals in the engine particulate is contributed by the metals in the fuel, lubricating oil, ambient dust and engine wear [33].

B emission is found in the range of 0-5 mg/g of particulate (Figure 6). B is higher for ethanol at low engine speed as well as high engine speeds. Engine lubricating oil is the main source of B. Ca is found in the range of 5-30 mg/g of particulate. Ca emission is lowest for methanol at higher engine load. It has a highest trace for ethanol at low load at 2400 rpm. The range of emissions of B and Ca is close to the range found for diesel particulates in CI mode [40]. It is observed from Figure 6 that B concentration in low load at 2400 rpm is higher in HCCI mode as compared to conventional CI mode for diesel [40]. The possible reason for higher B emission is higher rate of pressure rise in HCCI engine as compared to conventional mode. Higher rate of pressure rise during HCCI combustion might break lubricating oil film on the cylinder liner. This lubricating oil comes in exhaust after its in-cylinder combustion and gets collected as particulates, which is shows up in the form of higher B emissions.

Figure 7 shows concentration of Fe and Cu present in particulates for all test fuels. Iron (Fe) originates primarily from engine wear [33]. It has been found that the Fe concentration is in the range of 0-12 mg/g of particulates. Methanol shows significantly higher emission of Fe for low as well as high engine load. Fe emission at lower load in HCCI mode is comparable to conventional diesel combustion [40]; however it is higher at high load. At higher load rate of pressure rise is high in HCCI combustion, which may lead to higher wear. Trace emission of Cu is higher for gasoline at low as well as high engine loads at 1200 rpm. Cu emission for gasoline is lowest among other test fuels at 2400 rpm at high load (Figure 7). Copper originates from lubricating oil and wear of engine components [33].

Figure 8 shows concentration of Cr and Mn present in particulates for different test fuels. At low speed, gasoline shows higher Cr traces for low as well as high loads. At higher engine speed, butanol and ethanol shows higher traces. It is observed that the Cr traces are below 0.4 mg/g of particulates for all test conditions. The range is similar to the Cr found for diesel particulate [40]. Possible source of Cr is lubricating oil [39]. Mn shows higher traces at low engine speeds and is relatively higher for low loads (Figure 8). Methanol shows significantly higher emission at low engine loads. Gasoline, butanol and ethanol show consistent results. It is observed that Mn emissions are below 0.85 mg/g for all test conditions. Mn compounds are added as fuel additives [33].

Figure 9 shows concentrations of Mg and Zn present in particulates for all fuels at different engine operating conditions. Trace metals Zn and Mg are present in the lubricating oil [39]. The range of Mg trace is 0-3 mg/g of particulates. It is higher for alcohols and lower for gasoline. Zinc containing compound zinc di-alkyl-dithio-phosphate (ZDDP) is a commonly used additive in 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 the iron oxide in the combustion chamber to produce ZnO [33]. In high temperature environment, ZnO undergoes redox reaction to form Zinc and is emitted as trace metal. Zn emission is higher for high load for all fuels. Gasoline shows lower Zn emissions for low and high loads at both speeds. In general, it is observed that mass specific trace metal emission in particulates is higher at low engine load and lower for high engine loads for all test fuels in HCCI mode.

To compare the toxicity of metals, more detailed experimental investigation is required, for instance in-vitro toxicity test using collected engine exhaust particulate. The present study is limited to finding out overall concentration of these metals in the exhaust from the HCCI engine for gasoline like fuels. These metals are bound to particle sizes in the nm range, which have been shown to easily cross the alveolar membrane and can enter into the blood stream.

