

# Influence of Nano Cerium Oxide in Emission Reduction with Methyl Tert-Butyl Ether-Gasoline Blends at HCCI Engine

Dadapeer Doddamani <sup>\*1</sup> , Prakash Esamudra Sharanappa <sup>2</sup> 

<sup>1\*</sup>Research Scholar, Department of Mechanical Engineering, U.B.D.T College of Engineering, Davanagere.Karnataka, India.

<sup>2</sup> Professor, Department of Mechanical Engineering, U.B.D.T College of Engineering,

Davanagere. Karnataka, India.

(dadu.mech@gmail.com<sup>\*1</sup>, prof.esp.bdt@gmail.com<sup>2</sup>)

<sup>‡</sup>Corresponding Author; Dadapeer Doddamani, dadu.mech@gmail.com

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**Abstract-** This article is focused to analyse the Homogeneous Charge Compression Ignition (HCCI) engine operated with blends of nano CeO<sub>2</sub>, Methyl tert-butyl ether (MTBE)-gasoline blends. The blending proportions of MTBE are 5vol%, 10vol%, 15vol% and 20vol%. For CeO<sub>2</sub>, it is 30ppm, 60ppm and 90ppm. The mixing is carried out with high shearing ultrasonication process. The optimal air-fuel ratio and chamber pressure were identified as 2.52 and 2.5 bar. From the experimentations, The Brake thermal Efficiency was found to be improved up to 3% with CeO<sub>2</sub> + MTBE blends than pure gasoline, and the brake-specific fuel consumption was reduced up to 0.03 kg/kW hr compared with a conventional gasoline engine. The emission parameters such as NO<sub>x</sub>, CO and HC have been identified as relatively lower as 857ppm, 0.07vol% and 11ppm respectively with MTBE 15 + 90ppm than gasoline. The use of both MTBE and CeO<sub>2</sub> nanoparticles are found better to improve the performance and reduce the emission further.

**Keywords** Methyl Tert- Butyl Ether, Cerium oxide nanoparticles, homogeneously charged combustion ignition, Emission reduction.

## 1. Introduction

Internal combustion (IC) engines such as spark ignition (SI) and compression ignition (CI) engines are the well practising technologies for the past 100 years. Though a few problems still exist in both SI and CI engines, the problems may be caused by improper fuel-air supply, mixture and exhaust formation [1]. Many researchers are attempted to rectify those problems in various approaches such as blending the fuel additives, changes in operational parameters, modifications in engine geometries etc [2]. On the other hand, finding an alternative fuel for IC engines is another active research area, many fuels are tried in both spark-ignition engines and compression ignition engines. These fuels are tested on engines in order to check performance, combustion and emission. Conversion of SI engine to CI engine and vice versa has been tried by many people, in concern to use low octane and cetane fuels [3]. A homogeneous charge

compression engine has great potential in enhancing thermal efficiency with a controlled exhaust like an internal combustion engine. Here, a homogeneous mixture is produced like an SI engine and igniting a mixture is like a CI engine which will engage the hybrid combustion, thus reducing the soot particles in emission [4]. Also, the lean combustion suppresses the nitrogen oxides (NO<sub>x</sub>), and the thermal efficiency of the HCCI engine was improved in two techniques, by the low-temperature combustion process, and a high compression ratio to attain the auto-ignition of homogeneous charge [5]. The HCCI engine is able to reduce the NO<sub>x</sub> formation in next-generation fuels of CI engines, also it is more adaptable for both low and high-octane fuels, and thus it is mostly called a flexible-fuel engine [6]. From Iso-octane to n-heptane typed fuels are tested in HCCI engine with a variation of compression ratio between 10:1 to 28:1, intake air temperature between 30° C to 130° C with an increment of 20 °C. From the above experimentation, they were noted that

