

Dual-Stage Emission Reduction System Using Cu-Zeolite and Cobalt Oxide

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ABSTRACT: The increasing number of conventional vehicles (running on fossil fuels) have caused the pollution levels to soar. In this moment of urgency, it is necessary to minimize the vehicular emissions. Using efficient catalytic converters is one such solution. A dual-stage emission reduction system was developed with in-house preparation of Cu-Zeolite and Cobalt oxide (CoO). This helped in reducing the cost of production and also lower the light off temperature thereby converting even those pollutants which often escape untreated. Further, the efficiency of the catalytic converter was improved significantly by the proper packaging of the substrate. Modern techniques like the concept of fluidised bed and pre-heating of the catalyst increased the activity rate and surface area of the catalyst as well as the volumetric flow rate inside the catalytic convertor. Mounting and insulation of the convertor were also taken into consideration to make it commercially viable for light and heavy-duty vehicles. With the implementation of Bharat Stage-VI norms, the need for zeolites as cheap, sustainable catalysts for NO_x emission reduction is going to increase in leaps and bounds.

KEY WORDS: vehicular emissions, catalytic convertor, in house zeolite, fluidised bed, substrate

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I. INTRODUCTION

The fuel efficiency, longevity and torque provided by diesel engines have lured many a customer, so much so that they have been credited to being the front runners for the most impactful makeover in the automobile industry.[1] However, the diesel engines have some major trade-offs – from higher emissions of nitrous gases and carbon dioxide, both of which are major contributors to global warming to higher cost and incompatibility with other engines. Hence, they still have room for improvement.

Diesel emissions depend on the load of the engine and experiments have shown that the level of Carbon dioxide (CO₂) and water (H₂O) has shown an increase while there is a stark decrease in the level of Oxygen (O₂). Furthermore, most of these pollutants originate from various non-ideal processes during combustion, such as combustion of engine lubricating oil and combustion of non-hydrocarbon components of diesel fuel, such as sulfur compounds etc. Also emitted in diesel fumes nitrogen oxides (NO_x) which can penetrate deep into the lungs and cause cancer, chronic breathing problems and premature death in people with heart or lung disease. It also has indirect implications on the neighbouring eco-systems, inhibiting plant growth, ozone formation etc.

NO_x emission can be reduced by primary methods such as retard injection, fuel nozzle modification, change of compression ratio, water direct injection, water emulsification, exhaust gas recirculation (EGR) and secondary method such as selective catalytic reduction (SCR). SCR technology is designed to permit nitrogen oxide (NO_x) reduction reactions to take place in an oxidizing atmosphere. It is called "selective" because it reduces levels of NO_x using ammonia as a reductant within a catalyst system. The chemical reaction is known as "reduction" wherein the pollutants are converted into nitrogen, water and tiny amounts of CO₂. SCRs which were initially used in utility and commercial boiler, have now found large application in engines of automobiles, ships and other locomotives. The catalysts used in SCR are oxides of metals typically vanadium, titanium and

ceramics with highly porous structures such as zeolites. One or two layers of the catalyst may be applied and higher NO_x reduction can be achieved with the use of a higher amount of catalyst. The paper also provides a comparison of the efficiency of the prototype with the contemporary catalytic converters.

1.1 Metal Oxides as Catalysts: It is known that many oxides of the transition metals especially of groups 5,6,7,9,11 easily oxidise hydrocarbons like methane, butane, pentane etc. This is because the transition metals have vacant d-orbitals, small size (i.e. large nuclear force), large surface area. Thus, it tends to show variable oxidation states and form complexes. Experimental studies,[2] show that large scale screening of metallic oxides can be carried out through micro-catalytic chromatographic technique wherein the hydrocarbon is passed through the catalyst bed. Oxidation of the hydrocarbons occurs depending upon the temperature of the catalyst. The maximum operating temperature being 450°C. It is also observed that the degree of saturation, branching and whether the compound is open or cyclic, method of preparation plays an important role in the rate of oxidation. Considering all these factors, oxides of cobalt (CoO, Co₃O₄), manganese (MnO, Mn₂O₃), nickel (NiO), cerium (CeO₂), chromium (Cr₂O₃), titanium (TiO₂) are known to be more active.

