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Development of Automobile Catalytic Converter during Last Four Decades --A Review

K. Srinivasa Chalapathi[1], Dr. Ch.Bhavanarayana Murthy[2], Dr. B. Sudheer Prem Kumar3
[1]Assoc. Prof, [2]Professor, [3]Professor & Head, Mechanical Engineering Department
Anurag group of Institutions (formerly CVSR College of Engineering), JNTUH, Hyderabad

Abstract: Awareness regarding atmospheric pollution effects on the environment and the health of humans, plants, animals and other living organisms and flora and fauna World over has inspired many researchers. Extensive research was carried out all over the world with particular reference to Industrial & Vehicular pollution. Automotive catalysts designed to detoxify the exhaust were implemented in USA in the vehicles of the model year 1975. By 2014 about 40 years have been spent all over the world in the research of automotive catalytic converters. The published papers can be categorized into five groups mainly based on (i) Numerical models (ii) Computational Fluid Dynamic models (iii) Design of Catalytic converters per se (iv) Laboratory experimentation (v) Development of catalytic materials. This paper aims at reviewing how the present day catalytic converter used in automobiles has evolved in the last four decades. About 150 technical papers published in various journals were studied. Some 52 papers are described briefly which indicated the furtherance in the said research. Important conclusions drawn from a few papers are discussed in the end. An exhaustive list of 151 references on the subject is appended.

I. INTRODUCTION

Stringent pollution control over exhaust emissions from automobiles made Automobile industry to develop various means by which the emissions are rid of pollutants like CO, HC and NOx. Diesel emissions contain particulate matter additionally. The published literature can be divided under two branches of engineering namely Mechanical Engineering and Chemical Engineering. Again they can be further grouped into five categories:

1).Numerical and mathematical simulation for optimization of flow and temperature distributions: Governing equations are formed in Fluid Mechanics and Heat Transfer and they are solved mathematically and or numerically with certain assumptions in boundary conditions.

2) Using flow models of geometry and the Computational Fluid dynamics software the flow optimization is carried out in computers. With the extra ordinarily fast computer development large and complex problems can be simulated and solved quickly. Presently in the last few years almost every technical article is having this component.

3) Laboratory experimental test rigs are developed which are more realistic and extensive experimental data is collated to arrive at optimization of parameters.

4) The design of two way or three way catalytic converter per se is essential ingredient and this along with any one or more of the above are finding their place in modern journals.

5)Development of catalysts to replace expensive noble metals like Pt, Rh.

Some papers in each category are briefly described below. However review of the Catalytic converters is limited to first four grops listed, and Chemical Engineering aspects are not

Table 1. European Union emission norms for diesel powered vehicles in gm/km [94](Total Hydrocarbons & NMHC are not mentioned in this table as they are not stipulated in the norms)

Tier	Time Frame	CO	NOx	HC + NOx	PM
Euro 1	July 1992	2.72		0.97	0.1
Euro 2	Jan 1996	1.0		0.7	0.08
Euro 3	Jan 2000	0.64	0.50	0.56	0.05
Euro 4	Jan 2005	0.50	0.25	0.30	0.025
Euro 5	Sept 2009	0.50	0.18	0.23	0.005
Euro 6	Sept 2014	0.50	0.08	0.17	0.005

From the table 1 above ,It may be seen that the norms are kept constant for CO since Jan 2005 at 0.5, where as the values for NOx and HC+NOx have been steadily reduced after Jan 2005. This has triggered research for NOx reduction (termed NOx abatement [91]).The corresponding Indian pollution limits (termed Bharat stage) are lagging behind in implementation years. For example Euro 4 termed as Bharat Stage IV are implemented in Apr 2010. Still these norms are in place. The next stage cannot be implemented till some legislations are brought into force. Due to Indian economy background, retiring vehicles older than 15 years is not yet implemented. Also Catalytic converters are not yet made mandatory equipment in the cars used in India.

At the turn of the new century, fuel additives were developed which are inhibitors of pollutants. Also unleaded petrol was introduced.

Jeffrey A.cook et al [84] (2005) gave a review paper where they high lighted control oriented models of Gasolene and diesel engines and their after treatment. Initially researchers concentrated on improving the fuel quality and electronic engine control. Once these doors got closed (optimization has reached a dead end) they accepted pollutants as an acceptable hazard with the development of automobiles, they concentrated on after treatment methods and development of Catalytic converters.

II. PAPERS BASED ON NUMERICAL MODELS

P Kandylas et al[8] (1999) in their technical paper discussed about mathematical modeling of precious metals catalytic converters for diesel No*x* reduction. Precious metal catalysts for NO*x* reduction in lean diesel engine exhaust conditions are characterized by a narrow temperature range of efficient operation and require high availability of reducing species in significant concentration. Consequently, there exists a large optimization potential in the design and control of lean-NO*x* catalytic conversion systems. A mathematical model of the transport and chemical phenomena in platinum-based lean-NO*x* catalysts was formulated, based on the experience with analogous models for gasoline three-way catalysts. A simplified four-reaction scheme is employed, considering the oxidation of CO, H_2 and hydrocarbons (HCs), as well as the reaction between NO*x* and HCs. Results are compared with previously published laboratory and engine data in order to assess the capacity of this approach in representing real-world behavior of Pt-based lean-NO*x* catalysts. Initial results illustrate the power and flexibility of the model, which is able to predict the No*x* conversion characteristics in model gas tests as well as in full-scale engine tests with reasonable accuracy.

