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Influence of metal oxide catalysts on diesel engine emissions using catalytic converter

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Abstract: The demand for automobiles is rising each day on a global scale. Because of the lower cost of diesel oil compared to gasoline, more people own and operate private diesel vehicles than commercial ones. By 2030, it is anticipated that there will be 1300 million cars on the road. Emissions from fossil fuels contaminate the atmosphere, threatening air quality, the environment, and human health. Among these contaminants are Nox, HC, and CO. Researchers from all over the world concentrated on figuring out how to reduce pollution. Platinum and rhodium metals have been applied to catalytic converter (CC) monoliths in contemporary cars up until this point. These metals are pricey because they are rare. In the current investigation, ethanol alcohol and base metal catalysts like Al_2O_3, Ceo_2, and Zeolite (Ze) are utilized to create slurry using ultrasonication technique, which is then applied to foils made of metal. After testing, it was found that, when compared to a mix of the A50C40Ze40-E130, the modified CC has the ability to lower hazardous emissions like HC, CO, and NOx by 50, 57.89, and 43.82%, respectively.

***Index Terms* - CeO_2, Zeolite, Aluminium oxide (Al_2O_3), Ethanol alcohol, catalytic converter**

I. INTRODUCTION

As the population grows, so do the emissions from automobiles. The depletion of the environment caused by vehicle exhaust is a greater problem in this world [1,2]. Worldwide, more than 700 million cars are in use and more than 50 million cars are created each year. By 2030, it is predicted that the number of automobiles produced would have increased to about 1300 million. When fuels like gasoline, diesel, and other jet fuels burn—which is how most cars operate—hazardous gases including carbon monoxide (CO), nitrogen oxides (NOx), unburned hydrocarbons (HC), and other sulfurous oxides (SOx) are released in significant amounts [3,4]. The main pollutants produced by internal combustion engines are nitric oxide (NOx), hydrocarbons (HC), and carbon monoxide and minimal levels of particle pollution, lead (Pb), and sulfur oxide (SOx). Fossil fuels are burned to power internal combustion engines. Two thirds of the air pollution in metropolitan areas is caused by car emissions. One of the main issues facing the majority of countries worldwide is automobile pollution. Asthma, cancer, chronic illnesses, respiratory disorders, and other grave health consequences are brought on by these emission gasses. Emissions of CO and HC are caused by the combustion efficiency being less than 100%. The extremely high temperatures (>1500°C) of the combustion process cause the nitrogen in the air to be thermally fixed, forming NOx. The following gases, in the previously indicated quantities, are commonly found in exhaust .Water (H_2O, 10 vol. %), carbon dioxide (CO_2, 10 vol. %), oxygen (O_2, 0.5 vol. %), unburned hydrocarbons (HC, 350 vppm), nitrogen oxides (NOX, 900 vppm), hydrogen (H2, 0.17 vol. %) [5,6].

More sophisticated methods of management, such as modifications to the fuel system and engine design, engine parameter control, and the use of advanced exhaust after treatment equipment, have been adopted in an attempt to minimize emissions and the environmental strain they cause. Toxic gasses are reduced using both primary (within the engine) and secondary (outside the engine) techniques. The main techniques for lowering emissions include burning lean air fuel mixtures, multistage fuel injection, recirculating exhaust gases, and burning fuel gas after burning. These days Three-way catalyst adsorption, storage, and filtering processes, as well as oxidation, are examples of secondary methods for treating exhaust gases [7]. Three-way CCs (TWCs), which are capable of reducing CO, HC, and NOx emissions simultaneously, are now standard in automobiles. One of the most important contributions to reducing the environmental effect of vehicle emissions has been the widespread integration of CCs. CCs have a major role in reducing air pollution and promoting environmental sustainability by changing toxic pollutants into less toxic substances. Thus, in order to comply with present and future exhaust emission laws, the reduction of carbon monoxide (CO), hydrocarbons (HC), nitrogen oxide (NOx), and particle emissions is made possible [8-10].