Scanning Electron Microscopy

SEM images were taken for the samples collected on the filter paper (45 minutes sampling duration) from the partial-flow dilution tunnel at different engine operating conditions for each test fuel. Particulate collection is done for four test fuels at two engine speeds of 1200 and 2400 rpm. At each engine speed, particulate collection is done for two engine loads (high and low) for each test fuels. The mass of particulate collected on the filter paper under the given engine operating conditions are given in figure 4. SEM images have been taken for 1000X and 5000X resolution. SEM images of all the samples at 1000X and 5000X are shown in figures 10, 11, 12, 13, 14. From these images, the morphological behavior of different fuels used in HCCI engine can be compared. Figure 10 shows the SEM images of particulate collection on quartz substrates for high and low engine loads at 1200 and 2400 rpm respectively for gasoline. It is observed that particulates are higher at higher engine speed. At high engine speed, more fuel is injected in the combustion chamber, which leads to higher amount of particulate emission in the exhaust during same sampling time. Particulates are not uniformly distributed over the filter substrate. The particulates in gasoline seem to be absorbed in the fibers of filter paper and form flake kind of particulates. This type of particulate is observed only for gasoline. It can be noticed that the size and shape of the particulates varies over the substrate even for a fixed engine operating condition.

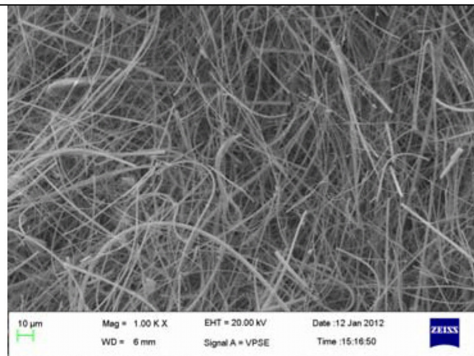
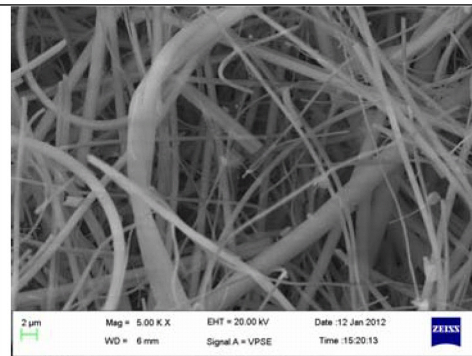
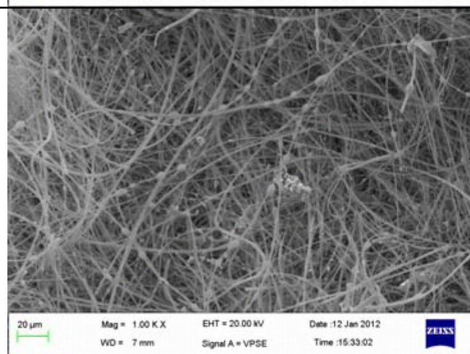
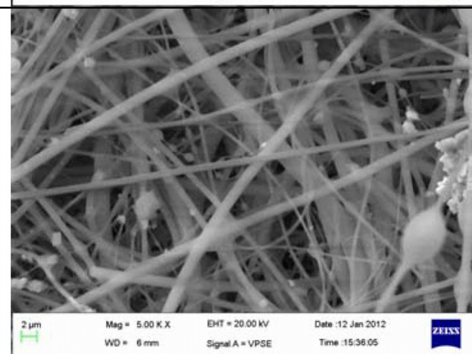
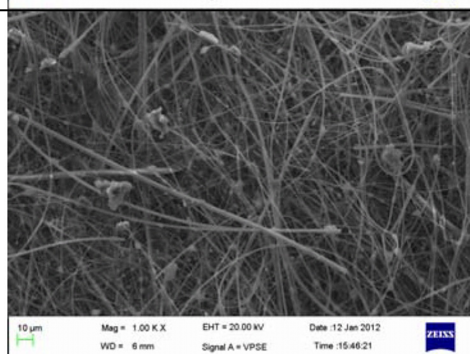
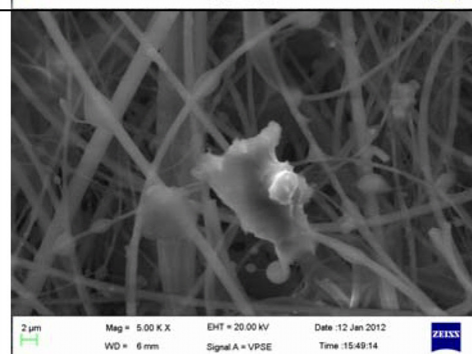
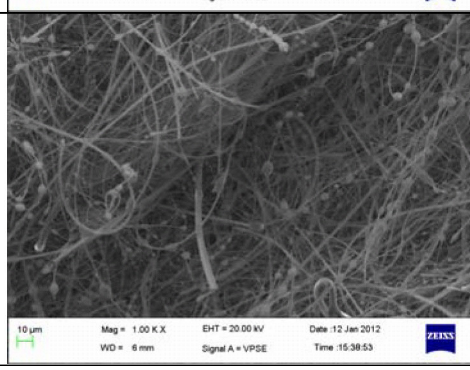
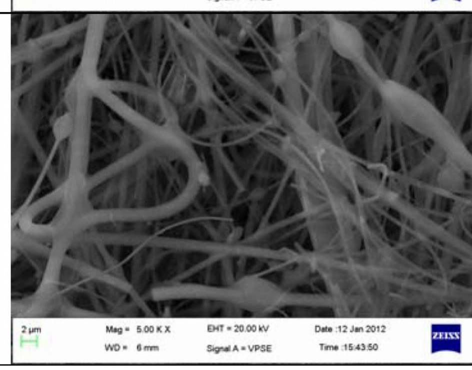
	1000X resolution	*5000X resolution*
Gasoline 1200 rpm High Load		
Gasoline 1200 rpm Low Load		
Gasoline 2400 rpm High Load		
Gasoline 2400 rpm Low Load		

