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Development and characterization of cerium oxide catalyst supported on ceramic honeycomb substrate to reduce emissions of spark ignition engine

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ABTRACT

This paper presents an innovative method to reduce cold start emissions of a four-stroke three-cylinder multi point fuel injection spark ignition engine. In this work, a glow plug is used as a heating source to maintain the activation temperature of a catalytic converter. This method is less complex than variable vacuum insulation method. In this work, cerium oxide (CeO_2) coated on the ceramic honeycomb substrate was used as a catalyst to lower the cost of a catalytic converter. A reduction of 34% carbon monoxide and 33% un-burnt hydrocarbon was observed at the idling condition with CeO_2 as the catalyst and glow plug as the heating source in the catalytic converter. The results obtained from the engine which is fitted with CeO_2 coated catalytic converter show the lowest emissions at all loads. Carbon monoxide and un-burnt hydrocarbon emissions (with catalytic converter) have reduced 68% and 71%, respectively, in comparison with a non-catalytic converter engine test at full load engine operation. The new catalytic converter competes with the existing noble metal-based catalytic converter due to the use of inexpensive CeO_2 as a catalyst.

Keywords: Catalytic Converter, Cerium Oxide (CeO_2), Ceramic material, Glow plug.

INTRODUCTION

Catalytic converter converts more harmful gases like carbon monoxide (CO), un-burnt hydrocarbon (HC), and oxides of nitrogen (NO_x) into less harmful gases like carbon dioxide (CO_2), water vapour (H_2O), and molecular nitrogen (N_2). In an internal combustion (IC) engine, the time required for the complete combustion and other processes is much less at a higher engine speed which causes the incomplete combustion of the fuel [1-3]. This leads to the formation of the HC, NO_x (NO and NO_2), and CO inside the engine cylinder. These emissions are particularly high during the idling and deceleration [1]. Carbon monoxide is a product of partial combustion of hydrocarbon in fuel. It is always present when there is a lack of oxygen during the combustion and thus, directly dependent on the applied engine air/fuel ratio [1]. There are several paths that cause hydrocarbons in the exhaust. The most obvious is, as to the cause of CO, a lack of oxygen when the air/fuel mixture is rich [1, 4]. NO_x is formed during combustion in the engine when oxygen reacts with nitrogen at an elevated combustion temperature [5-11]. Methods like after burner, exhaust manifold reactor, catalytic converter, and exhaust gas recirculation are used to treat the automotive exhaust gases [5, 12]. This paper focuses on catalytic converter technology.

In a conventional catalytic converter, materials such as platinum, rhodium, gold, etc. are conventionally used as catalysts which are highly chemically reactive with the exhaust gas emissions at high temperature [1]. Generally, two types of catalyst materials are used: a reduction catalyst and an oxidation catalyst usually made of noble materials [1, 13]. The reduction catalyst uses platinum and rhodium to reduce the NO_x emissions. When NO or NO_2 molecule contacts the catalyst, the catalyst rips the nitrogen atom out of the molecule and holds on to it, freeing the oxygen in the form of O_2. The nitrogen atoms bond with other nitrogen atoms and stuck to the catalyst, forming N_2 [14]. The oxidation catalyst is the second stage of the catalytic converter. It reduces the unburned hydrocarbons and carbon monoxide by burning them over a platinum and palladium catalyst. This catalyst aids the reaction of the CO and hydrocarbons with the remaining oxygen in the exhaust gas [15]. Figure 1 shows the catalytic converter chemical process.

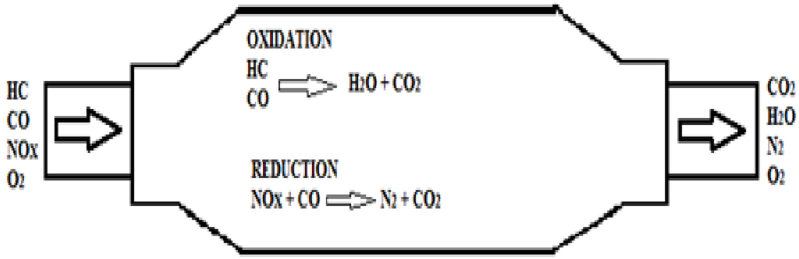


Figure1. Catalytic converter chemical process [16].

