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MEASUREMENT OF CARBONYL EMISSIONS FROM EXHAUST OF ENGINES FUELLED USING BIODIESEL-ETHANOL-DIESEL BLEND AND DEVELOPMENT OF A CATALYTIC CONVERTER FOR THEIR MITIGATION ALONG WITH CO, HC'S AND NOX.

Abhishek B. Sahasrabudhe[1], Sahil S. Notani[2] , Tejaswini M. Purohit[3], Tushar U. Patil[4] and Satishchandra V. Joshi [5]

[1,2,3,4]Student, B.E., Deptt. of Mech. Engg., Vishwakarma Institute of Technology, Bibwewadi, Pune, Maharashtra, India.
[5]Prof., Deptt. of Mech. Engg., Vishwakarma Institute of Technology, Bibwewadi, Pune, Maharashtra, India.

ABSTRACT

The research work is divided into (1) a portable sample collection technique (2) developing a suitable catalyst combination and (3) manufacturing a catalytic converter with novel design. Taking into account the hazards of aldehydes in ambient air, and carbonyl emissions compounds, an effort has been made to investigate the carbonyl compounds and measure their concentrations for diesel engines using Bio Ethanol (BE)-diesel fuel. From the said analysis, development of a potential catalytic converter is envisioned in order to reduce these emissions along with carbon monoxides, hydrocarbons and nitrogen oxides. Catalytic converter is specially manufactured for reduction of carbonyl emissions from the BE-diesel fuelled engine and its comparison and its integration with conventional three way catalysts is discussed. The retention time of the raw sample peak is comparable to the retention time of formaldehyde standard solution. Solitary formaldehyde peak is obtained. Peaks of acetaldehyde and acetone are not obtained due to their lower concentrations than the limit of detection, at the given loading condition. Retention time of each arrangement is close to that of formaldehyde standard. It is observed that CO, HC and NO_x conversion efficiencies remained constant irrespective of combination with specially designed ZrO_2 catalyst. Formaldehyde concentration obtained for one ZrO_2 catalyst sample is significantly lower than raw emissions. Added ZrO_2 catalyst showed further reduction. Thus, with optimum loading and surface area improvement methods, better results are achievable. Pt-Rh catalyst shows better carbonyl reduction than Pd-Rh catalyst. However, each of the three way catalysts is less efficient than ZrO_2 catalyst. ZrO_2 catalyst used in series with Pt-Rh catalyst shows the highest percentage reduction in formaldehyde concentration. Pt-Rh catalyst pair is effective in CO mitigation than Pd-Rh pair. The percentage reduction for HC and NO_x is comparable for both. Pt-Rh also depicts better carbonyl reduction ability. ZrO_2 is a better choice than noble metals in terms of availability and cost. Moreover it features a selective nature towards oxidation of aldehydes. Thus, Pt-Rh in combination with ZrO_2 becomes technologically effective and economically viable choice.

KEYWORDS: *Biodiesel-Ethanol-Diesel, carbonyl emissions, catalytic converter.*

I. INTRODUCTION

The global energy crisis, increasing prices of conventional fuels and increasingly stringent pollution norms have led to a greater focus on development of alternative fuels. A study has shown that (Jian-wei, Shah, and Yun-shan, 2009) due to several benefits in terms of fuel economy, power output and emissions, diesel engines rule over the fields of commercial transportation, construction, and agriculture [3]. Biodiesel Ethanol Diesel (BE-Diesel) blends have been considered as potential alternative fuels for diesel engines due to their renewable property, friendliness to environment and energy values comparable to fossil fuels. Studies have revealed that (Panga et al., 2006b) biodiesel can be used successfully as an amphi-phile to stabilize ethanol in diesel and the biodiesel–ethanol–diesel (BE–diesel) blend fuel can be stable well below sub-zero temperatures [1]. It was found that (Panga et al., 2006c; Ren et al. 2008a) particulate matters (PM), total hydrocarbon (THC) and CO were substantially reduced for BE–diesel in comparison with fossil diesel [1, 4, 15]. However the unregulated carbonyl emissions (aldehydes and ketones) due to the use of the said blends have seldom been investigated. Partial oxidation of hydrocarbons and alcohols in the blend is considered as the major cause of carbonyl emissions (Wagner and Wyszynski, 1996a) [5, 15].