S J Jeong et al [7] (2001) in their technical paper discussed about a three-dimensional numerical study of the effect of pulsating flow on conversion efficiency inside a catalytic converter. A study is made of the flow and conversion characteristics of the pulsating flow of an automotive catalytic converter. To investigate the unsteady flow effects of a dual monolithic catalytic converter of double-flow type, a numerical methodology coupled with wave action simulation based on gas dynamic theory is developed. The flow inside the converter is treated as three dimensional, unsteady compressible and isothermal. Conversion rates through the monolithic channels are calculated under the assumption of being diffusion controlled. The present study indicates that this integrated numerical model successfully represents the conditions of severe interaction among the exhaust flows, the extreme filling and the empty processes that affect the flow distribution and conversion efficiency. The simulation results also show that the level of flow maldistribution in the monolith heavily depends on the curvature and angles of separation streamline of the mixing pipe that homogenizes the exhaust gas from the individual cylinders. It is also found that, on a double-flow converter system, there are severe interactions of each pulsating exhaust gas flow at the junctions, and consequently junction geometry greatly influences the degree of flow distribution.

N Mladenov et al[23] (2010) in their paper presented a comprehensive numerical study for better understanding of mass transfer in channel flows with catalytically active walls at moderate temperatures. Altogether 18 models were compared which represent mass transfer in single channels of a honeycomb type automobile catalytic converter operated under direct oxidation conditions. Results of numerical simulation data is compared with experimental data.

V.K.Parvin et al [68] (2012) from P.D.A. college of engineering in Gulbarga have discussed numerical models of various catalytic converters to reduce particulate matter and back pressure in diesel engines. They used knitted steel wire mesh as filter material as the noble metals are expensive, for effective reduction of HC,CO and NOx. Ceramic monolith, ceramic foam,steel wire meshes are some of the types of materials from which they selected steel wire mesh. They studied experimentally and compared using CFD simulation.

T Shameem et al [15] described Mathematical and numerical model for simulating performance of automotive TWC converters which are employed to reduce engine exhaust emissions.

G.N.Pontikakis et al (2004) [74] said that since the introduction of catalytic converters in production vehicles, many numerical models appeared in the literature leading to confusion because of a complicated landscapes of approaches. They attempted to inverse this situation first by sketching an overview of modeling approaches, subsequently discussed their choice of compiling a methodology that provides the required high accuracy levels for the current state of the art exhaust after treatment systems design. They combined their work with development of a modeling code which gives better integration with modeling tools.

III. PAPERS BASED ON CFD ANALYSIS:

In 2003**, Joachim Braun** et al [22] at the University of Heidelberg carried out research in catalytic converter. They studied the temperature distribution immediately after startup of an engine and after about 41 seconds.. It is observed that uniform temperature distribution was obtained. Only after a specified time that is around 41 seconds after startup. They observed that this much time lag is required to make the catalyst effective for clearing the pollutions. In the same year **Julia Wildman** et al [36] carried out research at university of Heidelberg where they used a code developed by them named DETCHEM. They studied three dimensional transient velocity distributions in front of inlet face on the thermal behavior of monolith. In fact both these were carried out at University of Heidelberg at the instance of J.Eberspecher Gmbh & Co. Both the projects were done parallelly and they studied the temperature Distribution of the monolith.

In the year 2003, **Ming Chen** [19] of Ontario, Canada carried out research on design Optimization of Catalytic converters. He modeled substrate as porous media and used a CFD Package to simulate isothermal flow. As a specific example, the effects of perforated plate with an appropriate open area ratio are effective in removing non uniformities of velocity with a small penalty of pressure drop. Figure 6.5 the monolith model and the velocity distribution which become uniform with usage of a perforated plate.

PLS Muthaiah et al [13] (2010) in their paper indicated that the main draw back in Diesel engines is that it produces large amounts of CO, NOx, and unburnt HC, smoke etc. The simplest and best way to reduce NOx and particulate matter is to go for after treatment of exhaust gases. The catalyst and filter materials placed inside exhaust manifold increase back pressure on the diesel engine which causes more fuel consumption due to reduction in efficiency. This paper attempts to find out optimum solution to get maximum filtration efficiency with limited back pressure.

Rolf Bruck et al [88](2006) felt that solution for Euro 5 norm and beyond would be to use turbulent flow catalyst. Emitec has introduced two new channel structures that create turbulent like flow condition dramatically increasing the catalytical efficiency: Longitudinal structure (LS design) and Perforated foils (PF design). The development of these models were carried out using CFD simulation with turbulent flow model and experimental programmes.

IV. PAPERS BASED ON EXPERIMENTAL INVESTIGATIONS:

S Rajadurai [14] et al in their paper analysed and said that the primary requirements of exhaust after treatment systems are low back pressure , low system weight , better emission performance and lower cost. Combinations of these properties provide better engine performance and lesser fuel consumption. Knitted wiremesh substrate with different geometry and channels are used as carriers of diesel oxidation catalyst, three way catalyst and Selective Catalytic Reduction (SCR) NOx catalyst. This paper deals with optimization of substrate design using different materials and mesh designs.