Ceramic honeycomb and beads are the two types of substrates used in the catalytic converter [17]. Most cars today use honeycomb structure. The present catalytic converters use noble metals as catalysts which are rarely available in earth crust and they are exhausted one day. The cost of extraction of noble material from the earth's crust is high and hence, causes an overall increase in the cost of the catalytic converter. In addition to this, the activation temperature of the catalytic converter made of noble material is higher than the non-noble materials [18]. Considerable work has been done to use non-noble metals as catalysts [19]. One of the researchers has developed a wire mesh, copper catalytic converter for a volume of $1.54m^3$ [20] and the experiment was carried out on a four-stroke single cylinder compression ignition (CI) engine. It is found that the HC is reduced by 38% and CO by 33% at full load. Efforts have been made to develop a cost effective catalytic converter (CAT) for diesel engines by using catalyst materials consisting of a combination of metal catalyst such Cerium Oxide (CeO_2), zirconium dioxide (ZrO_2), silver nitrate ($AgNO_3$), and copper nitrate ($Cu(NO_3)_2$) on pellets substrate [21]. These catalyst materials are inexpensive than conventional catalysts (noble metals) such as palladium or platinum. It is reported that the catalyst combination ($Cu/CeO_2/ZrO_2$+ ($Ag/CeO_2/ZrO_2$) gives maximum back pressure (78 to 290 mbar) and the three major pollutants HC, CO, and NOx have been reduced with emission conversion efficiency of 62.29%, 64%, and 59.7%, respectively [21]. It is also reported that the catalyst combination ($Cu/Ag/CeO_2/ZrO_2$) gives minimum back pressure (46 - 148 mbar) and the three major pollutants HC, CO, and NOx have been reduced with emission conversion efficiency of 61.1%, 62%, and 64.3%, respectively [21]. Efforts have been made to study the performance and emission characteristics of a four-stroke multi cylinder spark ignition engine with a Multi Point Fuel Injection (MPFI) system operating with

Oxyrich air energizer [22]. It is concluded that a complete combustion can be obtained by increasing the oxygen quantity in air intake with a magnetic effect on the air. It is reported that 10% to 25% efficiency has increased and the specific fuel consumption has decreased (saving fuel up to 15%). The main pollutants of petrol engine (CO and HC) are also decreased. In this method, both pollutants are reduced up to 20% to 30%. The other pollutants of petrol engine which are CO_2, O_2, and N_2 have increased with the increase in load and oxygen blend quantity [22]. The effectiveness of a catalytic converter mainly depends on operating temperature and gas feed composition. The optimum operating temperature for catalytic converters is around 200°C to 300°C [23]. It takes a few minutes for the engine to warm up. During this warm up period, at least 60% to 80% of toxic emissions occur [24]. The toxic emissions that escaped unfiltered during warm up period of the engine are called cold start emissions.

Many approaches have been proposed to reduce the cold start emissions [24-26]. The electrically quick heating method was also tried to reduce cold start emissions. This method requires an energy input of about 2kW and 30 seconds to produce the operating temperature. However, this method does not eliminate cold emissions completely, it only reduces the cold start emissions level [24]. The cold start emissions can also be reduced by fitting the catalytic converter closer to the engine. It helps the converter to reach its operating temperature quickly. However, there is a danger of overheating of the converter [24]. A combination of vacuum insulation and phase change material helps to eliminate cold start emissions. Vacuum insulation prevents the transfer of radiant heat from the exhaust to the surroundings, preserving heat between the trips. Phase change material acts as a heat storage system and releases heat to the converter during cold start condition [24]. One of the researchers has made an attempt to improve the effectiveness of catalytic converters via reduction of cold start emissions [25-27]. This work involves the use of variable thermal conductance to improve the amount of heat that can reach the converter. Low conductivity helps to retain heat between trips, but high conductivity helps to reject excess heat while the catalytic converter is running. Vacuum insulation provides a practical solution to these requirements [26].

The main objective of this research is to develop a cost effective non-noble metal based catalytic converter to be used with a spark ignition engine. Hence, in this research, an attempt has been made to use CeO_2 as a catalyst material in a catalytic converter because of its lower cost and lesser activation temperature than the noble materials. In this research, an attempt has also been made to reduce the cold start emissions by using a glow plug as the heating element.