The atmospheric carbonyls in urban area are mainly emitted by vehicular exhaust (Panga et al., 2006d; Ren et al. 2008b) [1, 4]. Some carbonyls such as formaldehyde, acetaldehyde, acrolein and methyl ethyl ketone are mutagenic, and even carcinogenic to human body as listed by US Environmental Protection Agency (EPA) (Roy, 2008) [6]. Furthermore, carbonyls play a critical role on the troposphere chemistry. They are important precursors to free radicals (HOx), ozone, and peroxy-actylnitrates (PAN) (Panga et al., 2006e; Ren et al. 2008c) [1, 4]. Even short term exposure to aldehyde vapours show effect of eye and respiratory tract irritancy in humans. Also, the report on the health effects of aldehydes in ambient air (2000b) states that inhaled aldehydes are likely to cause teratogenic effects [2]. Thus mitigation of carbonyls emitted from diesel engines fuelled using BE-diesel blends is vital. To establish a reduction system, it is important to develop a technique for effective measurement of carbonyl emissions.

Among all the engine hardware auxiliary systems, the catalytic converter is considered to have the highest aldehyde reduction potential (Wagner, Wyszynski, 1996b) [5]. Relevant literature regarding the use of catalytic converters for carbonyl emission reduction is reviewed. The aldehyde reduction potential of oxidation catalysts with gasoline fuelled engines is 97-100 per cent. Three-way catalysts have nearly the same reduction potential (90-100 per cent). Aromatic aldehydes were completely removed by the catalyst, while highest inefficiency was shown for formaldehyde (three-way catalyst and oxidation catalyst) [7]. (Cooper, 1992). According to Weaver (1989) the catalytic converters applied to natural gas fuelled engines reduced formaldehyde by 97-98% [8]. As per the study by Colden and Lipari (1987), for methanol fuelled engines the conversion efficiency has been 98 per cent for a three-way catalyst (platinum-palladium-rhodium) and 96 per cent for an oxidation catalyst (copper chrome base metal) [9].Catalyst efficiencies for methanol fuelled diesel engines were analyzed by McCabe et al., (1990a) [10]. The use of Platinum palladium oxidation catalyst resulted in an increase in the aldehyde emissions instead of reduction. The effect was attributed to the oxidation of methanol to aldehyde caused by the platinum palladium catalyst. The substitution of palladium with silver resulted in a reduction of aldehyde emissions owing to high selectivity of the catalyst to convert formaldehyde to carbon-dioxide and water (McCabe et al., 1990b) [10]. The conventional noble metal catalysts in general have oxidative action on both alcohol and carbonyls and thus there is a strong likely hood of the exhaust leaving the catalytic converter still containing significant aldehydes produced through partial oxidation of the alcohol(Wagner, Wyszynski, 1996c) [5]. Thus the need for amendments in the existing catalytic converter technology for engines using alcohol fuel is realized. In the present paper, focus has been laid on the development and testing of a catalytic converter which would enable the reduction of carbonyl emissions for a diesel engine using BE-diesel fuel. Mitigation of CO, HC's and NO_x has also been considered along with aldehydes and ketones.

High performance liquid chromatography**,** HPLC followed by spectroscopy has been used by several researchers for measurement of carbonyl compounds in the engine exhaust [11]. Trapping method using a bubbler and a suitable solvent had been used by Lipari and Swarin (1982).Trapping methods using Di nitrophenyl hydrazine (DNPH) cartridges have also been reported [12]. The cartridge is eluted using suitable solvent and the sample is available as a liquid to be injected for HPLC (Yacoub, 1999). In the present research, a bag sampling method suggested by Roy (2008) [6] is used to trap carbonyls in engine exhaust. HPLC-UV technique is implemented for sample analysis.

II. CATALYTIC CONVERTER DEVELOPMENT

In case of ethanol blended fuels, the oxidation of ethanol and formation of aldehyde and oxidation of aldehyde proceed according to the following formulae:

$$C_2H_5OH \text{ (From BE-Diesel)} + O_2 \rightarrow \text{Aldehydes} + H_2O \qquad \text{---------} (1)$$

$$\text{Aldehydes} + O_2 \rightarrow H_2O + CO_2 \qquad \text{---------} (2)$$

The conventional noble metal catalysts progress the reactions (1) and (2) side by side but the reaction (1) may occur rapidly leading to great amount of aldehyde. It was realized that Zirconium Oxide (ZrO_2) is highly selective in its action and progresses the reaction according to formula (2) considerably faster than reaction (1). Thus selective oxidation of aldehyde is attained relative to alcohol and an excellent removal of aldehydes is achievable. When the proposed catalyst is placed downstream of a conventional three way catalyst, HC, CO, NO_x may be controlled at the upstream side of the arrangement and the carbonyls can be selectively controlled at the downstream side as shown in figure 1.0.