CATALYTIC CONVERTER: Eugene Houdry, a French mechanical engineer, was the first to create the CC in 1930. An automobile's means of eliminating pollutants is a CC. It transforms more harmful particles coming from car exhaust into fewer hazardous ones. Because of Environmental requirements dealing to the reduction of emissions of harmful gases, CCs were first used in American manufacturing cars in 1975. All new model vehicles manufactured after 1975 were mandated by the US Clean Air Act to reduce their emissions by 75%, and CCs were to be used to achieve this reduction. Cars that don't have CCs emit HC, CO, and NOx. In cars with internal combustion engines, there is a CC. Three distinct versions exist [11].

Oxidation catalytic converter: This device converts hydrocarbons into carbon dioxide and water as well as carbon monoxide and carbon dioxide instead. Diesel engines usually use this converter to cut down on emissions of carbon monoxide and hydrocarbons as shown in equation 1 and 2. By accelerating up the oxidation process, platinum and palladium burn HC and CO and turn them into CO_2 and water droplets [12].

$$HC + O_2 \rightarrow CO_2 + H_2O \qquad 1)$$

$$2CO + O_2 \rightarrow CO_2 \qquad 2)$$

Reduction catalytic converter :The reduction CC is needed since NOx is already an oxidized molecule and needs to be fitted upstream of the oxidation system in order to be converted back into its original elements, N_2 and O_2 as shown in equation 3. The initial phase of the catalytic conversion is the reduction mechanism. Rhodium (Rh) and platinum (Pt) are used to lower the emission of nitrogen oxides. The catalyst pulls the nitrogen atom from the NOx molecules and holds onto it, releasing the oxygen in the form of O_2, as soon as the molecules make contact with the catalyst bed. N_2 is created when the nitrogen atoms link to other nitrogen atoms that are adhered to the catalyst.

$$2NO \rightarrow N_2 + O_2 \qquad 3)$$

The simultaneous oxidation of carbon monoxide (CO), hydrocarbons (HC), and reduction of nitrogen oxides (NOx) is an additional benefit of TWCs. In TWCs, noble metals are typically utilized as the active phase. Particularly, palladium (Pd) catalysts are All the more so because palladium is by far the most affordable noble metal available, with superior hydrocarbon selectivity and activity. It is commonly acknowledged that rhodium, the additional crucial component of three-way catalysts, is the most effective catalyst for encouraging the conversion of NO_2 to N_2 and O_2.

CATALYSTS: Pollutants are often oxidized to produce less toxic gases by converting highly harmful gases to less toxic gases. Most frequently, a mixture of precious metals, primarily from the platinum group makes the catalyst itself. Although platinum is the most active catalyst and is widely used, its high cost and undesired more additional reactions make it unsuitable for all purposes. Two other precious metals utilized in the CC are rhodium and palladium. Palladium is employed as an oxidation catalyst, rhodium as a reduction catalyst, and platinum as a catalyst for both oxidation and reduction [13]. The various metal catalysts are discussed below:

Noble Metal Catalysts: The noble metals (Pt, Pd, Rh, Ir, Au, and Ag) are most frequently thought of as being primarily used in cars as CCs, which change the dangerous, toxic gases that are released from the engine of the car into less toxic gases like H_2O and CO_2. The low-temperature CO oxidation catalysts that are most frequently utilized are Pt/SnO_2 and Pd/SnO_2. One of the drawbacks of noble metal catalysts is their high material cost. Palladium is employed as an oxidation catalyst, rhodium as a reduction catalyst, and platinum as a catalyst for both oxidation and reduction in noble metal catalysts.