port injection was found better in the HCCI engine [7]. Though many advantages with the HCCI engine, pressure rise in the homogenous mixture is found controllable which reduces unstable combustion. In order to biodiesel operation, external mixture formation is the most effective technique for homogenous charge combustion [8]. External mixture along with Exhaust gas recirculation (EGR) in the HCCI engine produced lower NO<sub>x</sub> and smoke particulates but it increases the unburnt hydrocarbon (UBHC) and carbon monoxide in the exhaust. Also, they found noisy combustion at higher engine loads due to a higher heat release rate [9]. Ethanol has great potential as an alternative source of energy, many people started conducting experiments in both gasoline and HCCI engine in various aspects. The external homogenous mixture was prepared using diesel and ethanol (10 and 20vol %) and tested on a conventional diesel engine. It was noted that a reduction of engine peak pressure by 20% and homogeneous lean combustion were observed [10]. The ethanol in the HCCI engine was found more efficient than in the gasoline engine [11]. The lean homogenous combustion was achieved with an elevated intake temperature between 300- 500°C [12]. Also, water injection in HCCI found a further reduction in NO<sub>x</sub> formation [13]. Increased air intake temperature can cause a high heat release rate and knock, but high air inlet temperature is essential for self-igniting in HCCI engines [14]. Ethanol can have a tendency to auto-ignite a little earlier than other commercial fuels and adding 40% of water injection is aiding the combustion much more stable in HCCI engine [15].

Alcohol has a better supplement for IC engines without any modifications, various blend proportions of ethanol were tested along with gasoline in SI engines, and found better thermal efficiency and reduced level of specific fuel consumption [16]. Also, it has a tendency to reduce emissions and exhaust gas temperature. Moreover, the nanoparticles with base fuel can able to improve the thermal conductivity, thermal stability and cold flow properties [17, 18]. The optimal ethanol blending ratio for a gasoline engine is 15 vol% [19]. The methyl tert-butyl ether (MTBE) and CeO<sub>2</sub> nanoparticles were tested with ethanol-blended gasoline in SI engine, the result showed that the brake thermal efficiency was improved by 3% in 20vol% of MTBE blends and increased by 4% in 20vol% of MTBE + 100 mg/l of CeO<sub>2</sub>. There was a reduction in CO and unburnt hydrocarbon (UBHC). But the CO<sub>2</sub> and NO<sub>x</sub> were improved by 13% more than pure gasoline [01]. Other oxygenated additive di-isopropyl ether was tested in a gasoline engine, and they observed that 6% and 13% reduction of UBHC and CO, and a 2% increment in brake thermal efficiency [20]. The cobalt-chromium nanoparticles (30ppm) with citronella biodiesel blends tested in the HCCI engine, it was found an enhancement in brake thermal efficiency and heat release rate by 5.4% and 6.8%, this can be occurred by a reduction in ignition delay and enhancement in cetane number. Also, the reduction is observed in major emission components such as NO<sub>x</sub>, CO, and UBHC about 17.7%, 5.1% and 34.32% respectively [21]. Many other nanoparticles (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>3</sub> and CNT) are also tested for IC engines, especially in CI engines for enhancing the combustion and reducing emissions reference the global

regulations. Biogas is a mixture of gases that is mainly composed of carbon dioxide and methane with a production process involving biological processing of anaerobic digestion breakdown of different organic materials. The biogas energetic value is dependent on the methane content. Therefore, there is a need to boost the proportion of methane in the produced biogas [22]. Compared to conventional engines, the HCCI engine has some significant advantages in terms of NO<sub>x</sub> emission and thermal efficiency and difficulties in terms of combustion [23]. In addition, the HCCI mode gives better performance and economy compared to conventional engines. Continued advancement is necessary to bring it into the daily production of vehicles [24]. HCCI engines are expected to have higher efficiency due to their high compression ratio compared to SI engines. It emits less amount of PM and NO<sub>x</sub> emissions only due to lean premixed combustion [25]. It involves compressing a homogeneous fuel-air mixture until it auto-ignition. It differs from the diesel combination because the ignition is spontaneous and not spark-induced [26].

