STATE OF THE ART RESEARCH ON CATALYTIC CONVERTERS FOR AUTOMOBILES – A REVIEW

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Abstract
The purpose of this review paper is to present the recent developments that happened in the Catalytic Converters that are used to reduce the pollution levels from the exhaust of Diesel automobiles. Extensive research was carried out all over the world with particular reference to Industrial & Vehicular pollution. This paper aims at reviewing how the present day catalytic converter used in automobiles has been developed and improved during the recent past. The Euro norms are stressing on reduction of NOx and PM levels particularly from Euro 6 and 7, NOx and PM levels are drastically cut down. During last five years the research has been further conducted based on drastic reduction of NOx and PM. This paper also discussed about the development of NOx Traps to reduce the NO_x. During last five years sale of passenger diesel automobiles have picked up in comparison to petrol automobiles. Some published papers are described briefly which indicated the furtherance in the said research. Important conclusions drawn from a few papers are discussed in the end.
Keywords: Catalyst, Catalytic Converter, NO_X Trap, DPF, Monolith.

I Introduction

Euro norms are becoming more and more stringent through Euro I to VI. India is adopting these norms and named as “Bharat Stage” which is behind Euro norms by five years. That is present Bharat Stage V norms were announced by 2014 – 15 which is equivalent to Euro IV norms.

However the Euro norms are stressing on reduction of NO_x and PM levels particularly from Euro 6 and 7, NO_x and PM levels are drastically cut down. Table 1 [2] will give the values.

Table 1: European emission standards

Tier	**Date**	**CO g/km**	**THC g/km**	**NMHC g/km**	**NOx g/km**	**HC+NOx g/km**	**PM g/km**
Diesel							
Euro 1	July 1992	2.72	-	-	-	0.97	0.14
Euro 2	January 1996	1.0	-	-	-	0.7	0.08
Euro 3	January 2000	0.64	-	-	0.5	0.56	0.05
Euro 4	January 2005	0.50	-	-	0.25	0.30	0.025
Euro 5	September 2009	0.50	-	-	0.18	0.23	0.005
Euro 6	September 2014	0.50	-	-	0.08	0.17	0.005

This particular change has impacted the research on the diesel engine catalytic converters. If we compare the BS-IV and BS-V norms introduced [Table 2 [1]] it indicates that there is no change in CO (g/km) whereas $HC+NO_x$ (g/km) is reduced by 22%; NO_x is reduced by 28% and PM is reduced by 93%. Diesel engines emit more NO_x and PM.

Table 2: Comparison of BS-IV and BS-V emission norms for N1 class 3 vehicle

Emission Norms	**CO g/km**	**$HC+NO_x$ g/km**	**NO_x g/km**	**PM g/km**
Bharat Stage IV	0.74	0.46	0.39	0.06
Bharat Stage V	0.74	0.36	0.28	0.0045
% Less	NO change	22	28	93

The authors had reviewed Development of Catalytic Converters from 1975 to 2013 and published a review paper [1] in 2013. They have studied about 150 Technical articles and categorized the research into five groups mainly based on (i) Numerical & Mathematical / Computer Models (ii) CFD Analysis of flow (iii) Design of Catalytic Converters (iv) Laboratory experimentations (v) Development of Low cost Catalyst materials.

However during last five years the research has been further conducted based on drastic reduction of NO_x and PM. During last five years sale of passenger diesel automobiles have picked up in comparison to petrol automobiles. The reason for this is that earlier reputation of diesel engines as smoky, noisy and sluggish power has been changed. Today they are smooth, less noisy and with marked fuel economy.

India is facing urbanization problem. Assuming 32 % increase in urban population per decade, it is expected to increase from 377 million in 2011 to 500 million in 2021 whereas during 2000 s only 91 million were in urban areas.

Sanjay Kumar Singh [17] discussed the urban transport and its challenges in India. He felt there is urgent necessity to tighten Pollution Control laws, enhancing modes of public transport, encourage car sharing and in general government should revise its public transport policy.

R. Gopalaswami [18] has discussed the "Delhi model" in detail. He has given an account of pollution levels in Delhi. According to the available statistics pollution levels in Delhi from March to September is generally acceptable whereas in October it is unhealthy; November to February reaches hazardous levels. The government of Delhi has constituted a panel to study and give report. They have suggested various measures both technical and management wise. Significant findings are to prioritize evaluation of pollution control standards for different vehicles like passenger diesel cars & Heavy vehicles in top priority and then petrol cars and heavy vehicles. They suggested catalytic converter retrofits to old passenger cars / urban transport vehicles. They developed an "electronic Catalytic Converter". It consists of Nano structure coaxial wave guide within microwave dielectric cavity resonator. It draws power from the car's 12V battery. The panel finally concluded that India should go for zero pollution cars like electric cars.