Basic Metal Catalysts: The most active base metal catalysts are those made of Co, Ni, Cr, Fe, Mn, and Cu. For CO oxidation processes, it has been discovered that base metal oxides such as Co_3O_4, CuO, and MnO_2 exhibit significant catalytic activity per unit surface area. The application of low-cost, high-performance supported base metal catalysts to catalytic activity may be highly promising. The following is an arrangement of the various supported base metal oxide catalysts according to their catalytic activity for CO oxidation. $Cr_2O_3 > V2O_5 > MnO > NiO > Fe_2O_3 > CuCr_2O_4 > Co_3O_4 > Cu_2O$. The supported Cu oxide catalysts have been applied to the oxidation of NH_3 and VOCs in addition to CO. catalyst for copper supported by CeO_2 or When it comes to oxidizing CO and CH_4, Al_2O_3 is far more efficient than other base metal catalysts. The base metals have a lot of surface features that influence compounds' surface energies and chemical characteristics. It has oxygen atoms attached to transition metals in it [14].

In a research study, Dey et al. (2019) [15] examined how, since the development of internal combustion engines and their growing application in the automotive industry, pollution has grown to be a significant worry during the past 20 years. In the production of CCs, noble metals like platinum (Pt), palladium (Pd), and rhodium (Rh) are typically utilized. This review aims to investigate alternative materials, such as activated carbon, Zes, sponge iron, SCR, and TiO_2, that can be used in place of platinum, palladium, and rhodium in CCs to increase efficiency and convenience of use. [15]

Pardiwala J. M, et al. This suggests that certain operating conditions, high cost, and restricted availability have encouraged research into alternative catalyst compounds. [16]

Cheng Y, et al. (2009) Discusses worries about sulfur poisoning in systems using Diesel Oxidation Catalyst before Cu/Ze Selective Catalytic Reduction (SCR) Catalyst for diesel engine applications. [17]

Ramalingam et al. (2018) [18] , investigated that the Due to greenhouse gas emissions and global warming, there has been a significant change in the climate recently, resulting in famine, draughts, and floods. When cars use more gasoline and diesel, harmful gases leak into the atmosphere, harming the ecosystem. One of the main ingredients in greenhouse gases, which cause the greenhouse effect, is carbon dioxide. Increased emissions of carbon dioxide from vehicles and industries due to the burning of petroleum-based products. We have decided to use Ze to adsorb carbon dioxide from gasoline-powered vehicle exhaust in order to reduce the amount of carbon dioxide released into the atmosphere. The testing gasoline vehicle adheres to the EURO – V emission standards and the vehicle's release of carbon dioxide is decreased by more than 25%.

When it comes to catalyst varieties, the two most widely available goods on the market are metallic and ceramic substrates. The monolith has grown to be the most popular choice for the majority of applications that call for high flow rates and minimal pressure drop. Although being the most often utilized substrate material, extruded ceramic monoliths are primarily chosen due to their relatively low manufacturing costs. The use of foil metallic monolith substrates is growing in popularity. Due to their relatively low porosity, neither of the substrates is suitable as a support for a catalyst. The channel walls are coated with a thin layer of a porous substance to get around this. We call this layer the wash coat. A popular material for wash coats is Al_2O_3, which has a surface area of around 100 m^2/g. Designed to improve the catalytic oxidation and reduction of exhaust polluting gases from IC engines to more harmless ones, like water, carbon dioxide, and nitrogen, this wash-coat also serves as a support for precious metals, primarily palladium (Pd), platinum (Pt), and rhodium (Rh). Because of their capacity to store oxygen, Ze and cerium oxides (CeO_2) are utilized in the coating to increase catalytic efficiency. Aluminum is a common energetic addition for both fuel and energetic materials used in air breathing propulsion. This study produced a modified conventional CC that is coated with Al_2O_3, CeO_2, and Ze in order to reduce emissions from the DI diesel engine and enhance the CC's performance. The In comparison to a typical CC, the advantages of this one are its lower cost and larger substrate surface, which makes it more effective in oxidizing and reducing emissions. [19].

II. MATERIALS

The catalysts such as CeO_2, Zeolite, Al_2O_3 and Ethanol are supplied by Greater Scientific, Vijayawada, India.