A K M Mohinuddin et al [20] presented results of an experimental study of the performance and conversion efficiencies of ceramic monolith TWCC employed in automotive exhaust lines for the reduction of gasoline emissions. Two ceramic converters of different cell density, substrate length , hydraulic channel diameter and wall thickness were studied to investigate the effect of varying key parameters on conversion efficiencies. Based on the emission test results the conversion efficiencies of both converters were calculated and evaluated. After completing the test the converters were cut to extract substrate or honeycomb and being analysed for microstructure using scanning electron microscope. Simulation programmes using commercial CFD packages were used to verify experimental results.

S.Karthikeyan et al [57] (2011) had indicated that future emission legislation for light commercial vehicles can be met through appropriate design of after treatment devices like diesel oxidation catalyst (DOC) for HC, CO and partial PM reduction and cooled—Exhaust gas recirculation systems (C-EGR) for NOx reduction for low cost solution. Computational analysis offer new possibilities for optimal design of DOC and C-EGR systems for low cost truck applications. Further the reduction in NOx emissions within the new legislation , forces the increase of EGR rates, for which EGR cooler with higher thermal dissipation capacity is required. Corrugated tube design for the cooler pipe increases the thermal efficiency of EGR cooler without affecting engine performance. They indicated that their paper provided the overview on exhaust flow uniformity index, pressure drop across the DOC and hot spot prediction in cooler tubes, pressure distributions inside the EGR cooler using CFD. They said that with optimized DOC/C-EGR design the emission results were investigated on chassis dynamometer BS-IV diesel emission norms.

V. PAPERS ON CATALYTIC CONVERTER DESIGN

A Ghasemi et al [21] have discussed regarding monolithic catalytic converters, which in their opinion is still the main control devise for modern vehicles in order to reach the ever increasing legislature demands for low emission standards. The catalytic converters require a large expansion from the exhaust pipe to the front face of the monolith. Unfortunately packaging constraints often do not permit the use of long diffusers . Hence flow separation within the diffuser leads to a non uniform flow distribution across the monolith. A uniform flow distribution at the inlet monolith face is favorable for the conversion efficiency as well as the durability of catalytic converter. Therefore the main problem is to optimize the flow distribution at the catalytic converter. It should be noted that due to flow mal distribution in an enlarged inlet of catalytic converter , some parts of the monolith would be ineffective. In this research a new design for inlet diffuser of catalytic converter has been proposed and fabricated. The new inlet diffuser is composed of some tube to tube cones that distribute the flow uniformly at the entrance face of the monolith. Temperature, pressure drop and concentration of pollutants, before and after the catalyst, have been measured. The results show that the new design for inlet diffuser tends to a less uniform temperature field at the entrance of the monolith but the flow distribution becomes more uniform. Therefore an increased conversion efficiency of the catalyst will be obtained .

Ammann, M. et al[1] in their technical paper discussed about the three-way catalytic converter (TWC) is an effective device for reducing exhaust emissions in automobiles. For control purposes, the TWC can be regarded as an oxygen storage device. In order to reduce exhaust emissions efficiently, the oxygen storage should neither be completely full nor totally empty. Based on a simple model for oxygen storage in the TWC, an adaptive scheme for the control of the oxygen level is presented. The parameters involved in the model for oxygen storage are identified online by measuring the air-to-fuel ratios upstream and downstream of the TWC and using a recursive Gauss-Newton estimation method.

McKinley et al[2] in their technical paper discussed about the Selective catalytic reduction (SCR) is coming into worldwide use for diesel engine emissions reduction of on- and off-highway vehicles. These applications are characterized by broad operating range as well as rapid and unpredictable changes in operating condition. Significant nonlinearity, input, and output constraints, and stringent performance requirements have led to the proposal of many different advanced control strategies. This article introduces a model predictive feedback controller based on a nonlinear, reduced order model. Computational effort is significantly reduced through successive linearization, analytical solutions, and a varying terminal cost function. A gradient-based parameter adaptation law is employed to achieve consistent performance. The controller is demonstrated in simulation for an on-highway heavy-duty diesel engine over two widely different emissions test cycles and for 24 different plants. Comparisons with baseline control designs reveal the attractive features as well as the limitations of this approach.

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K Hirata et al [3] in their technical paper discussed about pressure-loss reduction and velocity-profile improvement in a catalytic converter by a flow deflector. In automobile exhaust systems, catalytic converters have become essential in reducing environmental pollution. However, the main components of catalytic converters produce large pressure drops in exhaust systems, which decrease engine power and increase fuel consumption. In addition to the need to reduce pressure loss, the flow passing through the catalytic substrate strata should be as uniform as possible, which provides a uniform thermal distribution and high catalytic conversion efficiency. The goal of the present study is simultaneously to reduce the pressure loss and to improve the flow distribution under spatial constraints. The authors herein propose new types of device and investigate their performances experimentally. Specifically, the possibilities of two types of flow deflector with a shell structure, which are placed inside the diffuser part of the catalytic converter in order to reduce flow separation, were investigated. In addition, using the particle image velocimetry technique and Pitot tube velocimetry, flow features such as the velocity profiles were elucidated. The tested converter has a standard cylindrical ceramic monolith substrate with channels of square cross-section. As a result, the two flow deflectors can reduce the pressure loss by 17 per cent and 22 per cent, compared with a no-deflector converter and can effectively improve the velocity profile.