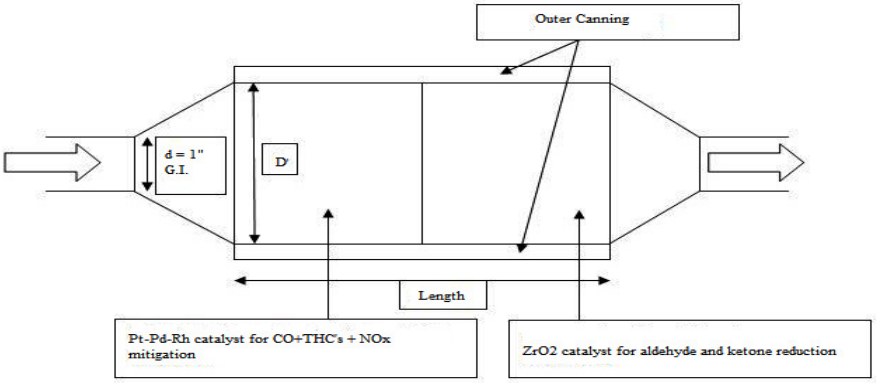

Fig 1.0 Schematic - catalytic converter arrangement.

Metallic substrates (stainless steel) having volume 150cc are used for the Zirconium oxide catalyst. Following properties of ZrO_2 are considered during catalytic converter development.

Table 1.0 Properties of ZrO_2

Sintering Temperature	>1000^{0}C
Melting Point	~2700^{0}C
Chemical inertness and corrosion resistance up-to	~2000^{0}C

Loading the powder at 200gm/litre of substrate volume is intended. Zirconium oxide powder, due to the lack of adhesiveness required for coating on the substrate, is mixed with Al_2O_3 and other suitable binding agent and chemicals to prepare slurry and is then coated on to the mesh surface. The slurry composition is as depicted in table 2.0.

Table 2.0 Slurry Composition

Component Name	**Function**	**Weight %**
Zirconium oxide powder	Catalyst	30
Alumina	Binding agent	20
Concentrated HNO_3	Control over pH and viscosity	0.5
Reverse osmosis water	Solvent	50

The components are mixed and slurry is agitated to attain desirable particle size distribution while monitoring continuously the pH and viscosity. Slurry thus obtained is used to wash coat the substrate. The substrate is then subjected to Vacuuming Process to attain a uniform thickness of the coating. Coated substrate is then taken through a drying cycle involving temperatures of the order of 400^{0}C and eventually subjected to adhesion loss test at temperatures up-to 1000^{0}C.The adhesion loss is recorded to be 2.13% which is within allowable limits.

Readily available, conventional three way catalytic converters loaded with Platinum-Rhodium (Pt-Rh) and Palladium-Rhodium (Pd-Rh) on metallic stainless steel substrate (150cc) are used for HC, CO and NO_x mitigation. Fig 2.0 shows the catalytic converters used.

Fig 2.0 Pt-Rh catalytic converter (Left), ZrO_2 catalytic converter (Right)