1.2 Zeolite as Catalysts: Zeolites have for long been associated with shape-selective catalysis. They are microporous, crystalline and hydrated aluminosilicates with a three-dimensional network of silicates in which some of the silicon atoms are replaced by aluminium atoms to form Al-O-Si framework. [3] Due to their shape-selective catalytic reaction, the packaging of zeolites is given importance. Usually, the substrates with honey-comb structures are preferred. They are commonly used in the Selective Catalytic Reduction (SCR) system of heavy-duty diesel engines.

The advantages of using zeolite are that it has a wide range of operating temperature (up to 600°C). [2] Thus it can be used along with several engines during diesel particulate filter regeneration. The conventional Platinum Group Metal (PGM) catalysts have a maximum operating temperature of 250-300°C. Moreover, the selectivity and conversion efficiency of zeolites increases with temperature. Thus, the heating element is a crucial component in such SCRs.

1.2.1 Zeolite From Fly-Ash: Fly ash has a complex chemical composition formed mainly from Silica (SiO₂), Alumina (Al₂O₃), Iron oxides (Fe₂O₃), Calcium Oxide (CaO), Magnesium Oxide (MgO) and small amounts of other oxides. [5] It is obtained as a solid waste residue from the combustion of coal, biomass and oil. It can be recovered from electric power plants or roadside food stalls. In recent years several new approaches have been taken up, to utilise fly ashes either to reduce the cost of disposal or to minimise environmental impact. One such method is the conversion of fly ash to zeolites which have many applications such as ion-exchange, molecular sieves, adsorbents and catalysts.

Zeolites, [5] being crystalline by definition are composed of tetrahedral [SiO₄]⁻⁴ and [AlO₄]⁻³ connected to the neighbouring tetrahedral with the oxygen atom. This generates a net negative charge on the framework. Hence to ensure neutrality, each Al⁺³ cation in the framework requires a compensating cationic charge to ensure neutrality. The compensating charges usually originate from extra framework cations within the structure like Na⁺¹, Cu⁺², Fe⁺² etc. to keep the entire structure neutral.

By treating the fused fly-ash with NaOH solution, CuCl₂ solution or FeCl₃ solutions obtain Na/Cu/ Fe-Zeolites.

II. CATALYST SELECTION

For finalizing the catalysts to be used in the catalytic converter, certain parameters were set like effectiveness, selectiveness, re-generability of the catalyst etc. Factors like light-off temperature (the temperature at which catalyst becomes active), cost, duration are also taken into consideration.

PARAMETERS	Pt-Pd-Rh	Activated Carbon	Hopcalite	Zeolite
Effectiveness	(9) Highly effective for oxidation of HC and CO	(8) Highest surface area for a given volume however, suitable only for the oxidation of CO	(8) Can oxidize CO and reduce O ₃ at low temperatures	(9) Suitable for the oxidation of CO and HC and reduction of NO _x emissions by approximately 50%
Light off temperature	(7) 220-250°C	(5) 700°C onwards	(9) 70-120°C	(8) 150-180°C