S F Benjamin et al [4] in their technical paper discussed about phosphorus deposition on a three-way catalyst under accelerated ageing conditions. Degradation of catalyst performance with time is described as ageing. There are two significant ageing mechanisms: poisoning and sintering. Experimental data on ageing have been obtained on an engine test bed using a specially designed catalyst core holder; the catalyst samples were subjected to different accelerated ageing regimes and durations. The ageing regimes were as follows: low temperature dosed (mainly poisoning); high temperature not dosed (mainly sintering); high temperature dosed (both sintering and poisoning). The experiments provided a series of samples from which the spatial and time dependences of the poisoning have been found. Portions of the samples were subjected to X-ray fluorescence analysis after ageing. A combined model of poisoning and sintering was developed and incorporated into a computational fluid dynamics model. This combined model can predict the level of deactivation as a function of length along the catalyst and as a function of time. Agreement between measured poison accumulation and predictions was achieved by tuning the sintering parameter.

A N Karkanis et al [9] in their technical paper discussed about emission reduction during cold start via catalyst surface control. The present paper is a preliminary investigation of a new approach to the reduction of pollutant emissions during a cold start. During a cold start the volume of the exhaust gases is considerably smaller than those under full load. Therefore, only a small portion of the catalyst active surface is required to process the gases. As the exhaust gases flow from the upstream surface to the downstream surface, they meet with the cold surface of the catalyst, which they should warm up first, before light-off. The larger that surface, the more time will be needed for its warm-up, which will increase the time required for a light-off. The experimental results presented here indicate that there can be a significant reduction of the pollutant emissions during the cold start of an engine, if a system can be devised that could adjust the catalyst active surface during start-up proportionally to the exhaust gas volume. There are strong indications that a quicker warm-up of the catalyst and a faster initiation of catalysis can be achieved by focusing the gas flow towards the centre core of the monolith. In this way the remaining ceramic body of the catalytic converter operates as a heat insulator. This idea may be utilized in the design of catalyst system with variable active surface.

A M Stamatelos et al [10] in their technical paper discussed about computer aided engineering in diesel exhaust after treatment systems design. Computer aided engineering (CAE) methodologies are increasingly being applied to assist the design of spark-ignition (SI) engine exhaust aftertreatment systems in view of the stage III and IV emissions standards. Following this trend, the design of diesel exhaust aftertreatment systems is receiving more attention owing to the capabilities of recently developed mathematical models. The design of diesel exhaust systems must cope with three major aftertreatment categories: diesel oxidation catalysts, diesel particulate filters and de-NO_x catalytic converters. An integrated CAE methodology that could assist the design of all these classes of systems is described in this paper. It employs the following computational tools: a computer code for modeling transient exhaust system heat transfer, a computer code for modeling the transient operation of a diesel oxidation or a de-NO_x catalytic converter, a database containing chemical kinetics data for a variety of oxidation and de-NO_x catalyst formulations and a computer code for modeling the loading and regeneration behavior of a wall-flow filter, assisted by catalytic fuel additives. Application of the CAE methodology, which helps the exhaust aftertreatment system design engineer to meet the future emissions standards, is highlighted by referring to a number of representative case studies.

M I Soumelidis et al [11] in their technical paper discussed about a chemically informed, control-oriented model of a three-way catalytic converter. Chemical activity inside a three-way catalytic converter (TWC) is highly complex and usually is not taken into account when developing TWC control-oriented models. Such models still remain to a large extent empirical and do not perform satisfactorily under a wider range of operating conditions. This work demonstrates how a very simple model, based on the basic chemical processes that take place inside the catalytic converter, can successfully capture a large part of the strongly non-linear TWC dynamic behavior. The proposed model is based on the reactions of ceria oxidation and carbon monoxide oxidation, which appear to dominate the fast dynamics of oxygen storage and release respectively. In addition, the water-gas shift reaction is incorporated into the model, which is responsible for the slower dynamic response of the catalyst under rich operating conditions. With some mild assumptions, a discrete-time version of the model was implemented in MATLAB. The model is sufficiently simple in structure for in-vehicle use and can be used for control and on-board diagnostic purposes.

E Korin et al[12] in their technical paper discussed about Reducing cold-start emission from internal combustion engines by means of a catalytic converter embedded in a phase-change material. Under normal operating conditions, catalytic converters appear to be the most effective means of reducing air pollution from internal combustion (IC) engines. The conversion efficiency, however, declines very steeply for temperatures below about 350°C and is practically zero during the starting and warming-up period. Improving the conversion efficiency under these conditions is important, particularly in large cities, where the number of starting per vehicle per day tends to be high. Among the more successful solutions are preheating of the catalyst electrically, warming up of the catalyst in an external combustion chamber, installation of an auxiliary small-capacity catalytic converter, and employment of an adsorbing unit between two catalysts. Although these methods are quite effective, their disadvantage lies in the fact that they require an external energy source, an additional component (a control unit) or a three-stage catalyst. In the present work an investigation was made of a solution based on the exploitation of thermal capacitance to keep the catalyst temperature high during off-operation periods. A phase-change material (PCM) with a transition temperature of 352.7°C, which is slightly above the light-off temperature of the metallic catalyst, was specially formulated, and a system comprising a catalytic converter embedded in the PCM was designed and tested. Under normal engine operating conditions, some of the thermal energy of the exhaust gases was stored in the PCM. During the time that the vehicle was not in use, the PCM underwent partial solidification, and the latent heat thus produced was exploited to maintain the catalyst temperature within the desired temperature range for maximum conversion efficiency.