III. METHODOLOGY

3.1 Preparation of Substrate in Catalytic Converter:

CC generally consists Platinum, Palladium and Rhodium as a catalyst but they are very expensive so in this experiment the CC is modified with different stainless steel foil/metallic foil which are less expensive when compared to monolith. The stainless steel is prepared according to the shape and size of substrate. After coating with the prepared slurry the metallic foil is fixed inside CC in such a way that it does not move when exhaust gases flow past them. A 60 foils are cut and arranged in the place of substrate. Finally, modified CC is used to test on a diesel engine.

3.2 Wash coating

Aluminum oxide, was utilized as the wash coat ingredient to strengthen the coating. A 50 gms of Al_2O_3, 10 gms of CeO_2, 10 gms of Ze and 70 gms of Ethanol are used to prepare the slurry in 1:1 ratio using ultrasonically and blend is termed as A50C10Ze10-E70. Similarly, A50C20Ze20-E90, A50C30Ze30-E110, A50C40Ze40-E130 blends are prepared and applied to the metallic foil. After applying by dip coating, the foils are heating in the furnace at 120 for 1 hr. Then, the prepared metallic foil is arranged in the CC as shown in figure 1. The modified CC is directly used to measure the exhaust gasses passing through it by Mars gas analyzer. The prepared blends are listed in the table 1.

Figure 1. Represents the modified catalytic converter

Table 1. Concentrations of various Catalysts and Ethanol

Sl. No.	Name of the catalyst	Wt. (in grams)	Wt. (in grams)	Wt. (in grams)	Wt. (in grams)
1	Al_2O_3	50	50	50	50
2	CeO_2	10	20	30	40
3	Ze	10	20	30	40
4	Ethanol	70	90	110	130
5	Name of the wash coat blend	**A50C10Ze10-E70**	**A50C20Ze20-E90**	**A50C30Ze30-E110**	**A50C40Ze40-E130**

3.3 Engine set up

Experiments were conducted on Kirloskar TV1, four stroke, single cylinder, water cooled diesel engine. The rated power of the engine was 3.5 kW at a speed of 1500 rpm. The engine was operated at a constant speed of 1500 rpm and a standard injection pressure of 220 bar. Details of the engine specification are given in Table 2. The Mars gas analyzer is used to measure the exhaust gas emissions. The engine setup and mars gas analyzer are represented in figure 2 and 3.

Table 3. Engine specifications

Sl. No.	Engine parameters	Specifications
1	Engine model	Kirloskar TV1
2	No. of cylinders	1
3	No. of strokes	4
4	Power	3.5 kW
5	Type of cooling	Water cooled
6	Rated speed	1500 rpm
7	Cylinder bore	100 mm
8	Length of stroke	105 mm
9	Compression ratio	18:1
10	Injection pressure	220 bar
11	Ignition timing	23˚ bTDC

Figure 2. Represents the engine set up

Figure 3. represents the gas analyzer

IV. RESULTS AND DISCUSSIONS

4.1 HYDROCARBON EMISSIONS (HC)

The HC emissions vs load are shown in figure 4. As the load increases the HC emissions are decreased. The HC emissions are reduced to 48, 42, 38, 32, and 24 ppm for without CC, A50C10Ze10-E70, A50C20Ze20-E90, A50C30Ze30-E110, and A50C40Ze40-E130. The HC emissions are decreased by 50% for A50C40Ze40-E130 blend when compared to without CC which is due to the oxidation process.