Method and ease of preparation	(6) PGM catalysts are usually available in the form of ores beneath the earth	(6) Produced from carbonaceous source materials like wood, lignite, coal and petroleum by physical or chemical activation	(7) A mixture of Cu and Mn oxides prepared by $KMnO_4$ co-precipitation method followed by washing, drying & successive heating of the precipitate at various temperatures	(7) The mixture of fly-ash, $Na_2SiO_3 \cdot 5H_2O$ & ion carrying solution is mixed, heated, ground, stirred and filtered for a long period
Cost	(5) Very Expensive	(8) Relatively cheap	(7) Relatively cheap but more expensive than activated carbon	(7) Relatively cheap as chemicals required for its preparation are easily available
Selectivity	(8) Alumina supported Pt catalysts help to carry out the selective reduction of NO (at around 200°C)	(9) No adverse effect as it cannot reduce NO_x	(8) No adverse effect as it can oxidize NO_x in the presence of Cr	(9) No adverse effect as metal-enriched zeolites are known to effectively catalyze NO_x
Life	(9) Long term of about 4-5 years	(6) A short life, as carbon filters can withstand only for 3 days	(6) Loses activity at temperatures above 500°C and also in presence of moisture	(8) Long term 1.5-2 years experimentally
Regeneration/Reactivation	(8) Reactivation of the catalyst involves dissolution in HCL, an oxidant like (Cl_2 , H_2O_2) & a reducing agent like HCOOH	(8) Carbon is reprocessed in rotary counterflow furnace with a gradual increase in temperature from 20 to 830°C. Addition of 20% acid solution is an alternative	(7) Catalyst is mixed with a fluid a reactivating agent that is at or above a critical point of the fluid reactivating agent. Addition of gaseous O_2 can also reactivate the surface.	(8) Passing the brine solution to the cured sample, followed by ion-exchange method The trickling down effect improves the reactivation process
Weighted rank	52	50	52	56

Table 1: Matrix of Catalyst Rating

Note: The above ratings are given primarily according to the experimental set-up wherein the exhaust gas reaches a temperature of only 130°C around due to the limited horsepower of the engine.

2.1 METAL ION EXCHANGE OF ZEOLITES: Based on the above results, **Zeolites are best suited for our purpose.** To decide on the ion exchange, an experimental set up was prepared wherein a commercial catalytic converter and test convertor with the different catalysts are attached to the engine exhaust manifold. The engine was then run at the same load and speed conditions as it was when running without catalytic converter. The concentration of CO, HC, CO_2 , O_2 and NO_x were measured in each case. Certain readings have been obtained by extrapolating the graph based on findings.[4] The engine specifications are as follows:

Engine	M19 Vanguard Commercial engine
Model/ Type	19L232-0054 G1, 305 cc
Bore Diameter/ Stroke	3.12" / 2.44"
Maximum Power	10 HP (~7.5 KW)
Maximum Torque	19.6 Nm
Compression Ratio	8.1 to 1

Table 2: Engine specifications for experimental setup

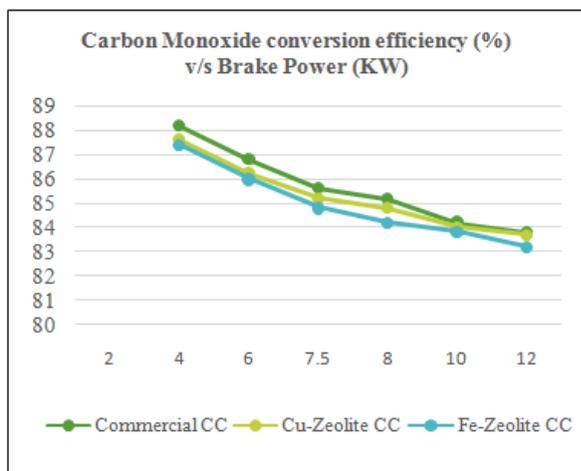


Figure 1: It is observed that at 7.5 KW, CO conversion rate is best in case of Cu-Zeolite without much difference in comparison to the commercially used CATCONS.