J M Deur et al [17] in their paper discussed a variety of after treatment systems which have been or being developed to reduce emissions of NOx and other pollutants from automobile and truck exhausts. In addition to three way catalytic converters for automobiles, several other catalytic technologies are being devised to reduce emissions. These include Selective catalytic reduction(SCR), Lean NOx Traps(LNT), Catalysed soot Filters(CSF). CFD packages are used for optimizing these.

Nestor Martinez et al [27] studied the modeling of vibrations in a catalytic converter. A Three dimensional model is used to first obtain the temperature distribution and theheat transfer coefficients. This information is then used to model the thermo mechanical performance of the converter in order to obtain the vibrations and the noise under real operation conditions. Abaqus, a commercial code is used and the methodology of construction of model in its context is described. The system includes manifold,and exhaust tube with catalytic converter which greatly contribute to total vibrations of the system. However focus is made on the catalytic converter in order to fulfill the new standards of Noise and Vibrations.

Tae Joong Wang et al [30] have developed a porous medium model for modeling flow through the monolith of catalytic converter. In this model Nusselt and Sherwood numbers were studied . They felt that mass and energy balance formulations should be based on fluid mean temperature instead of fluid bulk mean temperature. They obtained Nusselt number for square and circular cross sections under two different thermal boundary conditions namely constant heat flux and constant temperature at the wall.

V K Chakravarthy et al [29] used a multi channel model to study impact of flow non-uniformity during cold start transient operations of a Catalytic converter. It is seen that inlet zone recirculation can lead to significant non-uniformity of flow in the monolith and this can lead to significant differences in the ignition characteristics among the channels. These ignition differences are pronounced at lower exhaust temperatures where the axial location of the ignition can vary from one channel to another. It is suggested that this strong effect of temperature on ignition may explain some of the apparently contradictory conclusions about the impact of flow non-uniformities in the literature. They showed that the simulations made by them, show that the index of non-uniformity as defined in many past studies is an inadequate measure of the full impact on ignition characteristics. For the same index of non-uniformity , the non-uniformity effects on ignition become less significant with increase in exhaust flow rate. This implies that more detailed simulations of flow and temperatures non-uniformities caused by the recirculation zones , heat losses at the boundaries and insufficient mixing upstream of monolith can be relevant to practical applications.

P R Kamble & S S Ingle [32] used a perforated copper plate as a catalyst for catalytic converter. It is designed and developed for a volume of 1000cm3. The experiment is carried out on 4-stroke single cylinder CI engine. The conversion efficiency of the converter was increasing with increase in number of plates. The total number of copper baffle plates tried inside the converter shell are 20 numbers, found to be optimum, though upto 28 were tried. They said that though Copper is not a noble metal it works to certain extent in a limited volume catalytic converter (1000 cc) and copper area of 3800cm2. However back pressure increases which reduces engine efficiency. They found that it is feasible to develop Copper as a catalyst for pollution control in automobile exhausts. Manuel Presti et al (2002) [63] studied the effects of internal geometry of Catalytic converter channels on flow characteristics; exhaust back pressure and overall conversion efficiency, both by mathematical modeling and experimental investigations. They developed a sinusoidal cell and studied wash coat distribution.

VI. PAPERS BASED ON RESEARCH IN CATALYTIC MATERIALS:

Seppo Niemi et al [90] had studied an Ag-alumina based prototype HC-SCR catalyst for removal of NOx emissions in a turbo charged, inter cooled direct injection off road diesel engine. The fuel post injection of the engine was first optimized to produce sufficient amount of hydro carbons into exhaust gases. The efficiency of the catalyst was investigated in a few sets of engine operating conditions using a number of HC/NOx ratios. They reported that highest efficiency of 70% was obtained. However they said that it is not enough as 90% efficiency was achieved with urea based SCR catalysts.

G.J.K.Acres et al [105] in their article on Design and preparation of supported catalysts, have placed particular emphasis on catalyst design as opposed to preparation. They presented case studies on Alumina based catalysts,Silica catalysts, Zeolite catalysts, Ruthenium-Zeolite catalysts, and Carbon supported catalysts. They discussed different methods like Impregnation, Adsorption from solution, Co-precipitation, Deposition, Chemical vapour deposition, Calcination or reduction. They discussed catalyst design parameters like Activity, Stability, Selectivity, and Regenerability.

S.Chauhan (2010)[99] in his technical article expressed his opinion that Noble metals like Pt, Rh and Rd are best option, even though they are expensive and limited in supply. He discussed about other catalysts like Iridium, Ruthenium, Nickel, Copper and Zeolite.