II. NOx Traps

CO_2 emissions of diesel engines are less compared to petrol engines. But threat is because of NO_x & PM levels. Hence J. Hussain, Palaniraja et al [11] discussed in detail regarding the necessity of NO_x traps and NO_x – PM trade off. The formation of NO_x and PM depends closely on combustion process which depends on engine design variables such as combustion chamber design, fuel injector design, pressure and tuning of injection, Swirl ratio, valve timing, compression ratio etc. Soot particles which heavily contribute to the total mass of particulate matter are formed in the engine during rich regions of combustion. Soot burn up is favored by high temperatures of the engine combustion. But high temperatures favor formation of more and more NO_x. Hence there is an optimization of NO_x - PM is required which is a trade off. Recent years have seen exclusive research on $NO_{x\ traps}$ and also evolution of 4 – way Catalytic Converters which involves in Diesel Particulate Filters.

P. V. Walke et al [3] discussed about evolving a Cat – trap consisting of pellet type catalytic converter and foam type particulate trap for reduction of NO_x and PM levels in diesel exhaust. The CAT was developed using CeO_2, ZrO_2 and Ag NO_3 catalysts on pellet substrate. The foam type particulate trap arrests particulate matter.

Seung Gwan Lee et al [4] have suggested that instead of removing NO_x after its formation, it is better that it is suppressed using NH_3 selective catalytic reduction using vanadium on Zeolitic micro porous TiO_2. They claimed to have demonstrated that vanadium Catalyst supported on Zeolitic micro porous TiO_2 obtained from hydrothermal reaction of bulk TiO_2 at 400 K in the presence of LiOH suppresses significantly the NO_2 emission compared to conventional catalyst.

The addition of LiOH, NaOH and KOH to the hydrothermal medium resulted in the formation of Zeolitic micro porous TiO_2, nano tube and nano rod respectively which seems to be cost effective process. The obtained micro porous nano crystalline TiO_2 showed large surface area of 250 m^2/g. Thus they indicated the use of Nano technology in the coating of catalysts on substrate.

Syed Aalam et al [5] have suggested the usage of nano aluminum oxide catalyst for reduction of CO and HC. They have studied NO_x emission levels for different nano particle concentrations.

Diesel exhaust without Catalytic Converter showed 1110 ppm NO_x whereas the level decreased to 780 ppm for 1 g Al_2O_3 coatings and 680 ppm for 0.5 g Al_2O_3 nano particle coatings.

Jhonson Matthey Institute has published an article of “Urea – SCR technology for de NO_x after treatment of diesel exhausts” [6]. Two ways or three way Catalytic Converters efficiently remove CO, HC and NO_x at high exhaust temperatures where as this efficiency of removal falls drastically at low exhaust temperatures. NO_x – PM trade off was broken by fitment of Diesel Particulate Filter. The second NO_x control technology is using Selective Catalytic Reaction by using NH_3 SCR which breaks NO_x into Nitrogen and water.

Jitin Malhotra et al [7] from Amity University have used a catalytic converter formed by discarded components. These components still contain noble metals like Platinum, Palladium, and Rhodium. This hypothetical device is attached to original Catalytic Converter which further reduces pollution levels. NO_x was claimed to have reduced from 250 ppm to 179 ppm using this eco-friendly system.

Kaustubh. P. Ghodke [2] discussed in his paper on how to combat upcoming Indian Emission legislation in view of implementation of Euro 6 norms. He suggested that combination of EGR, SCR and DPF will help counter the issue. He said that DPF is successfully employed to reduce soot content of the emission. EGR though has many drawbacks, when coupled with DPF can be effectively used to reduce NO_x production.

Liuhanzi Yang et al [8] of International Council on Clean Transportation (ICCT) in their white paper on NO_x control technologies for Euro 6 diesel passenger cars have studied 32 Euro 6 diesel passenger cars with 11 SCR, 16 LNT (Lean NO_x Traps) and 5 EGR equipped. It has been found that they are not Euro 6 compliant in spite of using pollution reduction devices; exhibiting over 2 or 3 times the stipulated limits of NO_x. The transition from Euro 5 to Euro 6 has driven technological changes in the control of NO_x. In Euro 6 norms NO_x limit is 80 mg/km compared to Euro 5 NO_x limit of 180 mg/km. However ICCT has studied extensively many brands of cars fitted with pollution reduction devices like SCR, LNT or EGR. They concluded that though laboratory results of reduction were good; the real driving conditions were not simulated. The biggest challenge to diesel passenger car manufacturers worldwide will not arise from laboratory test under certification cycle (NEDC or WLTC) but impending real driving emission test. NO_x emissions are not properly controlled under the NEDC based testing. It may be necessary to allow more than 80 mg/km limit of NO_x value i.e. raise the emission levels than Euro 6 to conform real road performance assessment.