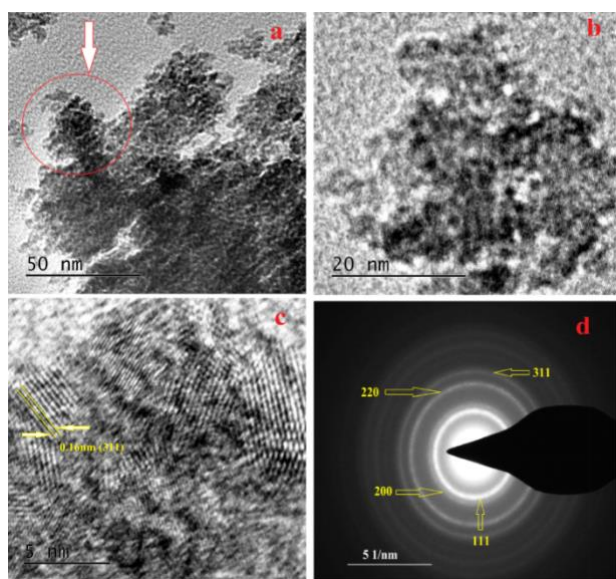
From previous literature, it is confirmed that the HCCI engine is suitable for controllable particulate emission and ethanol is a better alternative to fossil fuel. And, MTBE has a great tendency to enhance combustion and reduce emissions in engine operations. To the knowledge of the authors, no work was attempted in the case of using CeO<sub>2</sub> nanoparticles with MTBE blends in a homogenous charge combustion engine. The work focused to analyse the influence of cerium oxide on emission reduction in HCCI engines along with MTBE blends. In this way, the performance, combustion and emission characteristics of the HCCI engine when it is charged with Gasoline + MTBE+ CeO<sub>2</sub> nanoparticles.

## 2. Materials and Methods

To provide the controlled emission without compromising the performance, the HCCI engine was selected and it was planned to operate by MTBE blended gasoline with CeO<sub>2</sub> nanoparticles for further emission reduction. Here, the CeO<sub>2</sub> nanoparticles are the provoking agent to accelerate the oxidization process which can reduce the NO<sub>x</sub> emission. Here, CeO<sub>2</sub> is mixed in the proportions of 30ppm, 60ppm and 90ppm with MTBE gasoline blends. The nanoparticles morphology was analysed using Transmittance Electron Microscope (TEM) which is shown in Fig 1. The specification of TEM Made: FEI from the Netherland, model: Tecnai 20 G2, Resolution: 1.8Å°, and Point: 2.40 Å°. And the specification of CeO<sub>2</sub> nanoparticles is given in Table 2. The MTBE is blended in the proportion of 10vol%, 20vol% and 30vol%. MTBE and CeO<sub>2</sub> nanoparticles were purchased from Validyn Engineering Solutions Pvt Ltd, India. Also, the Gasoline was purchased from the Indian Oil fuel Station, India. The thermal properties of various samples are measured and listed in table 1. The fuel density does not vary in a noticeable amount, but the flashpoint, fire point and calorific value have been found to significant hike as comparable with commercial gasoline. This is due to reducing the aromatic compound volume by adding the MTBE.

**Table 1.** Thermal properties of fuel blends

Properties	Gasoline	MTBE 5	MTBE 10	MTBE 15	MTBE 15+30ppm	MTBE 15+60ppm	MTBE 15+90ppm
Density @15° C (kg/m <sup>3</sup> )	745	743	741	735	742	743	743
Flash Point (°C)	-43	-43	-44	-46	-45	-45	-47
Fire Point (°C)	-38	-39	-40	-41	-42	-43	-43
Kinematic Viscosity @40° C in cSt	0.63	0.6	0.58	0.56	0.58	0.58	0.59
Gross Calorific Value (MJ/kg)	47.16	43.56	43.12	43.83	43.15	43.15	43.18
RON	87	92	96	99	96	95	95



**Fig. 1.** TEM images of CeO<sub>2</sub> nanoparticles

**Table 2.** Specification of CeO<sub>2</sub> nanoparticles

Particulars	Specifications
Particles	Cerium Oxide (CeO <sub>2</sub> )
Manufacturer	M/S Validyn Engineering Solutions, India.
Molecular mass	172.11 g/mol
Average particle size diameter	Lesser than 80 nm
Density	7.15 g/cm <sup>3</sup>
Colour	Pale Yellow
Melting point Temperature	2340°C