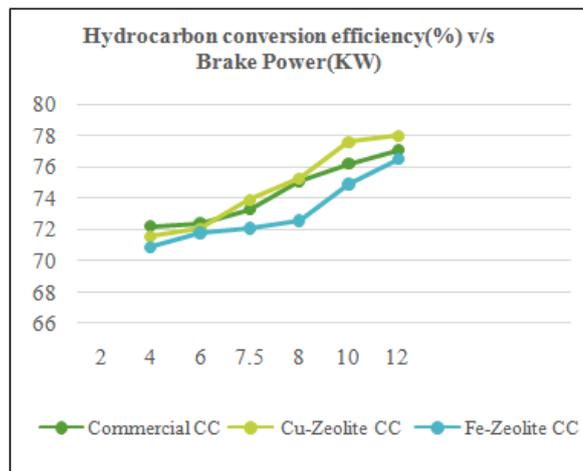


Fig. 2: At 7.5 KW, HC conversion rate using Cu-Zeolite is better compared to commercially used CATCONS.

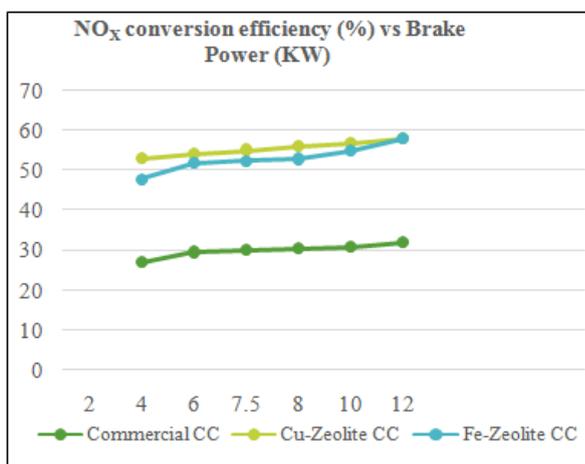


Figure 3: At 7.5 KW, NO_x conversion rate of Cu-Zeolite is better than Fe-Zeolite and much better than commercially used CATCONS.

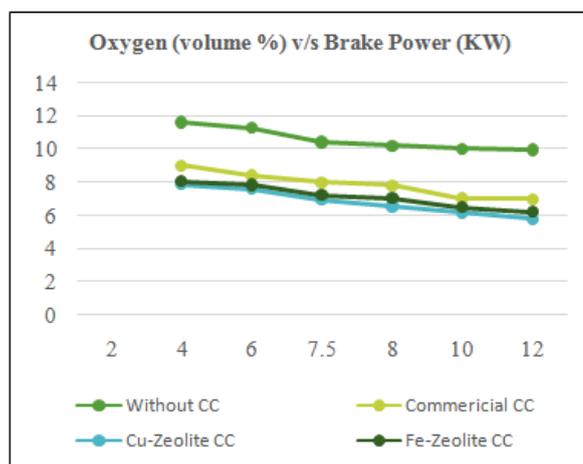


Figure 4: There is a negligible difference in the oxygen volume levels between Cu and Fe-Zeolite. However, there is a significant decrease in comparison to those without CC because O₂ is being used to oxidize CO.

Thus, **Copper Zeolite was finalised** as the catalyst, due to its relatively low light-off temperature, ease of manufacturing, long shelf life, high activity rate and selectivity.

III. CATALYSTS PREPARATION

3.1 Cu-ZEOLITE [4]

- The fly-ash sample is passed through a sieve to filter out large impurities.
- The filtered sample is then treated with concentrated HCl to remove finer impurities.
- Mixing treated fly-ash, an aqueous solution of cupric chloride CuCl₂ and sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) in the ratio of 1: 0.5: 1 by weight.
- A highly exothermic reaction occurs. The resultant mixture is immediately poured into an aluminium tray and heated in a furnace at 550°C for an hour. The grey mixture then begins to a greenish-brown in colour.
- The fused fly-ash is then allowed to cool for about 15 minutes before grinding it into finer powders.
- Distilled water is then added in the ratio of 100 ml per 10 grams of the powdered fused fly-ash.
- A magnetic stirrer is used to stir the resultant solution for 24 hours until a single-phase homogenous solution is obtained. A mechanical stirrer can also be used based on the quantity of the solution available.
- Once the solution is more or less homogenous, the curing process is carried out in the oven at 90°C for 6 hours.