Parthasaradhi Bera and M.S.Hegde (2010) [53]in their technical paper discussed recent advances in Automobile exhaust catalysts.They felt that Cerium oxide has been found to play a major role in this area due to its unique redox properties. They proposed a new preparative method of dispersing metal ions by solution combustion technique over CeO_2 and TiO_2 resulting in many different combinations alongwith noble metals like Pd, Rh and Pt.

M.Shaleef & Mc Cabe in the year 2000 reviewed[41] the successes of heterogeneous catalysts over the period 1975-2000. They reviewed briefly the history of Automotive catalysis right from 1975. They had inferred that a a key distinction between past automotive catalysis experience and that projected for the future is an increased focus on catalysis in upstream of power plant applications like in Fuel cells.

Grigorios C. Koltsakis & Antonio M.Stamatelos (1999) [61] in their article had discussed a mathematical model which helps in catalyst optimization. They presented an approach embodying certain types of dynamic phenomena into an existing quasi steady model.They validated their model with experimentation.

Nitin Labhsetwar et al (2006) [39] discussed application of supported Perovskite-type catalysts for vehicular emissions. They said that although noble metals have dominated the scene, efforts are on to develop low cost catalytic materials. They studied perovskite type compounds with ABO_3 structure , which in their view are having thermal stability characteristics. They presented their work on synthesis of various improved pervoskite type mixed oxides supported on modified alumina-washcoated cordierite honeycomb., their characterization and detailed catalytic evaluation.

Hasan Mandal (2008) [48] discussed advances made in ceramic filters for diesel engine emissions. He felt that, as long as fossil fuels are used as primary energy source the world will face great environmental problems and development of ceramic technology may be a key to the solution. Ceramic supports, filters and substrates will have increasing attention in the coming years.

VII. RESEARCH IN THE LAST THREE YEARS

It has been seen from literature search that in the initial years i.e at the start of the 21st century, for almost six to seven years, researchers concentrated on the mechanical construction of the catalytic converters , like the location of catalytic converter in the exhaust pipe, design optimization of inlet and exit diffusers, the cross sectional design of monoliths and the effects of cold starts and the effect of catalysts and their efficiency at various temperatures. As the pollution norms became more and more stringent, particularly after Euro-III and Euro IV, research was centered around the monolith material development, cleaning efficiency of catalysts and the most recent research i.e after 2010, for the last three years, materials for substitution of noble metals to reduce manufacturing costs of catalytic converter. Some recent contributions world over are discussed below:

Gary Thomas [97] in the year January 2013, discussed regarding materials used in automobile catalytic converters. He stated that the core is usually ceramic monolith with a honeycomb structure. Metallic foil monoliths are made of Iron-Chromium-Aluminium combinations, which are less expensive. Both these are designed to provide a high surface area to support the catalyst wash-coats.

The catalyst wash coat is a carrier of catalytic materials, which is used to disperse them over a large surface area. Titanium dioxide, Aluminium oxide, Silicon dioxide or a combination of Silica and Alumina can be used. In some applications, Cerium, Iron and manganese are also used.

Prof Bharat.S.Patel et al in their review paper on Catalytic converters for Automobile applications [98] in the year 2012 , stated that by the year 2030 vehicular population increases to 1300 million. As the Pollution norms are becoming more and more stringent, number of alternate technologies like improvement of engine design, fuel pre treatment or better tuning for efficient and complete combustion. , are being considered to reduce emission levels further. They found that among all technologies, Catalytic converter using Platinum group of metals as catalytic materials were found to be more effective.

Julie M Pardiwala et al [44] presented a review paper on Catalytic converter for automotive exhaust emission in the year 2011. They felt that by the year 2030 vehicle population is projected to grow to 1300 million compared to about 700 million used world wide at present, (in 2011). Number of alternative technologies like improvement of engine design, fuel pretreatment, use of alternative fuels , fuel additives, exhaust treatment or better tuning of combustion process etc are being considered to reduce emissions. They concluded that of all the methods using catalytic converters based on Platinum (noble) group metal is the best way to control

A.K.M.Mohinuddin & Ataur Rehman [38] (2012) have discussed about simulations for development of low cost catalytic converter. They discussed use of non-precious metals in catalytic converters to bring down costs. Copper powder and nickel were chosen as alternative catalysts which have shown that they are effective in reduction of NOx in rich air/fuel mixture and reduction of CO and HC in lean mixture conditions. They used commercial softwares like COMSOL and FLUENT and showed improvement in catalyst conversion efficiency and reduction in back pressure on the Engine.

Elizabeth Lynn Belcastro [75] (2012) in her M.S thesis discussed life cycle analysis of a three way catalytic converter. In this thesis many materials for wash coats and catalysts along with ceramic monolith were discussed and their life cycle is analysed.

N.V.Deshpande & P.V.Walke from GHR College of engineering, Nagpur[83] in the year 2011 have devised a cost effective catalytic converter for diesel engine. They used cerium oxide, Zirconium dioxide , silver nitrate and copper nitrate with pellet substrate. They have shown that optimization of both minimum back pressure and maximum collection efficiency are possible using these catalyst pellets.

N.Rajasekhar Reddy & Dr. K.Madhava Reddy [82] (2012) have designed and optimized exhaust muffler at G.Pulla Reddy college of Engineering, Kurnool .