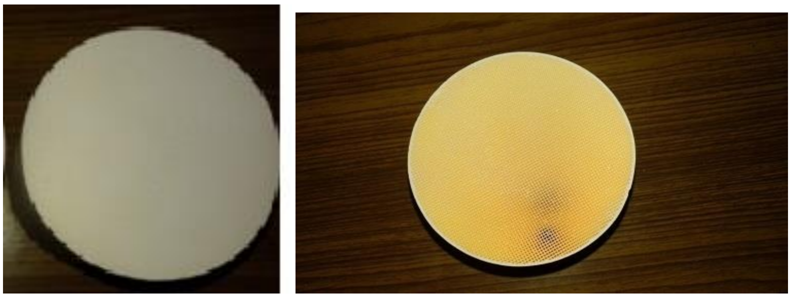
MATERIALS AND METHODS

Table 1 shows the materials used for the fabrication of a catalytic converter. The outer casing is made of stainless steel in order to provide structural strength. The honeycomb structure is the main structural component of a catalytic converter. Ceramic honeycomb is selected because it has a good thermal stability, high catalytic activity, high strength, and long life. Ceramic honeycomb structures offer maximum surface areas with minimal volume. Figure 2 shows the Ceramic Honeycomb Monolith Substrate. In this work, two ceramic honeycomb structures are used as substrates. One is a simple ceramic honeycomb structure and the other is a ceramic honeycomb structure coated with CeO_2. Non-coated and CeO_2 (catalyst) coated ceramic cylindrical shape honeycomb substrates were imported from the Nanjing Depurate Catalyst Co., Ltd Nanjing, China. The cylindrical honeycomb structure has 100 mm diameter and 100 mm length. Figure 3 shows a non-coated and CeO_2 coated ceramic honeycomb substrate materials. The cylindrical honeycomb structure has a weight to volume ratio of 0.40 (g/cm^3) with a cell density of 62 (cells/cm^2). The substrate has a length of 100mm and diameter of 100mm. The substrate has a low pressure drop, chemical inertness, and structural stability at temperature up to 500^{o}C. In this work, cerium oxide is used as a catalyst to promote oxygen storage, which in turn improves oxidation stability. Cerium absorbs excess oxygen and releases it under low oxygen conditions which improve the oxidation efficiency of HC and CO [24]. In addition to this, Cerium Oxide is inexpensive than noble metals.

Table 1. Materials used for the fabrication of catalytic converter.

Sl. No	Part Name	Material	Reasons
01	Outer casing	Stainless steel	Longer life, durability, minimum expansion, deformation
02	Monolith Substrate	Ceramic (honeycomb shape) mixed with precious metals and wash coat has been formulated for the storage of oxygen	Good thermal stability, high catalytic activity, high strength, long life.
03	Glow Plug		Heating element
04	Cerium Oxide		Catalyst

Figure 2. Ceramic honeycomb monolith substrate.



(a) Non coated

(b) CeO_2 Coated

Figure 3. Ceramic honeycomb substrate.

Table 2 describes the product test report of the ceramic honeycomb substrate (non-coated type and catalyst coated type) which were obtained from the Nanjing Depurate

Catalyst Co., Ltd Nanjing, China. Table 3 describes the product test report of the coating material.

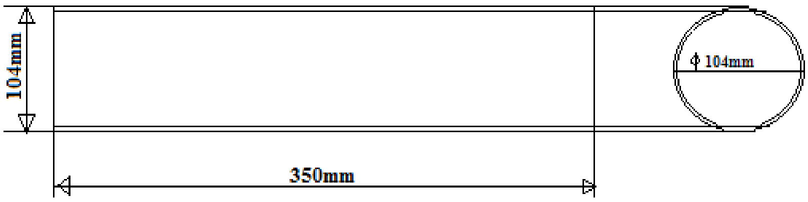
Table 2. Product test record of ceramic honeycomb substrate (non coated and coated).