- The cured sample (dark grey colour) is then passed through vacuum filtration to remove the excess copper chloride and other soluble impurities.
- The precipitated solids (of grey or dark green colour) are then dried at 80°C for 12 hours in the oven. The greyish-green lumps thus obtained yields Cu-Zeolite. It can be further ground to finer powders.

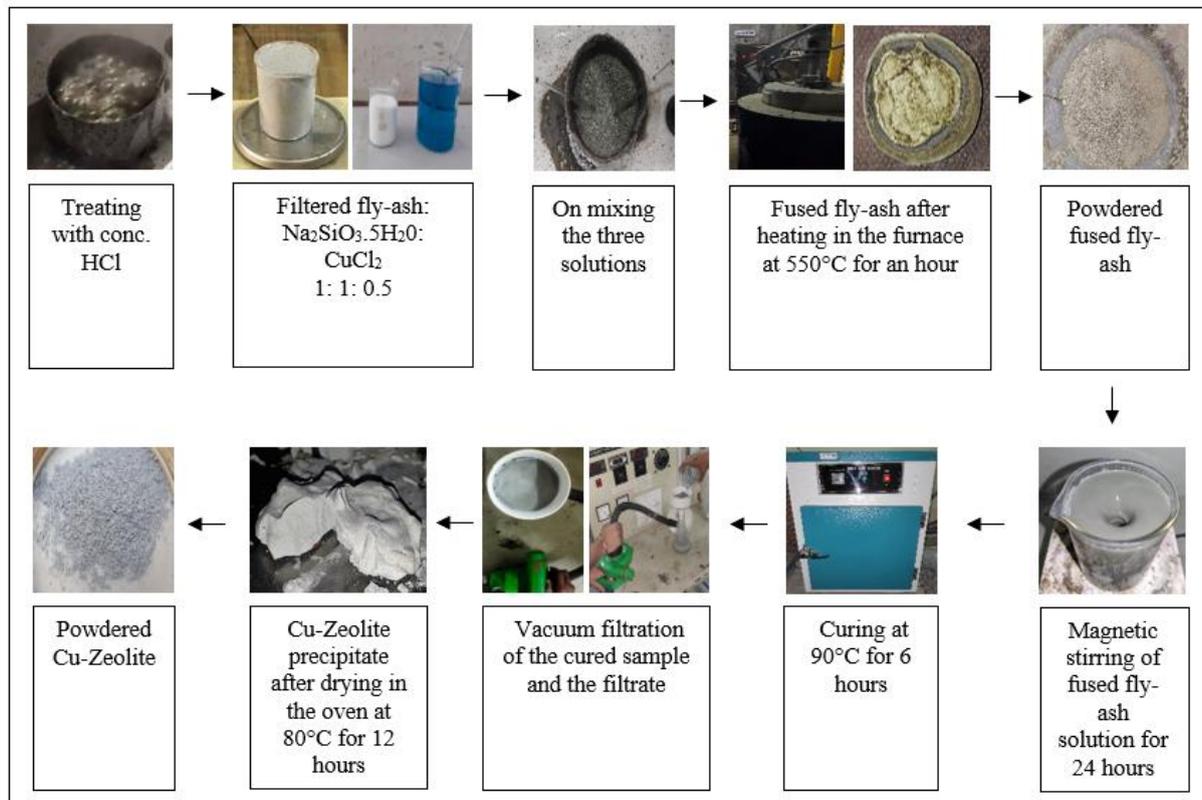


Figure 5: Preparation of Cu-Zeolite

Based on the test sample results, it was observed that the hydrocarbon reduction isn't significant enough in a wet environment. This led to the preparation of Cobalt (II) Oxide which is a metal oxide capable of oxidizing most of the hydrocarbons (n-hexane, n-pentane, benzene, dimethyl butane, pentyne etc.) at below 200°C. [2] The comparatively low light-off temperature of cobalt oxide makes it more suited to our set up.