Figure 10. FE-SEM image of particulate sample for gasoline at 1200 and 2400 rpm.

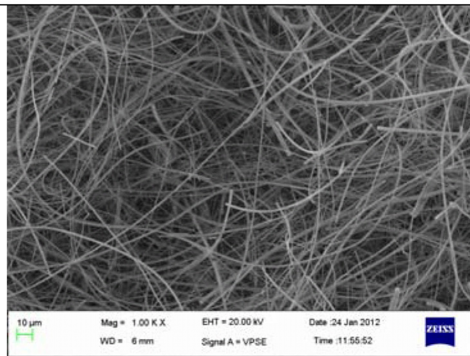
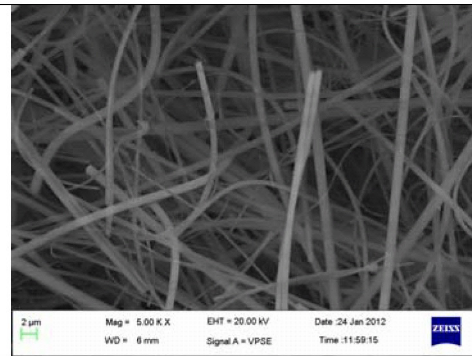
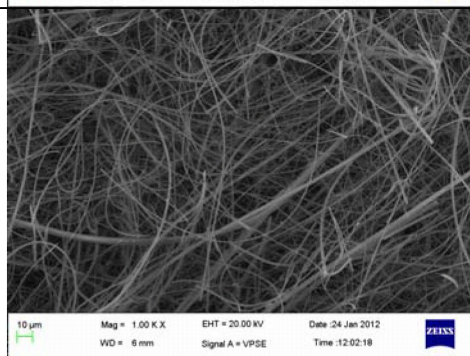
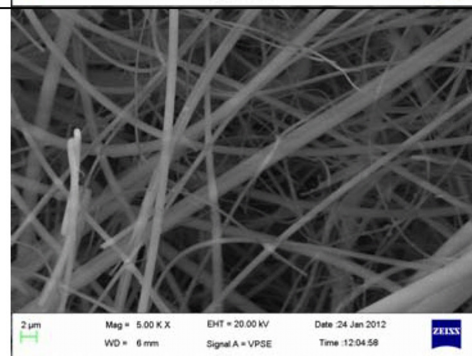
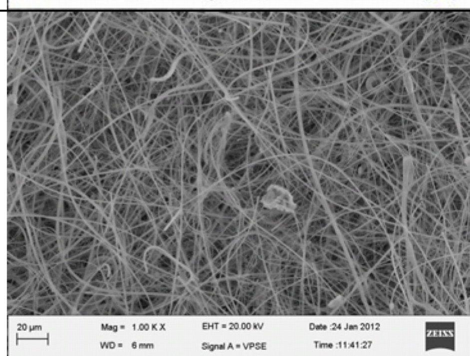
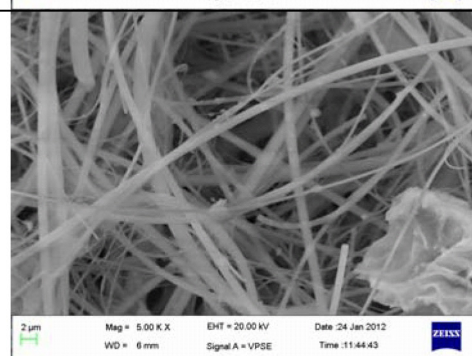
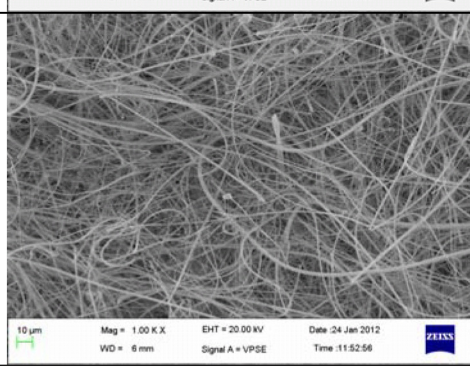
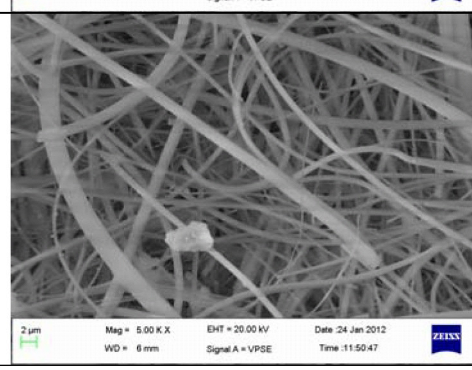