Item Name	Standards	Test result (Non coated)	Test result (CeO_2 coated)
SiO_2 (%)	49.7±1.5	50.35	50.35
Al_2O_3 (%)	35.4±1.5	35.80	34.54
MgO (%)	13.5±1.5	13.10	13.9
Cell Density (cell/cm^2)	62±3	62	62
Wall Thickness (mm)	0.18±0.02	0.17	0.17
Volume Weight (g/cm^3)	≤0.55	0.40	0.42
Moisture Absorption (%)	25±5	25.9	26.1
Thermal Expansion Coefficient ($*10^{-6}/^0C$)	≤1.8	1.27	1.30
Thermal Shock Resistance (Air cooled)	No cracking as putting in temperature of 500^0C than take out to nature cooling for three times	No cracking as putting in temperature of 500^0C than take out to nature cooling for three times	No cracking as putting in temperature of 500^0C than take out to nature cooling for three times

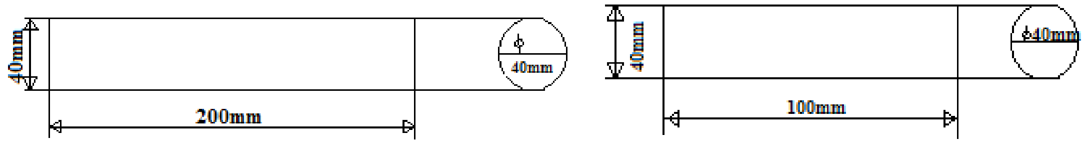
Table 3. Product test record of coating material.

Item Name	Standards	Test result
Zr (Hf)O_2	24±1	24.07
CeO_2	68±1	67.94
La_2O_3	8±1	7.99
Na_2O	<0.01	<0.01
SiO_2	<0.05	<0.05
Fe_2O_3	<0.01	<0.01
SO_4^{-2}	<0.03	<0.03

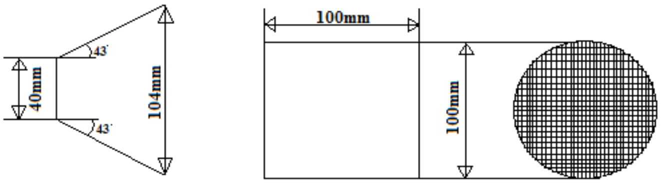
The Catalytic converter is made cylindrical because it is easy to fabricate and easy to maintain. It requires minimum assembly time and it is rigid. Catalyst volume (1570796.23 mm^3) and space / residence time / holding time (10135.26 /hr) were calculated using the standard formulae. The fabrication of Figure 4 shows the details of parts of the catalytic converter. Figure 5 shows the assembled catalytic converter. The outer casing has a diameter of 104mm and length of 350mm. The casing contains a 100mm diameter and 100mm length two honeycomb ceramic substrates which are surrounded by a 2mm thick stainless steel mesh to hold the material tightly. The inlet cone length of the casing is 200mm and outlet cone is 100mm. The inlet cone length is kept larger than the outlet cone length in order to reduce the thermal stress.



(a) Catalytic Converter Casing



(b) Inlet Cone (c) Outlet Cone



(d) Cone angle (e) Cylindrical honeycomb substrate

Figure 4. Parts of catalytic converter.

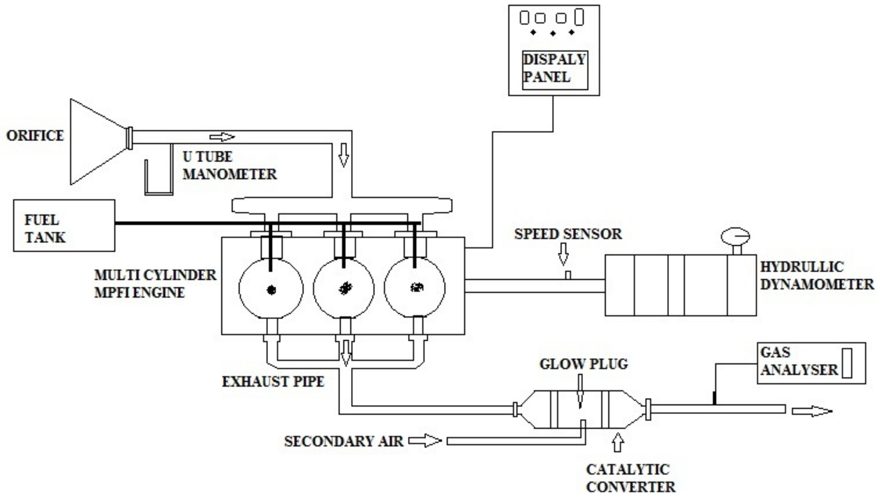
Figure 5. Assembled catalytic converter.