The CeO<sub>2</sub> nanoparticles can provoke the combustion process in a later stage by acting as an oxygen buffer, which reduces the NO<sub>x</sub> emission. The fuel blend has been prepared using high shear ultrasonication process in a systematic approach which satisfies the kinetic stability, dispersion stability and chemical stability [19, 20]. The ultrasonication process (shown in Fig 2) was carried out for 50 minutes and the stability of particles was checked by placing the blends in a graduated glass tube for 20 hours under static conditions. And, it was found that the particles were stable for up to 17 hours. To the author's Knowledge with previous investigations, no major work was carried out in using CeO<sub>2</sub> nanoparticles and MTBE blended Gasoline on the HCCI engine. The optimal MTBE blending ratio is 15vol%, which was considered for further blending of CeO<sub>2</sub> nanoparticles in the ratios of 30ppm, 60ppm and 90ppm. HCCI engine operated all those blends, and the performance, combustion and emissions were compared with commercial gasoline.



Fig. 2. Ultrasonication unit



Fig. 3. Photograph of HCCI engine Experimental set-up

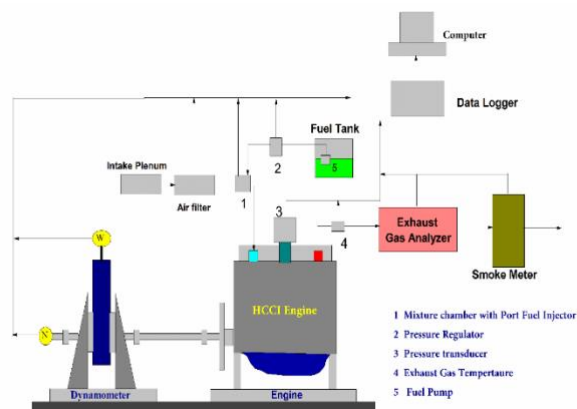


Fig. 4. HCCI engine Experimental set-up lay-out

### 3. Experimental Set-up

A single-cylinder, 4 strokes, the diesel engine was used for the testing which is shown in Fig 3 and Fig 4. The specification of the engine is given in Table 3. The dynamometer is used to measure the shaft torque. The fuel samples used in this engine were listed and their properties are given in Table 1. The following modification is carried out to convert the diesel (specification given in Table 3) to HCCI mode by placing the Port fuel injection system and electronic control was used to control the fuel flow automatically based on engine running conditions.

Here, the pressure transducer was used to measure the engine in-cylinder pressure, and average pressure traces are used to calculate the heat release rate (HRR), cumulative heat release and combustion timing. Also, the exhaust gas from the tailpipe was tested with AVL 444 digas analyser and AVL 437 smoke meter. Digas analyser is used to measure the NO<sub>x</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, and unburnt hydrocarbon. The smoke meter is used to measure the smoke intensity. The overall uncertainty was calculated by equation 1 using the different values given in table 4.

Cumulative Uncertainty,

$$U = \sqrt{\left(\sum U_{\text{individual}}^2\right)} = \pm 0.45 \quad (1)$$

Where U is total uncertainty and U<sub>individual</sub> is individual uncertainty of various factors which included pressure sensors, flow sensors, crank angle encoder, thermocouples, digas analyser, and smoke opacity. The total uncertainty percentage obtained was about ±0.45.

**Table 3.** Engine Specification

Details	Kirloskar, single-cylinder, 4 strokes, air-cooled and CI engine with 661 cc
Cylinder bore in mm	87.5
Stroke length in mm	110
Rated Power output in kW	5.2 with 1500 rpm
Dynamometer arm length in mm	185 mm arm length, eddy current, water-cooled.
Lube oil sump capacity	3.7 l

**Table 4.** Equipment with uncertainties

Instruments	Uncertainties in %
Pressure transducer (Cylinder pressure)	±1
Crank angle encoder	±0.2
Load cell(Strain gauge)	±0.2
Speed sensor	±0.1
Thermocouple K type	±0.15
Fuel flow sensor	±0.5
Airflow sensor	±0.5
AVL digas analyser	±0.41
AVL smoke meter-Smoke opacity	±1

**Table 5.** Engine Testing Conditions

Compression Ratio	12:1
Air-Fuel Ratio	1.75
Chamber Pressure	2.5 bar

The modified engine was operated in HCCI mode with a compression ratio of 12 and air-fuel ratio of 1.75 given in Table 5. The air-fuel ratio was optimized by previous experimentations.