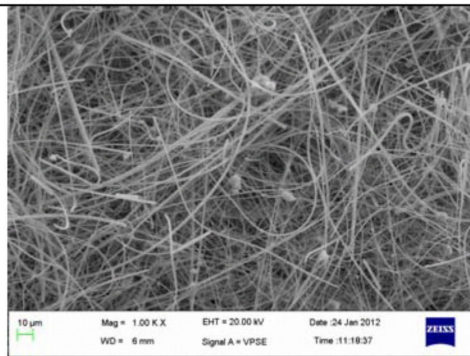
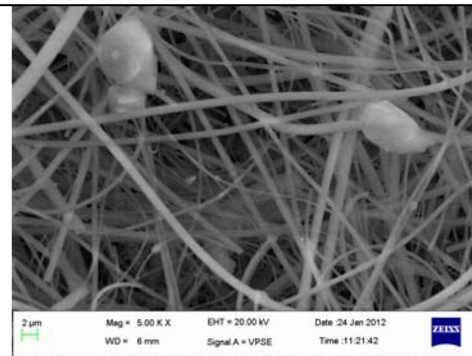
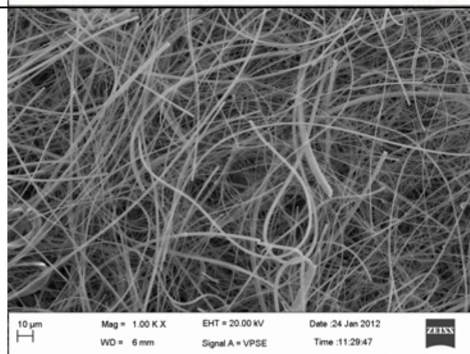
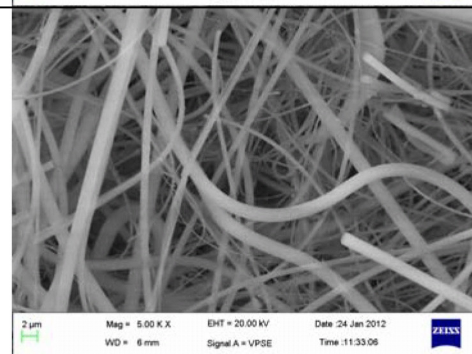
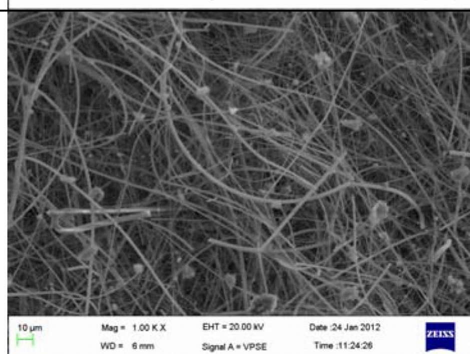
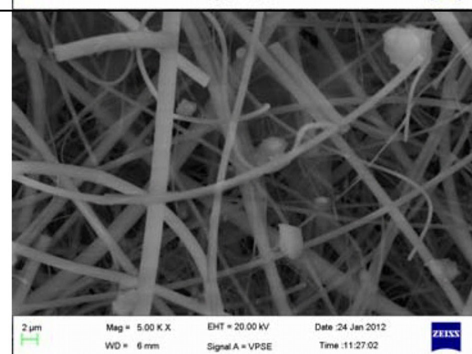
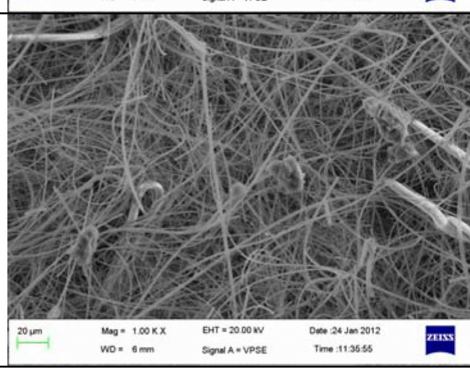
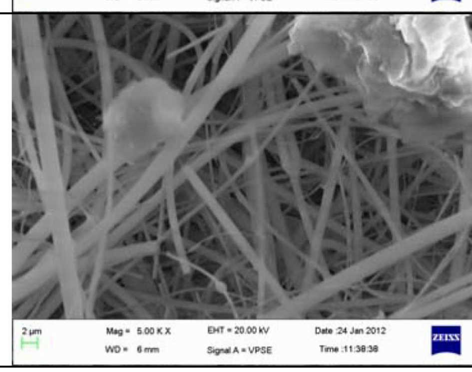
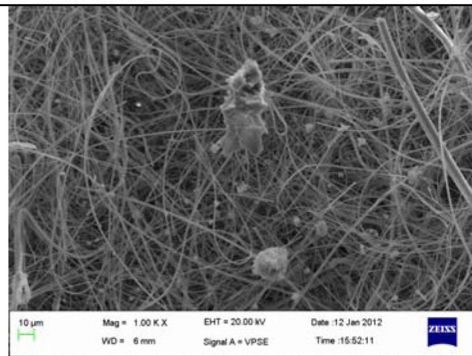
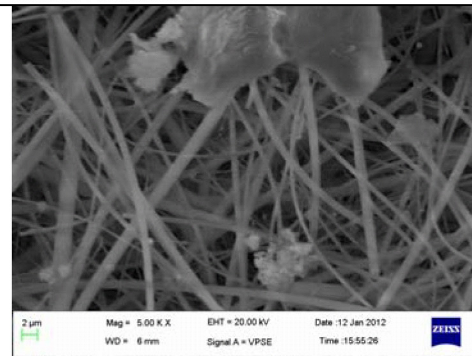