3.2 COBALT OXIDE

- Cobalt nitrate crystals are treated with sodium bicarbonate solution to obtain cobalt carbonate.

$$\text{Co}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CoCO}_3 + 2\text{NaNO}_3$$
- The cobalt carbonate solution (blood red) is then heated in a furnace at 350°C for 1 hour.
- The black powdery substance thus obtained is Cobalt Oxide (CoO). It can be further ground to finer grains.

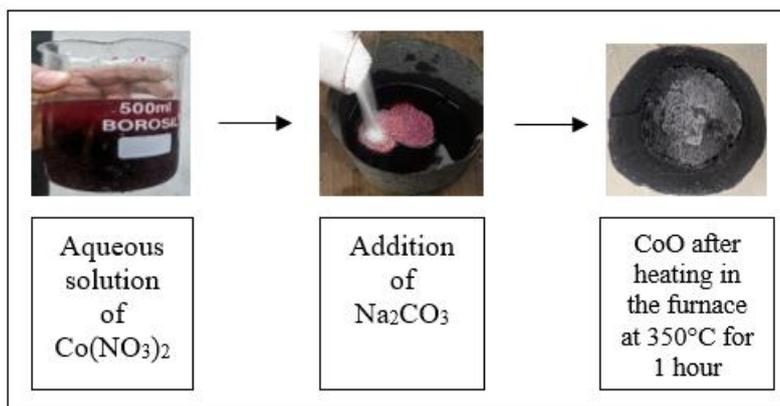


Figure 6: Preparation of Cu-Zeolite

IV. PACKAGING:

Two methods of packaging are selected based on economic factors and effectiveness:

4.1 Non-Woven Filter Bags: Non-woven fabric is a material made of the staple (short) and long (continuous long) fibres, bound together by chemical, mechanical, heat, or solvent treatment. The term is used in the textile manufacturing industry to describe fabrics such as felt, which are neither woven nor knitted. When densified or supported by a backrest, some non-woven materials lack adequate resistance.

Non-woven filter bags are widely used as insulation material and also commonly used as dust collectors on an industrial level. A non-woven glass fibre filter bag having a pore size of 5μ pore size and temperature resistance of about $400^\circ - 450^\circ \text{C}$ is employed for the same purpose to trap unburnt hydrocarbons during the combustion and process of catalysis. Keeping the pore size small allows the combustion gases to pass through the bag but traps other particulates and carbon.

4.2 Dip Coating Over Ceramic Substrate: Ceramic is a substance that is inorganic, non-metallic, often crystalline, nitride, or carbide. Those elements may be called ceramics, such as carbon or silicon. Ceramic materials are brittle, rigid, compressive, and poor in stress and shear. They can tolerate chemical oxidation occurring in other materials that are subject to acidic or caustic conditions. Ceramics can typically withstand very high temperatures between $1,000^\circ \text{C}$ and $1,600^\circ \text{C}$ ($1,800^\circ \text{F}$ to $3,000^\circ \text{F}$). Glass is not always treated like a ceramic due to its amorphous (non-crystalline) nature. Glassmaking, however, requires several steps in the ceramic process, and it has similar mechanical properties to ceramic materials.

A ceramic substrate with the catalyst adsorbed on its surface is used to provide more area of contact between the exhaust gases and the catalyst. The process used for the adsorption is dip coating:

Dip coating refers to submerging a layer into a tank that contains coating material, extracting the component from the tank and allowing it to drain. Then, the coated piece can be dried by force-drying or baking. It is a common way to create thin film-coated materials along with the process of spin-coating.

4.3 Stages of Dip Coating:

In general, the dip-coating process can be split into 3 stages:

- **Immersion:** The substrate is immersed in the coating material solution at a steady velocity ideally free from the judder.
- **Dwell time:** The substrate remains fully submerged and motionless to allow the coating material to adhere to the substrate
- **Withdrawal:** The substrate is removed, again at a constant pace to prevent any judder. The quicker the substratum is drained from the finer the coating material being added to the plate.