Wafa.M.Dabbas [54] (2010) had worked on vehicle emission inter dependencies from urban air quality perspective for his doctoral work in University of Malasia . He used test data of some 542 vehicles emissions in six different drive cycles and worked a compromise of reduction in CO,HC and NOx emissions.

Mallikharjuna Rao et al [86] (2012) discussed evaluation of particulate traps for reduction of diesel engine smoke. NOx and particulate matter of diesel engine's tail pipe emissions in exhaust still pose challenges with regards to their trade off. In order to meet stringent emission norms , it has become mandatory to use exhaust after treatment devices besides adopting good quality of fuel. Present work deals withexperiments carried out on a six cylinder diesel engine

J.Hussain, Palaniraja et al [91] (2012) in their review paper had studied the diesel engine emissions with particular reference to NOx and PM in the diesel exhaust. Diesel Engine's reputation as a noisy , smoky and sluggish power plant has changed due to modern diesel engine technology which allows one to combine inherent low fuel consumption with excellent driving performance and low emission characteristics. After CO2 was identified as a green house gas contributing to global warming , diesel engines have emerged as an alternative to gasoline engines due to their low fuel consumption and hence low CO2 emissions. While CO emissions are negligible in CI engines due to lean operation, emissions of unburnt hydrocarbons can be handled with oxidation catalysts, the emission of oxides of Nitrogen (NOx) and particulate matter (PM) are of concern.

With respect to after treatment solutions, the focus will have to be on NOx traps because their regeneration requires tight control over air path. The formation of NOX as well as PM is closely linked to combustion process which depends on the engine design variables such as combustion chamber and fuel injector design, pressure and timing of injection (Modern injection systems such as Common rail also allow multiple injections), Swirl ratio, Valve timing compression ratio etc. In general these variables can only be optimized for reduction of one of these two pollutants which is called NOx—PM trade-off policy used by Euro norms.

Soot particles which heavily contribute to the total mass of Particulate matter emitted by the engine are formed in the cylinder in the locally rich regions of the inhomogeneous combustion. The subsequent soot burn up at the boundary of the diffusion flame sheath is favoured by high temperatures. However high temperatures also favour generation of NOx. Hence decreasing the combustion temperature (e.g. by exhaust gas recirculation) for lower NOx emissions results in increase of PM. This dilemma is known as NOx –PM trade off.

S.H.Amirnordin et al [73] (2011) have studied pressure drop prediction of square cell honey comb monolith structure. They said that optimum geometry of honeycomb monolith had to be determined, while maintaining low pressure drop. They adopted sub grid scale modeling in their paper.

Abhishek. B.Sahasrabudhe et al [89] (Nov 2011) carried out measurement of carbonyl emissions from exhaust of engines fuelled using biodiesel-ethanol-diesel blend and development of catalytic converter for their mitigation alongwith CO,HC,and NOx. They divided their research work into three sections namely (1) Portable sample collection (2) Developing a suitable catalyst combination and (3) Manufacturing a catalytic converter with a novel design. They discussed catalyst materials suitable for such catalytic converter.

S H Aminordhin et al [65] (June 2011) studied about the high efficiency catalytic converter in vehicle exhaust system. The structure requires a high surface area and low pressure drop in the engine. They studied a square and hexagonal shape subgrids to optimise the geometry of monolith channel. They stated that the high efficiency catalytic converters must have high surface area of honeycomb monolith, as catalyst is applied on these surfaces. They predicted pressure losses using square and hexagonal shaped cells in honeycomb with subgrid scale modeling which represents actual variations in the pressure drop between inlet and outlet of catalytic converter for various combinations of wall thickness and cell density. They made a comparison of experimental results with numerical results established from the published literature. They stated that engine looses about 300W power per 1000Pa pressure drop. They concluded that hexagonal shaped cell gave 43% less power loss.

Partasarathi Bera and M.S.Hegde [94] (2010) have reviewed recent advances in auto exhaust catalysis. They had discussed about a new preparative method of dispersing metal ions by solution combustion technique over CeO2 and TiO2 resulting particular catalysts. Structure of these catalysts and their catalytic properties towards exhaust catalysis and mechanism of catalytic reactions were accounted. They established a new direction in heterogeneous catalysis.

MECA report [87] (2007) gives an exhaustive account of emission control techniques for diesel powered vehicles. Technologies designed to control particulate emissions include diesel oxidation catalysts(DOC), Diesel particulate filters(DPF), closed crank case ventilation (CCV); and technologies designed for control of oxides of nitrogen include exhaust gas recirculation (EGR), Selective catalytic reduction(SCR), Lean NOx catalysts(LNC) , and lean NOx traps(LNT).

Stephen Ademola Adegbite (2010) [151] in his Ph.D thesis discussed vividly about coating of catalyst supports, links between slurry characteristics, coating process and final coating quality. In his study an automatic film application is used for coating gamma-alumina slurries onto Fecralloy, an integral component of metallic monolith catalysts to achieve the desired coating properties.

VIII. SOME CONCLUSIONS THAT CAN BE DRAWN FROM THIS LITERATURE STUDYARE

An attempt was made to study about 150 published technical papers during the period 1973-2013. Papers during the period 1970-1980 mainly concentrated on general aspects like fuel quality, General automobile design and Engine tuning. Later in the next two decades that is till turn of the century researchers concentrated on mathematical modeling and numerical analysis of the flow of gases of combustion.