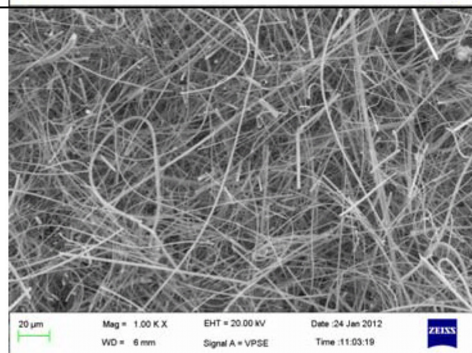
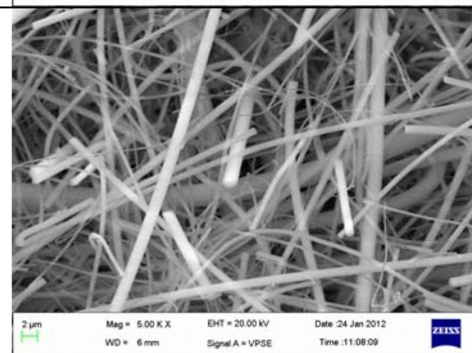
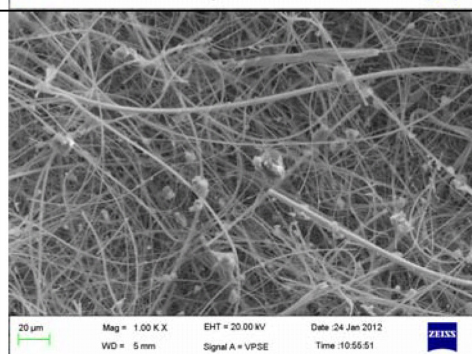
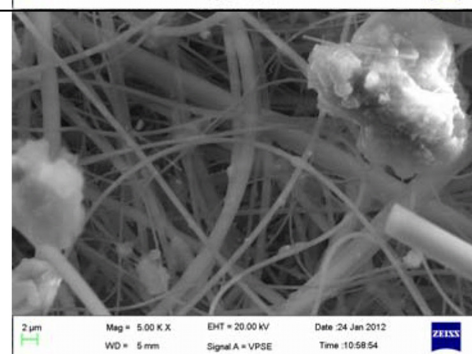
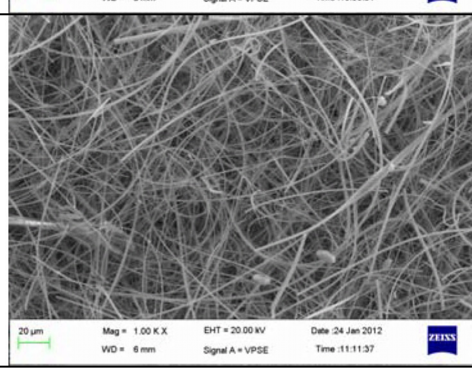
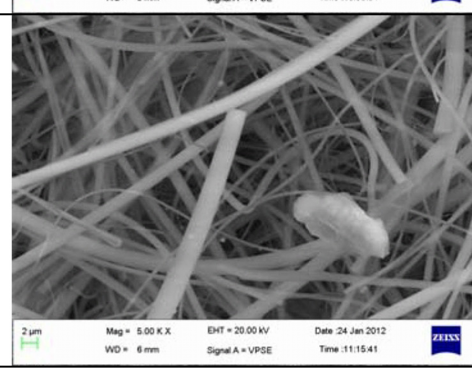
	1000X resolution	*5000X resolution*
Butanol 1200 rpm High Load		
Butanol 1200 rpm Low Load		
Butanol 2400 rpm High Load		
Butanol 2400 rpm Low Load		