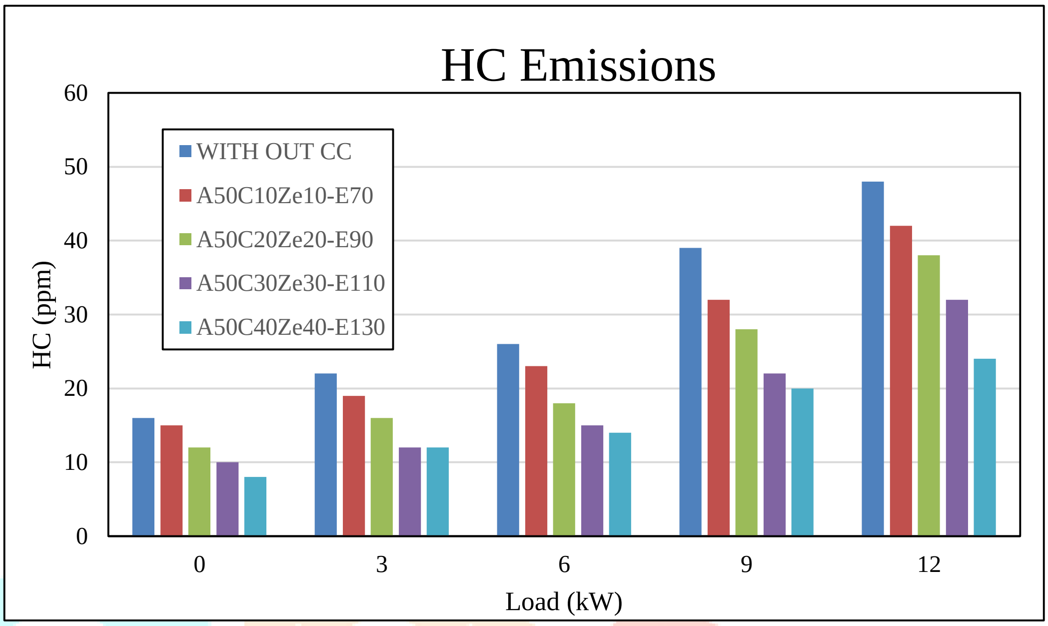

Figure 4. Shows the HC emissions vs Load

4.2 CARBON MONOXIDE EMISSIONS (CO)

The CO emissions vs load are depicted in figure 5. The CO emissions are decreased along the increased load. The CO emissions are reduced to 0.114, 0.102, 0.096, 0.089, and 0.048 % for without CC, A50C10Ze10-E70, A50C20Ze20-E90, A50C30Ze30-E110, and A50C40Z40-E130. The CO emissions are decreased by 57.89% for A50C40Ze40-E130 blend when compared to without CC which is due to the addition of oxygenated elements in the CC.