#### 4. Results and Discussions

The HCCI engine was tested with various fuel blends in different loading conditions. The influence of CeO<sub>2</sub> and MTBE is analysed and the performance, combustion and emission parameter results are compared with commercial gasoline.

##### 4.1. Engine Performance

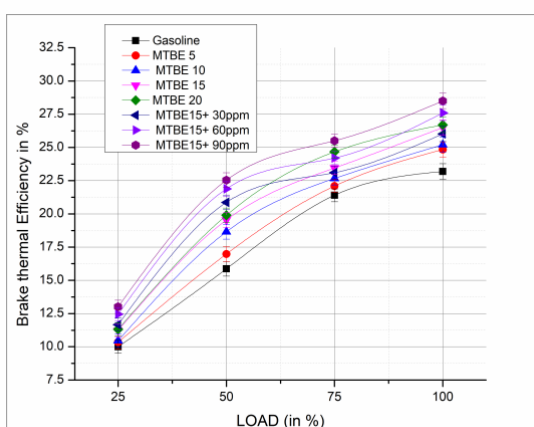
The suitability of fuel blends depends on performance parameters such as Brake Thermal Efficiency (BTE), Brake Specific Fuel Consumption and Cylinder pressure. These parameters are mainly relying on the properties of fuel blends, the air-fuel mixture and air pre-heat temperature.

##### 4.1.1 Brake Thermal Efficiency

The brake thermal efficiency is the calibre of fuel blend efficiency, here the BTE was increased with increasing the MTBE blend volume as shown in Fig 5. It is because of the higher in calorific value and research octane number (RON). The maximum BTE was found with MTBE 15 as compared with other blends and gasoline. Also, adding the CeO<sub>2</sub> Nanoparticles with MTBE 15 will be increasing the BTE further between 0.2 and 2% in different loading conditions. Here, the 90ppm of CeO<sub>2</sub> has produced a higher BTE about 28.5% at a higher load than other samples. Compared with SI engine operations, the BTE was found to be increased up to 2% in HCCI mode operations reported in Table 6. It is because of more pumping loss in SI engine compared with HCCI engine.

**Table 6.** Comparison of performance parameters with SI engine at high loads

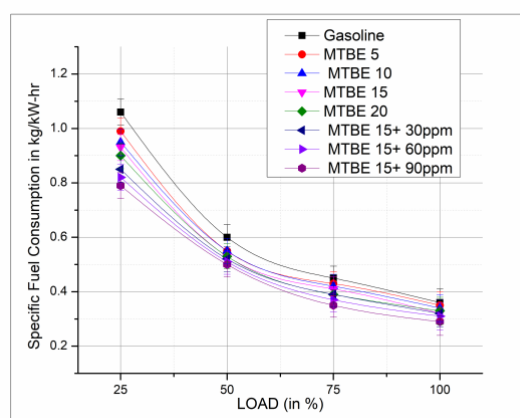
	MTBE 15 @ SI Engine	MTBE 15 + 100 mg/l @ SI engine	MTBE 15 @ HCCI	MTBE 15 + 90ppm @ HCCI
Brake Thermal Efficiency in %	25.21	26.85	26.5	28.9
Specific Fuel Consumption Kg/kW h	0.36	0.31	0.32	0.29
Cylinder Pressure in Bar	23.5	25.6	25.6	26.8
Reference	[1]	[1]	-	-



**Fig. 5.** Brake Thermal Efficiency vs Engine Load

#### 4.1.2 Brake Specific Fuel Consumption

Brake specific fuel consumption is a quantity to compare the fuel efficiency with shaft work. The BSFC of MTBE blends was found to be reduced with the increase in MTBE volume as shown in Fig 6. The MTBE and CeO<sub>2</sub> nanoparticles are accelerating the oxidizing ability of the mixture which causes the lower BSFC. In HCCI mode operations, the mixture was pre-heated up to 160° by compression, the vaporization requires a low quantity of work, thus reducing the BSFC and increasing the BTE. It was found that BSFC was brought down to 0.29 Kg/kWh with MTBE 15 + 90ppm from 0.31 with MTBE 15 + 100ppm at the SI engine.