Figure 11. FE-SEM image of particulate sample for butanol at 1200 and 2400 rpm.

<table>
<tr><th></th><th>1000X resolution</th><th>5000X resolution</th></tr>
<tr><td>Ethanol
1200 rpm
High Load</td><td>
</td><td>
</td></tr>
<tr><td>Ethanol
1200 rpm
Low Load</td><td>
</td><td>
</td></tr>
<tr><td>Ethanol
2400 rpm
High Load</td><td>
</td><td>
</td></tr>
<tr><td>Ethanol
2400 rpm
Low Load</td><td>
</td><td>
</td></tr>
</table>

Figures 12. FE-SEM image of particulate sample for ethanol at 1200 and 2400 rpm.

	1000X resolution	*5000X resolution*
Methanol 1200 rpm High Load		
Methanol 1200 rpm Low Load		
Methanol 2400 rpm High Load		
Methanol 2400 rpm Low Load		

Figures 13. FE-SEM image of particulate sample for methanol at 1200 and 2400 rpm.

Figure 11 shows the SEM images of particulates from HCCI combustion of butanol and very little or no particulate collection is seen on the substrate. Some traces of particulates can be observed when engine speed is 2400 rpm. This may be because of higher fuel quantity injected, which leads to the higher amount of particulate formation. It can be observed that particulates collected are low on mass basis in all the fuels compared to conventional combustion engines. However, particle number concentration is comparable and cannot be neglected in HCCI engines.

Figures 12-13 show the SEM images of particulate samples for ethanol and methanol. It has been observed that in ethanol and methanol, higher amount of particulates are collected in comparison to butanol. Lower loads show lower particulates for ethanol and methanol at both engine speeds. The structure of particulate in ethanol and methanol is quite different from gasoline particulates. At higher resolution SEM image, the shape and structure of particles is visible more clearly. Main difference between all these fuels from a chemical aspect is the size of carbon chain length of molecule and oxygen content. Gasoline has no oxygen molecule while other three fuels have one oxygen molecule. From these SEM images, it can be noted that butanol shows lowest amount of particulates. HCCI engines generally emit significantly lower overall PM emissions (by mass), which is once again confirmed by the present results. However particulate emissions are significant in terms of numbers. Overall PM emission from HCCI engines may potentially pose health risks due to complex morphology of these particles. Morphological studies in SI engines have shown that carbon nanotubes and fullerenes represent a significant portion of the particulate matter [41]. Detailed and exhaustive studies are however required to characterize the morphology of HCCI particulates and their health effect.

CONCLUSIONS

Experimental investigation has been conducted to characterize toxicity and morphology of particulate emission from HCCI engine using gasoline, ethanol, methanol and butanol at two engine speed 1200 and 2400 rpm. The PM was analyzed chemically in order to understand their toxic potential so that appropriate particulates control technology can developed and selected for HCCI engine. BSOF results showed decrease in its level with increasing engine load for all the test fuels. BSOF is higher in HCCI engine particulates. The particulate samples were analyzed for trace metals (B, Ca, Fe, Cu, Mg Cr, Mn and Zn). It was found that concentrations of B, Ca, Fe, Cu, Mg and Zn were higher than those of Cr and Mn for all test conditions. Mass specific concentration of trace metals decreases with engine load for the test conditions. The range of emissions of some of the trace metals close to the range found for diesel particulates in CI mode and a few engine operating conditions, some trace metals have higher specific concentration than diesel CI mode. SEM images show that the PM deposited on the filter paper increases with increase in speed.

In summary, the gasoline and alcohol HCCI lead to lower particulate emissions and the toxic potential of the particulate emitted is higher at higher engine load. Considering the toxicity of particulates, PM emission from HCCI engines cannot be neglected.

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DEFINITIONS/ABBREVIATIONS

BDC - bottom dead center

BSOF - benzene soluble organic fraction

CAI - controlled auto-ignition ignition

CI - compression ignition

COV - coefficient of variation

DI - direct injection

HCCI - homogeneous charge compression ignition

ICP-OES - inductively coupled plasma-optical emission spectrometer

IMEP - indicated mean effective pressure

IVC - intake valve closed

IVO - intake valve open

NVO - negative valve overlap

PM - particulate matter

RI - ringing intensity

SEM - scanning electron microscope

SI - spark ignition

SOF - soluble organic fraction

TDC - top dead center

THC - total unburned hydrocarbon

T_i - inlet air temperature