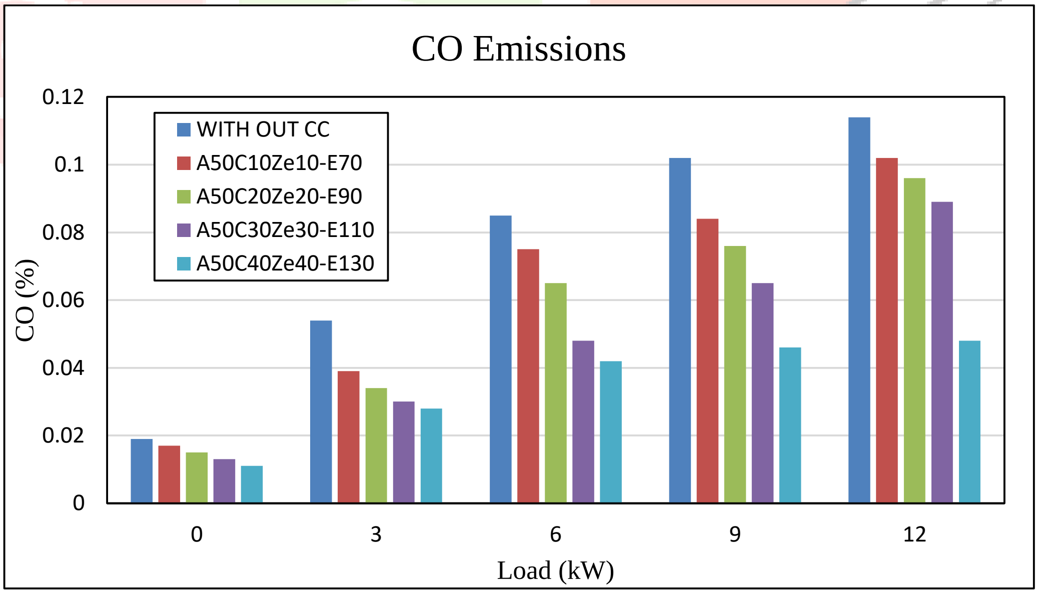

Figure 5. Shows the CO emissions vs Load

4.3 Nitrogen oxide emissions (NOx)

The NOx emissions vs load are represented in figure 6. The NOx emissions are The NOx emissions are converted into N2 and O2 duet the reduction process in which the oxygen molecules are absorbed by the catalyst. The NOx emissions are observed to be 890, 790, 662, 584, and 500 ppm for without CC, A50C10Ze10-E70, A50C20Ze20-E90, A50C30Ze30-E110, and A50C40Ze40-E130 respectively. The NOx emissions are decreased by 43.82% for A50C40Ze40-E130 blend when compared to without CC.

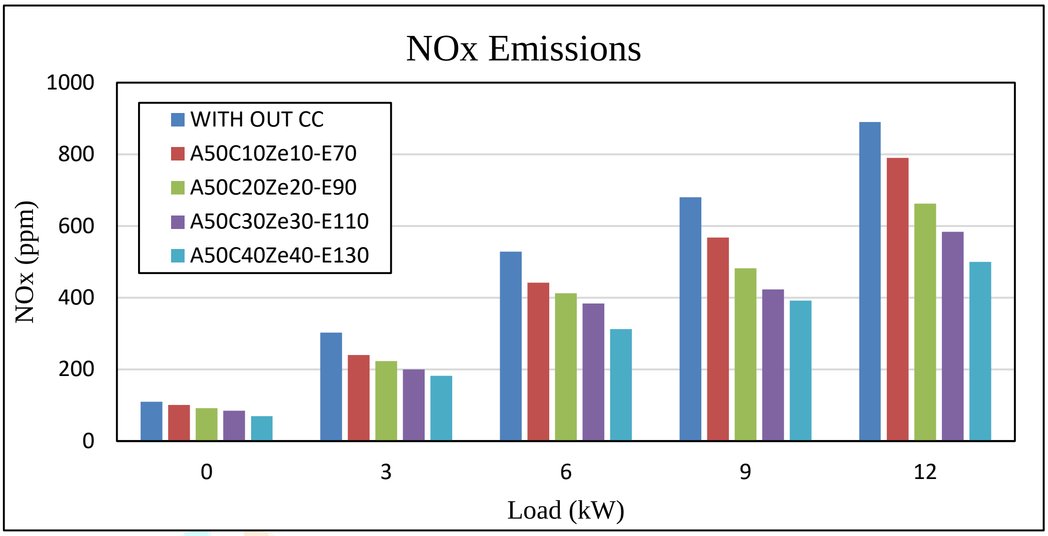

Figure 6. Shows the NOx emissions vs Load

V. Conclusions

The base metal oxide catalysts such as Al_2O_3, CeO_2, Ze along with Ethanol alcohol used in CC reduced the HC, CO, and NOx emissions. The following inferences are made based on results and discussions.

- The influence of selected catalysts resulted in reduced HC emissions by 50% for the A50C40Ze40-E130 blend as compared to with no CC due to the abundant oxygen in the catalysts.
- The synergistic effect Al_2O_3, CeO_2, Ze, and Ethanol decreased CO emissions by 57.89% for the A50C40Ze40-E130 blend due to oxygen storage capacity of catalysts.
- The effect of wash coat slurry (A50C40Ze40-E130 blend) resulted in lowered NOx emissions by 43.82% when compared to without CC due to reduction reaction process.

Finally, the above investigation concludes that the catalysts Al_2O_3, CeO_2, Ze, and Ethanol alcohol are potential to reduce diesel engine emissions with low cost modified CC.

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