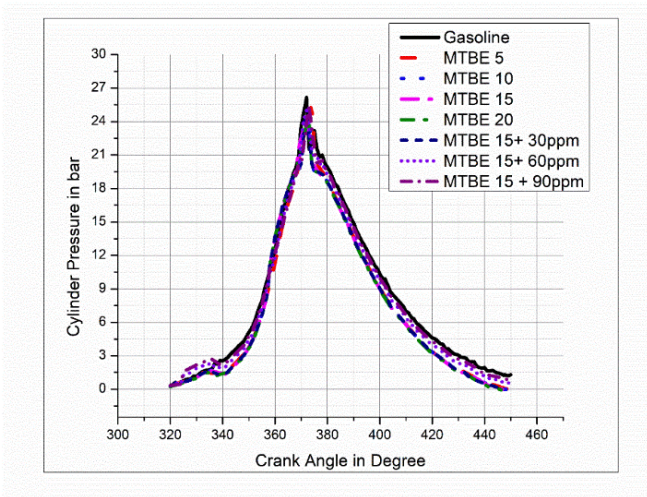


**Fig. 6.** Brake Specific Fuel Consumption Vs Engine Load

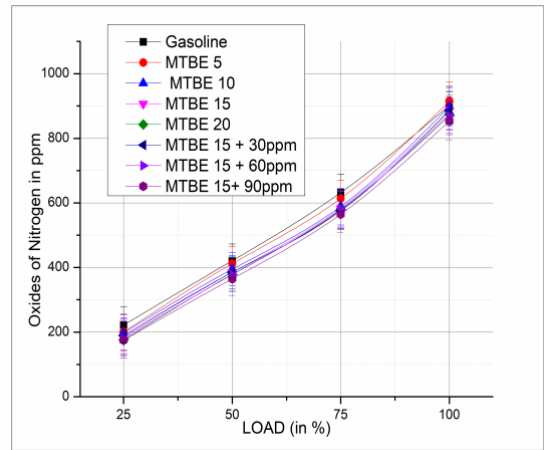
#### 4.1.3 Cylinder Pressure

The cylinder pressure with all the blends in the HCCI engine was found higher than the SI engine. In the HCCI mode of operations, the cylinder pressure was reduced while increasing the MTBE blends as shown in Fig 7, this is due to the enhancement of the Research octane number (RON) and front-end octane number (FEON), which produce better combustion. Also, enhancement of calorific value with MTBE will induce to start of the combustion a little earlier with lower pressure. The addition of CeO<sub>2</sub> with MTBE and gasoline blends will increase the cylinder pressure more than gasoline, this is because of particle surrounding fuel requires little higher pressure and temperature to start the combustion. The maximum peak pressure was attained at 370°CA, 373 °CA and 374°CA for gasoline, MTBE 20 and MTBE 15+ 90ppm respectively.