EXPERIMENTATION DETAILS

Exhaust emission tests were carried out on a three-cylinder, the MPFI petrol engine which is coupled with an electrical dynamometer. Table 4 shows the engine specifications. Five gases analyzer (Indus make PEA 205 model) is connected to the tail pipe of the engine to measure CO, CO_2, HC, and O_2. A probe is mounted at the exhaust pipe which supplies exhaust gasses samples to the gas analyzer. The amount of CO, CO_2, HC, and O_2 present in the exhaust can be read at the indicator panel of the exhaust gas analyzer. Engine tests were conducted by varying the loads (0, 2, 4, 6, 8,10kg) and keeping the speed constant (2000RPM). In this work, the speed of the engine is kept constant because the load has a greater effect on the performance and emissions characteristics of the SI engine. By keeping the speed constant, it is possible to study the effect of brake power, air-fuel ratio, and torque on the performance and emissions characteristics of the SI engine. Figure 6 shows the experimental setup used in this work. In the first stage, exhaust emission test was conducted by fitting a 100mm diameter catalyst (CeO_2) coated catalytic converter to the tail pipe of the test engine. In the second stage, exhaust emission test was conducted by fitting a 100mm diameter non-catalyst coated (without CeO_2 coating) catalytic converter to the tail pipe of the test engine. In the third stage, cold start exhaust emission test was conducted by fitting a 100mm diameter catalyst coated (CeO_2 coating) catalytic converter with a glow plug in the tail pipe of the test engine. In the last stage, exhaust emission test was conducted by fitting a 100mm diameter catalyst coated (CeO_2 coating) catalytic converter to the tail pipe of the test engine by supplying secondary air. The results obtained in these tests have been compared to the exhaust emissions of the engine without a catalytic converter.

Table 4. Engine specifications.

Engine	MARUTI 800
BHP	12 hp
Fuel	Petrol
No. Of cylinders	3 cylinders
Bore	68.5 mm
Stroke length	72 mm
Starting	Self start
Working cycle	Four stroke
Method of cooling	Water cooled
Method of ignition	Spark ignition



(a)

(b)

Figure 6. Schematic diagram and real experimental engine setup.

RESULTS AND DISCUSSION

Variation of CO Emission

Figure 7 shows the CO emission at different loads. As the load on the engine is increasing, the CO emission is also increasing. The CO emission has increased from idling to full load when the catalytic converter is not used. The same trend was observed for all other test conditions. When the coated catalytic converter is fitted to the tail pipe, CO emission was reduced by 58% at full load in comparison with CO emission when the catalytic converter is not used because the catalyst coated on the honeycomb substrate oxidizes CO to CO_2. In addition to this, at higher engine load, conversion of CO to CO_2 is more because of higher exhaust gas temperature, which increases the catalytic activity of the catalyst [1]. There is an appreciable reduction in CO emission in the lower load range when glow plug is operated. The results indicate that CO emission has decreased to a value of 72% from 75% when the glow plug is heated up in the load range of 4kg. This is because the glow plug keeps the converter hot when exhaust gas temperatures are low. A reduction of 50% CO emission was observed when a non-coated catalytic converter is used compared to a non-catalytic converter engine at full load operation because the honeycomb substrate material has SiO_2, Al_2O_3, and MgO which act as catalysts and boost oxidation of CO to CO_2. It was also observed that CO emission has increased 19% when the non-coated catalytic converter is used compared to the coated catalytic converter engine at full load operation due to the use of CeO_2 as a catalyst.