After the entry of new millennium, researchers have understood that all the efforts towards improving fuel quality, engine design and engine tuning have reached a saturation and hence they believed that certain amount of pollutants cannot be avoided. Hence they concentrated on the design construction of three way catalytic converters, though two way converters were existing. From the year 2000 through 2014, Euro norms 3 to 6 started reducing CO and NOx levels steadily. This have driven researchers to concentrate on other aspects like catalytic reduction & oxidation, removing particulates and complete combustion of Hydrocarbons. In the early stages Alumina pellets coated with noble metals were used for catalytic reduction & oxidation. Researchers tried experimentally using Perforated plates and wire meshes as NOx traps. Parallelly CFD softwares were used for optimizing the Catalytic Converter dimensions.

Particularly optimization of channel geometry and shape were optimized.

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Studies both experimentally and through computer simulation of the monoliths were carried out. Initially corrugated metal sheets were used for fabrication of metal monoliths coated with Platinum/Rhodium/
Palladium. Later ceramic monoliths were extruded and used. As this extrusion of ceramic materials and using noble metals as catalysts are highly expensive, the most recent papers are devoted for finding alternative catalysts which are cost effective.

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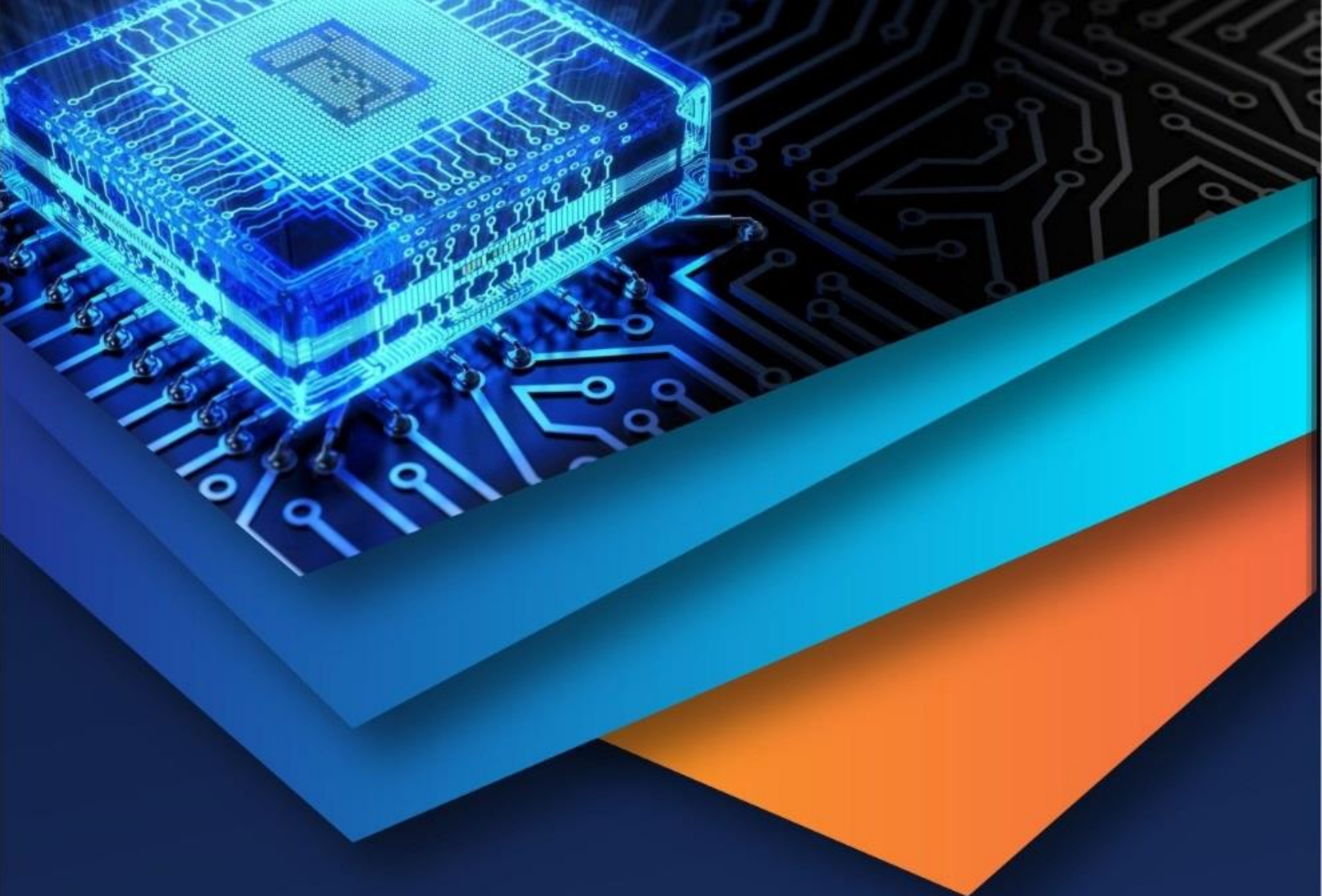

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