**Fig. 7.** Cylinder pressure Vs Crank Angle at High Load



**Fig. 8.** NOx Vs Engine Load

**4.2 Emission Parameters**

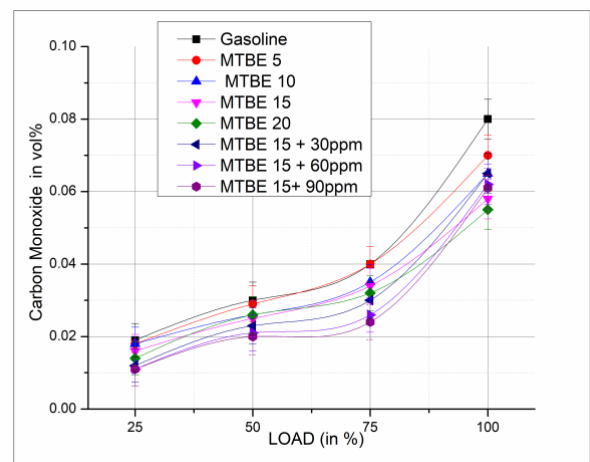
The emission regulations for IC engines have become more stringent around the world. Generally, NOx and PM emissions are quite low in HCCI engines than SI engines whereas HC and CO contents are found higher. All the emissions are depending on various parameters such as engine design, fuel properties, engine operating conditions etc. In general, the NOx emissions are formed due to the combustion of lean homogeneous mixture whereas the HC emissions are formed due to incomplete combustion process in HCCI engine. Moreover, both HC and CO are mainly formed in the crevices and near the cylinder walls at high equivalence ratio. The NOx and CO emissions of 931ppm and 0.065 vol% with SI engine which is found higher than HCCI mode. Though, the HC emission is found higher with HCCI which is 23 PPM. In an HCCI mode, the addition of CeO<sub>2</sub> nanoparticles of 90ppm with MTBE 15 significantly reduces the NOx and HC emissions whereas slightly increases the CO emissions.

**4.2.1 NOx Formation**

The NOx formation will have occurred at elevated engine temperature, it is actually a reaction between nitrogen and oxygen to form a NO and further NOx. The NOx production was reduced while increasing the MTBE volume in blends shown in Fig 8. The enhancement in O<sub>2</sub> concentration is due to MTBE and CeO<sub>2</sub> addition thus reducing the NOx formation. On the other hand, mostly the engine in HCCI mode will operate with a lean mixture which will not allow the flame temperature to reach above 2000K. Thus, the reactions which are responsible to form NOx are inactive. Due to that, the NOx from HCCI is found low than SI engine.

**4.2.2 CO Emission**

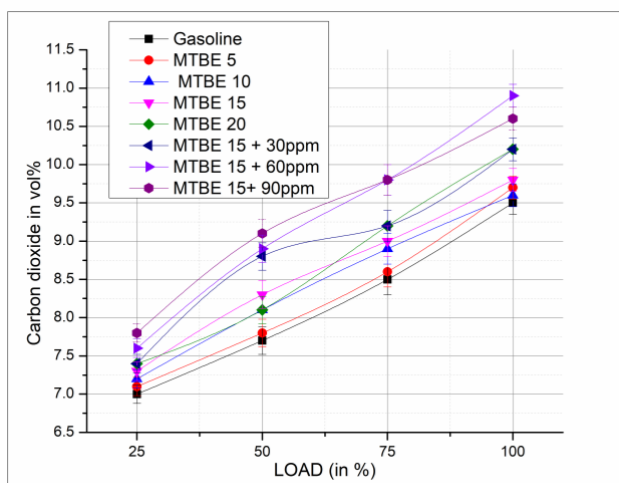
Generally, the CO emission from the HCCI engine is higher than that of the SI engine because the CO is mostly formed in crevices of the cylinder, where the complete combustion is not possible at all because being in a cold region. To reduce the CO emission, the temperature will be higher than that of 1500 k, but it would increase the NOx. In HCCI operation, the CO emission was increased significantly when MTBE is mixed with gasoline shown in Fig 9. The CO was increased with the increase of MTBE volume due to a decrement in CO oxidation during expansion and exhaust strokes caused by the lean mixture. This can be rectified by adding CeO<sub>2</sub> nanoparticles because CeO<sub>2</sub> provides the oxygen to enhance the co oxidization, thus converting the CO to CO<sub>2</sub> given in Table 7. With reference to the CO emissions, the CO<sub>2</sub> emission is increased with the increase of CeO<sub>2</sub> nanoparticles shown in Fig 10.