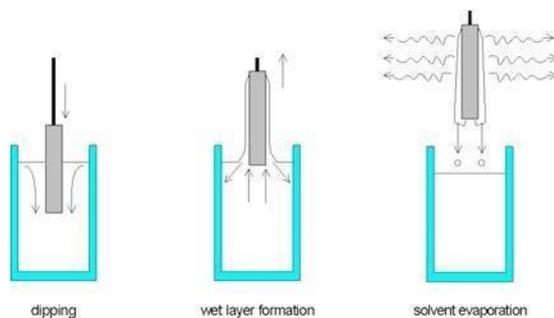


Figure 7: Stages of the dip-coating process



Figure 8: Non-Woven filter bags and substrate



Figure 9: Ceramic substrate coated with a catalyst

V. TESTING:

To decide the arrangement of the catalysts and the ideal environment for catalytic activity, a small-scale catalytic convertor was created.



Figure 10: Prototype of catalytic convertor used for testing



Figure 11: Dual bed arrangement of catalyst in the prototype

POLLUTANTS	WITHOUT CATALYTIC CONVERTOR	WITH CATALYTIC CONVERTOR	
		DRY COTTON WOOL	MOIST COTTON WOOL
CO (in %)	4.22	3.42	0.51
CO ₂ (in %)	4.77	4.49	2.53
HC (ppm)	27	12	54
O ₂ (in %)	10.49	13.70	16.48

Table 3: Emission results of the prototype

It is noted that in the moist environment, carbon monoxide conversion efficiency increases by 68.9% and oxygen levels by 26.5% compared to the dry environment. However, the oxidation of hydrocarbons falls drastically. Thus, cobalt oxide was also prepared to oxidise the hydrocarbons in a wet environment at low temperatures.

VI. EFFICIENCY OF THE CATALYTIC CONVERTER:

6.1 FLUIDISED BED: Due to the dual bed arrangement of the catalytic converter, the exhaust gases flow initially through the first chamber consisting of Cu-Zeolite powders followed by the second one consisting of CoO powders. However, the major problem is the difference in composition because of which these fine pellets or powders tend to split and choke the later chamber(s). [6] This reduces the exhaust gas flow thereby increasing the backpressure and decreasing the volumetric efficiency of the system. It can result in a loss of engine power. Based on this general observation, it was decided to incorporate the fluidized bed to prevent the plugging action. The fluidized bed [7] works on the principle that if the air is allowed to pass through the non-woven filter bags (also known as FBD bags) of powdered catalyst at a velocity greater than the settling rate of the particles, then they are blown up and remain suspended in the air stream. Due to this action, the catalyst powders provide a larger surface area for adsorption thereby increasing its efficiency. As the bed resembles a boiling liquid, it is often referred to as fluidised bed.

Using the principles of Bernoulli's theorem, the exhaust gases from the engine are passed through an inlet pipe of the converter with fine holes drilled in it, so that the velocity is sufficient enough to cause the turbulent motion of the powdered particles in the bed. The catalyst material in the first chamber is fluidised thereby activating the oxidation reaction of carbon monoxide and hydrocarbons.

6.2 HEATING ELEMENT: Every catalyst has activation or light-off temperature at which the oxidation and reduction reaction occurs. Using a temperature sensor, it was observed that the exhaust temperature reaches 120°C. Thus, the catalysts with relatively low light-off temperature (150-180°C) were selected. Nichrome wire was wrapped around the inlet pipe so as to increase the exhaust temperature up to that of the catalyst. The large value of resistance provides the required heating effect. A relation between the length of the wire (L), time for heating (T) and voltage rating of the battery (V) was established by equating Joule's law of heating with Ohm's law to decide the voltage rating of the electrical circuit.

$$V = [(14.238 * L^2)^{1/2}]/T$$

A buck and booster set up can also be used in the electrical circuit for either varying the voltage as per the requirements.