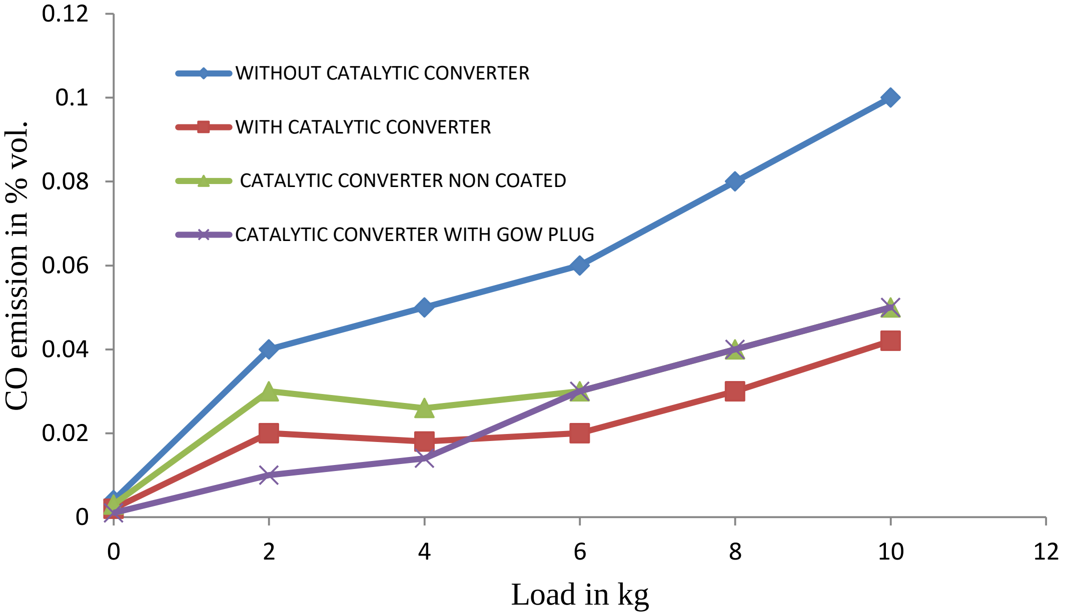


Figure 7. Effect of load on CO emission at different operating conditions.

Variation of HC Emission

Figure 8 shows the HC emission at different loads. It is clear from Figure 8 that HC emission (in ppm) increases with the increase in load for all test conditions. It was observed that HC emission has decreased 55.56% at the idling test condition and 69.23% at full load test condition when the CeO_2 coated catalytic converter is used as compared to non-catalytic converter engine operation because the catalyst coated on the honeycomb substrate oxidizes un-burnt hydrocarbons to water vapor and oxygen. In addition to this, at higher engine load, conversion of un-burnt hydrocarbons to water vapor and CO_2 is more because of higher exhaust gas temperature, which increases the catalytic activity of the catalyst [1]. The results indicate that the HC emission has decreased to a value of 55.6% to 81.6% when the glow plug is heated up in the load range of 0kg to 4kg. A reduction of 36.21% HC emission was observed when a non-coated catalytic converter is used compared to a non-catalytic converter engine at full load operation because the honeycomb substrate material has SiO_2, Al_2O_3, and MgO which act as catalysts and boost oxidation of CO to CO_2. It was also observed that HC emission has become 2.25 times when the non-coated catalytic converter is used compared to the coated catalytic converter engine at full load operation due to use of CeO_2 as a catalyst [1]. Thus, there is a steady decrease in HC value with the introduction of the coated catalytic converter.