III. EXPERIMENTAL SET-UP AND SAMPLING PROCEDURE

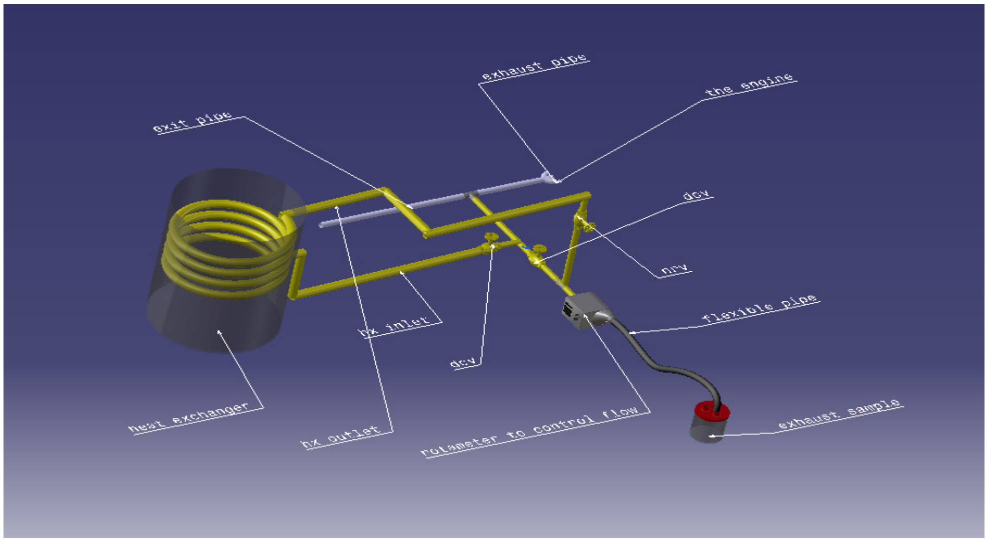

Fig 3.0: Schematic- Sampling setup

Fig. 3.0 shows schematic of experimental set-up modeled in CATIA for collection of exhaust sample. Direction Control Valves and Non Return Valves are used to guide exhaust flow. The low temperature engine exhaust (at low load conditions) can directly be collected without allowing it to pass through heat exchanger. The high temperature engine exhaust (at high load conditions) is cooled (lower than the sustainable temperature of equipment in setup) by using a coiled heat exchanger, before its collection in the sampling bag. The volume flow rate of exhaust is measured by gas rotameter. Tedlar gas sampling bags, made from a special inert material are used for the collection of the sample. The sample collected is subjected to chemical treatment to stabilize the carbonyls in the collected exhaust. Thereafter the stabilized solution is analyzed to understand the carbonyl concentration using HPLC-UV technique.

Particulate filters are used in the actual set-up to prevent clogging in the ancillary equipments. RTD and K type thermocouples are used to determine the temperature of the exhaust gas at different locations in the set-up. The image of actual setup is shown in figure 4.0.

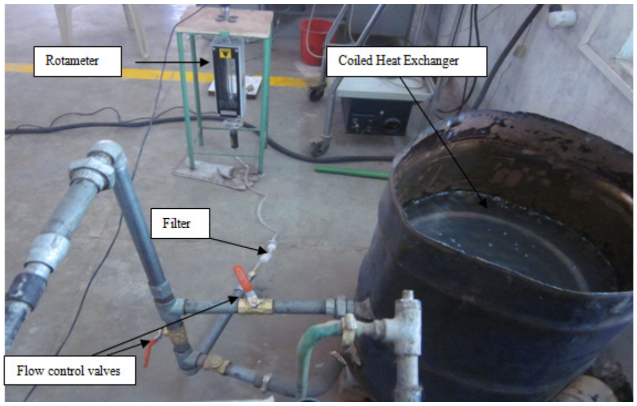

Fig 4.0: Image of sampling setup

The catalytic converter substrates are 64 mm in diameter and 60 mm in length. The diameter of the exhaust pipe from engine is 40mm. Converging and diverging nozzles are manufactured to connect the exhaust pipe to catalytic converters. Catalytic converters are fitted inside an insulated tin canning having diameter slightly greater than outer diameter of the substrate. Two or more converters, (when used) are placed end to end in the canning with a small gap (around 2mm) in between. The arrangement is shown in figure 5.0.

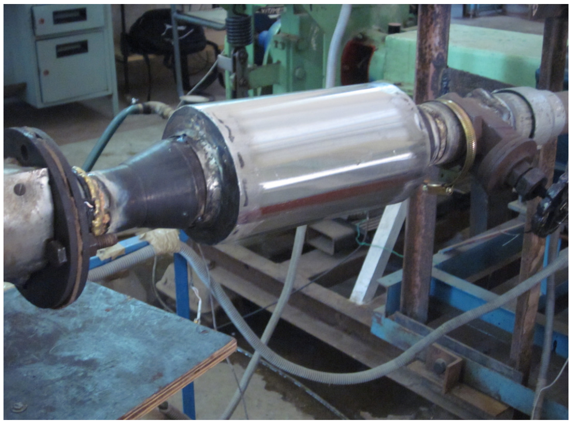

Fig 5.0: Image- catalytic converter arrangement in exhaust line

'Kirloskar' make naturally aspirated DI diesel (shown in fig 6.0) Gen-set/Tractor engine is used for trials.