6.3 REGENERATION OF THE CATALYST: When the entire surface of the catalyst has been used up for adsorbing the pollutants, it is necessary for reactivating its surface. Bypassing brine solution [8] through the catalyst bed, the zeolite can be regenerated. Further, by ion exchange method, Cu-Zeolite can be obtained. During commercial use, it can be incorporated by including an inlet pipe in the upper half of the converter so that the brine solution can seep through the entire bed. This process is commonly used for replenishing the zeolite beds used in softening hard water.

VII. MOUNTING AND INSULATION:

7.1 CANNING AND MOUNTING are carried out using SS 304 wires for packaging, protection, vibrational damping and to hold the substrate and FBD bags in position. After packaging, the entire set up is placed inside an aluminium body of the catalytic converter. Brackets are welded along the sides for mounting purposes.

7.2 INSULATION of the inlet pipe using e-glass wool and silicon rubber sheets due to the inclusion of the heating element. Their easy availability, low cost and noise-damping properties make them ideal for insulating the converters/ mufflers. Critical thickness of insulation was calculated using the given formula:

$$R_c = \frac{\text{thermal conductivity (k)}}{\text{film co-efficient of outer surface (h}_o)}$$

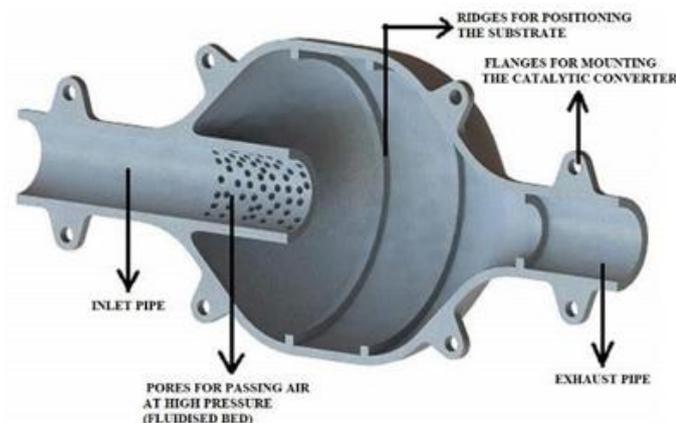


Figure 12: Final Design of Catalytic Converter



Fig.13: Inner packaging, mounting and assembly of Catalytic Converter

VIII. RESULT

Based on all the design considerations and the testing results, the emission test was conducted on the catalytic converter. The testing procedure comprised of running the engine at full throttle for 2 minutes before taking the reading.



Figure 14: Testing results of final Catalytic Converter model

POLLUTANTS	WITHOUT CATALYTIC CONVERTOR	WITH CATALYTIC CONVERTOR
CO (in %)	0.446	0.110
CO ₂ (in %)	1.10	0.29
HC (in ppm)	34	21
O ₂ (in %)	18.74	20.10

Table 4: Emission results of the catalytic convertor

It is observed that carbon monoxide and carbon dioxide emissions reduce by 75.34% and 73.63% respectively. By introducing cobalt oxide powders, the hydrocarbons get oxidized too thereby reducing its emissions by a significant 38.24%. Lastly, oxygen levels improved by 7.26%.

Note: The above results were taken using a limited amount of the catalyst. The results can be improved by increasing the amount of catalyst used.

IX. CONCLUSION

The exhaust gas flow inside the catalytic converter can be studied with the help of Computational Fluid Dynamics (CFD) techniques. This will help in reducing back pressure even further. Based on the findings, suitable changes can be incorporated to improve the mass flow rate and volumetric efficiency of the catalyst. Further, by examining the pore size with appropriate apparatuses the coating process and technique can be chosen accurately. The catalytic converter can be used commercially as well in heavy-duty vehicles due to its pollution control efficiency, small packaging, durability and cost-effectiveness.

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