**Fig. 9.** CO Vs Engine Load

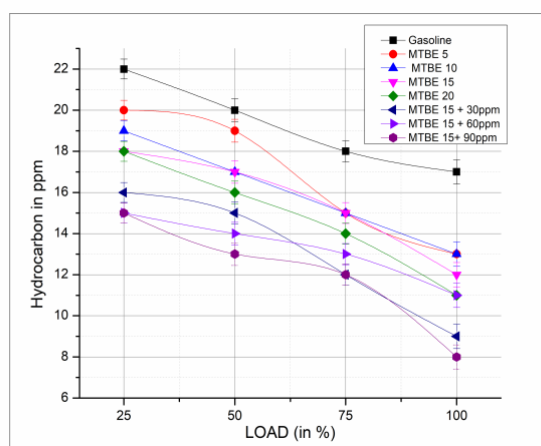
**Table 7** Comparison of emission parameters with SI engine at high loads

Parameters	MTBE 15 @ SI Engine	MTBE 15 + 100 mg/l @ SI engine	MTBE 15 @ HCCI	MTBE 15 + 90ppm @ HCCI
NOx in ppm	931	958	884	857
CO in Vol%	0.065	0.07	0.06	0.07
HC in PPM	21	18	23	11
Reference	[1]	[1]	-	-



**Fig. 10.** CO<sub>2</sub> Vs Engine Load

The unburnt hydrocarbon from the HCCI engine was observed higher with gasoline operation than in other samples as shown in Fig 11. This is due to the occurrence of flame quenching nearer to the wall. The HC from the SI engine with MTBE 15 was noted at about 21ppm, and then it was reduced to 16ppm with MTBE 15+ CeO<sub>2</sub>, whereas HCCI produced 17ppm and 11ppm for MTBE 15 and MTBE 15+90ppm of CeO<sub>2</sub>. The reduction occurred due to reducing the flame quenching effect by HCCI mode combustion and providing the oxygen by CeO<sub>2</sub>.



**Fig. 11.** Hydrocarbon Vs Engine Load

### 5. Conclusion

The automotive sector for heavy industries still plays a vital role, thus stringent emission regulations were implemented in many countries to reduce the emission drastically. For this, it is mandated to find alternative and advanced combustion methods. HCCI engine is a hybrid combustion engine to overcome the problems associated with conventional IC engines. In general, the HCCI engine produces more HC and CO in emissions. To overcome this, the current research focused on reducing the HC and CO emission from HCCI engines using CeO<sub>2</sub> nanoparticles. The performance, combustion and emission were analysed and the following concluding points are derived from the analysis. Compare to gasoline engines, HCCI produced high BTE with MTBE and gasoline blends. Further, the BTE was enhanced up to 3% when it operated with MTBE and CeO<sub>2</sub> blends. The SFC of the HCCI engine was found to be reduced than that of SI engine operation with MTBE and CeO<sub>2</sub> blends. The homogeneous charge and CeO<sub>2</sub> enhanced the fuel efficiency, the SFC was dropped up to 0.01-0.03 kg/kW hr. The cylinder pressure is found high with HCCI mode, but it would be reduced while introducing the MTBE and CeO<sub>2</sub> nanoparticles.



The reduction was found up to 3 bar than SI engine operations. The NO<sub>x</sub> was reduced with HCCI operations than SI engine operations, due to low cylinder temperature. And it was reduced further when it operated with CeO<sub>2</sub> and MTBE blended operation. The maximum reduction was observed between 5% and 7%. The HC and CO were found higher with HCCI mode operation than SI engine operation, due to low in-cylinder temperature which cannot able to brake the CO and HC particles into another form. But, both HC and CO started to reduce when the gasoline was blended with MTBE and CeO<sub>2</sub> nanoparticles. From the whole analysis, the MTBE 15 + 90ppm of SiO<sub>2</sub> blend provided better performance along with controlled emission for HCCI mode operations.

### Nomenclature

1. HCCI – Homogenous charged Compression Ignition
2. CeO<sub>2</sub> – Cerium Oxide
3. MTBE- Methyl Tert-Butyl Ether
4. TEM- Transmittance Electron Microscope
5. SI-Spark Ignition
6. CI-Compression Ignition
7. BTE- Brake Thermal Efficiency
8. SFC – Specific fuel Consumption
9. CO – Carbon Monoxide
10. CO<sub>2</sub>- Carbon dioxide
11. HC - Hydrocarbon
12. NO<sub>x</sub>- Nitrogen Oxide
13. RON-Research Octane Number

### Conflict of Interest

This article has no conflict of Interest

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