III. CO_2 Emissions: Projected changes by 2025

In July 2012 the European Commission proposed a mandatory CO_2 emission target of 95 gm/km to be achieved by 2020 [9]. In the recent BEUC report it has been indicated that there is clear lack of post 2020 vision with a target of 70 gm/km emission of CO_2 as CO_2 is a greenhouse gas which increases global warming. Present environmental havocs are due to global warming, which everybody is aware. EU in collaboration with ICCT suggests that relative to 2015 baseline of 130 gm/km of CO_2 to be lowered to 70 gm/km would give fuel savings. However car manufacturers with internal combustion engines are likely to increase car prices. Studies suggest that CO_2 levels can be lowered to 75 gm/km without the need to sell ultra low carbon vehicles. Despite higher initial price of ultra low carbon vehicles they will be preferred if they are CO_2 compliant. Hybridization of cars may be solution that is cars running with more than one type of energy.

IV. Non Noble Material based Catalytic Converters:

As noble metals like Platinum, Rhodium and Palladium are expensive and proved to be hazardous if released into the atmosphere; researchers have searched for other cheaper catalysts.

Chirag Amin & Pravin Rathod [10] have studied and found that there are several types of problems associated with noble metal based Catalytic Converter. The failure of Catalytic Converter with noble metal catalysts may be due to (i) converter meltdown (ii) Carbon deposit (iii) Catalyst fracture (iv) Poisoning. The noble metals Pt, Ph and Pd are supposed to promote Oxidation process. The authors found substituting with Iron – exchange Zeolite (formed from AlO_4 & SiO_4) also does the job. The TiO_2 and Cobalt Oxide also are alternative materials. Copper or Chromium or Nickel were coated on the top of piston and cylinder head surface using standard electroplating process. They found copper very effective among the three. At a high compression ratio of 9:1 and lean mixture (A/F = 15.7) copper catalyst increases Break thermal efficiency from 17.7 % to 22.8 %; decreases HC emission from 3200 to 2300 ppm and lowers CO emission from 3.6 to 0.25 % by volume (Normal CR = 7.4; A/F = 13.2) compared to normal engine of 2kw, 3000 rpm.

Narendra Singh Makwana et al [19] have tested a catalytic converter with non-noble metal (Nickel) catalyst.

Anurag Dubey [12] in his review paper has stated that methods exist for control of CO, HC, NO_x, CO_2, PM for stoichometric and lean burn gasoline engines and diesel engines. Continuous improvements in substrate and coating technologies as a part of integrated system comprising of electronic control and fuel quality allow more stringent norms.

Promit Choudhury & Srisha Deo [13] has used copper as catalyst in the form of plates. A number of perforated copper plates of I mm thickness is assembled on a bolt and housed in a canister through which the exhaust gas is passed. They found it is quite effective.

Parthasaradhi Bera & M.S. Hegde [14] has studied dispersing metal ions over CeO2 and TiO_2 by solution combustion technique resulting in $Ce_{1-x} M_x O_{2-\delta}$ and $Ti_{1-x} M_x O_{2-\delta}$. This special preparation technique for dispersing ionic metals could be extended to other reducible transition metal oxides supports such as SnO_2, V_2O_5, WO_3 and MoO_3. Though this paper was written in 2010 it gives a lot of insight in development of many new catalysts.

Ugo Bardi & Stefano Caporali [15] has studied availability of Pt, Rh, and Pd called noble metals. They have written an article on alarming position of depletion of these rare earth metals. According to them electric vehicles may be only solution to substitute cars with these rare earth metals.

Sylvain Kiev et al [16] discussed about the application of structured perovskite based catalysts in three way catalytic converters. As such perovskite type oxides exhibit good oxidation activity which can be improved by including a fraction of noble metals like Pd, Pt or Rh. The main advantage of these perovskite type catalysts is the possibility to accommodate simultaneous different metal cat ions at A^- and B^- sites which allows tuning catalytic properties.

V. Concluding Remarks

The authors have reviewed technical papers from 1975 to 2013 on development of catalytic converters for diesel automobiles. However they found that recent years 2014 to 2016 have seen researchers concentrating on NO_x reduction and developing traps. From Euro 5 onwards NO_x and PM levels are drastically cut by 28 % and 93 % respectively.

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