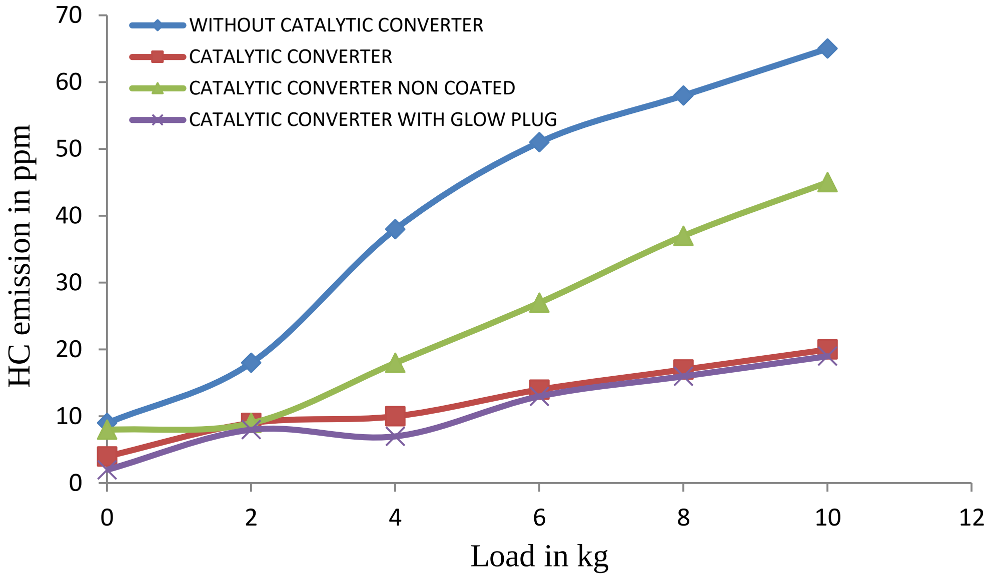


Figure 8. Effect of load on HC emission at different operating conditions.

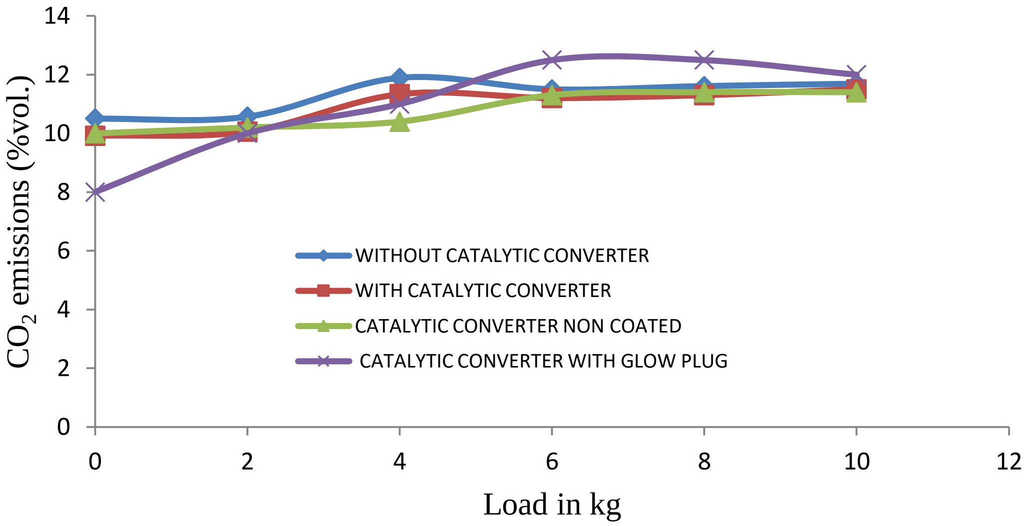


Figure 9: Effect of load on CO_2 emission at different operating conditions.

Figure 9 shows the CO_2 emission at different loads. It was observed that CO_2 emission increases with the increase in load for all test conditions. It was observed that CO_2 emission has decreased 5.52% at idling test condition and 1.63% at full load test condition when the CeO_2 coated catalytic converter is used compared to a non-catalytic converter engine operation because catalyst (CeO_2) oxidizes CO to CO_2. The results indicate that CO_2 emission has decreased to a value of 5.39% from 23.81% when the glow plug is heated up in the load range of 0kg to 4kg. A reduction of 2.48% CO_2 emission was observed when a non-coated catalytic converter is used compared to a non-catalytic converter engine at full load operation because the honeycomb substrate material has SiO_2, Al_2O_3, and MgO which act as catalysts and boost oxidation of CO to CO_2.

CONCLUSIONs

It can be concluded that the CO, HC, and CO_2 emissions can be reduced by using CeO_2 coated catalytic converter at all engine load operations. It can also be concluded that cold start emissions can be controlled using a glow plug along with the CeO_2 coated catalytic converter. The catalytic converter made of the non-noble (CeO_2) material has significant advantages such as inexpensive than the catalytic converter based on the noble material and a lower operating temperature than the noble metal and also the easy availability of the non-noble material. The non-noble material catalytic converter is the best option for reducing pollution when noble materials are not available.

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NOMENCLATURES

CO – Carbon Monoxide
CC – Catalytic Converter
HC – Hydrocarbon
SiO_2 – Silica
MgO – Magnesia
Al_2O_3 – Aluminum oxide
La_2O_3 – Lanthanum oxide
Na_2O – Sodium oxide
Fe_2O_3 – Ferric oxide
SO_4^{-2} – Sulfate