Fig 6.0: Image-Engine Set-up

Its specifications are given in table 3.0

Table 3.0 Engine Specifications

Rated Power	27.9 KW
Rated Speed	1500 rpm
Cooling System	Water cooled
Dynamometer	Hydraulic Controlled
Lubrication	Inbuilt engine operated pump
No of cylinders	3
Compression Ratio	18.10
Nozzle Diameter	0.20 mm
Injection Time	21^0 After BTDC
Fuel Injection Pressure	500 Bars

The BE-Diesel fuel used has following composition and properties (Refer Table 4.0).

Table 4.0 Fuel composition and Properties

Ethanol	30% by volume
Bio-diesel	20% by volume
Diesel	50% by volume
Density at 15^0C	835 kg/m^3
Kinematic Viscosity at 40^0C	2.4 cSt
Calorific value	38965 kJ/kg

The engine exhaust, after flowing through the catalytic converter arrangement is partly diverted towards the gas sampling line. All trials are conducted at 20kg dynamometer load (mean load in five mode test) and 1500rpm engine speed. Different catalytic converter arrangements using Pt-Rh or Pd-Rh and the specially manufactured ZrO_2 catalyst are used. Gas is sampled in Tedlar bags of 5 liters capacity to measure the concentration of carbonyls. 0.5 grams of DNPH in 400ml of ACN with few drops of perchloric acid is used as absorbing solution. 20ml of the said DNPH solution is inserted in the bag before sampling. A flow rate of 1 LPM is maintained at the bag inlet by using a flow control valve and sampling is carried for 4 minutes. 4 liters of exhaust gas is thus collected in the bag as shown in fig 7.0. It is ensured that the ambient conditions during the collection of samples for different trials are constant. The collected sample is thoroughly shaken to homogenize the mixture and accelerate the formation of respective hydrazones. To stabilize the mixture, it is cooled at -30^0C for around 30 minutes in refrigerator. The stabilized condensate is then collected in small vials for further analysis. An AVL make gas analyzer (refer Fig 8.0) is used to observe and record concentrations of HC, CO and NO_x.

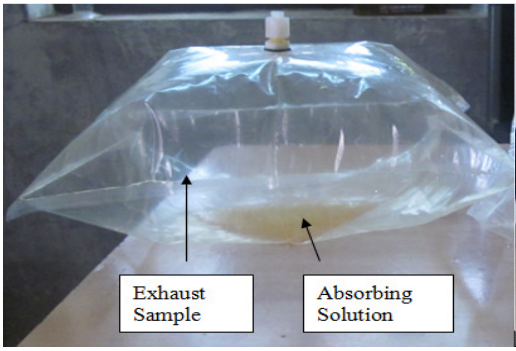

Fig 7.0: Exhaust collection in Tedlar Bags

Fig 8.0: Gas Analyzer

IV. SAMPLE ANALYSIS:

The exhaust sample collected is analyzed using High Performance Liquid Chromatography (HPLC-UV) technique [13, 14]. The HPLC system used is shown in Fig 9.0.Chormatographic conditions are given in table 5.0.

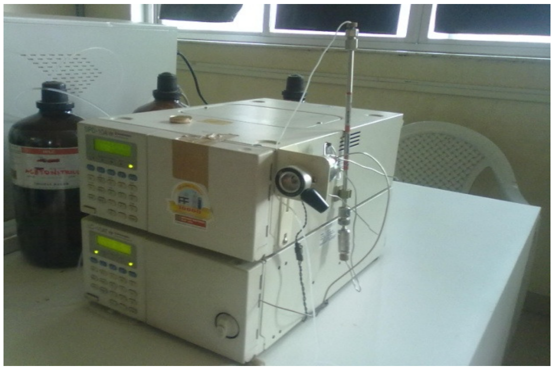

Fig 9.0 HPLC-UV apparatus

Table 5.0 HPLC Chromatographic conditions:

Parameter	Remarks	Description
Column:	Analytical column:	Inertsil C-18(ODS), 4.60mm*250.00mm,5 micron particle size
Column oven temperature	Ambient temperature	32 degrees.
Detector:	UV- Visible	360nm wavelength (Lambda maximum)
Sample:		20 micro-liters
Flow-rate:		1mL/min
Mobile phase	ACN	HPLC grade
HPLC system		LC-10AT vp, Shimadzu make(Japan)
Data acquisition	PC controlled	Spinchrome software

The results obtained from the HPLC-UV apparatus consist of a chromatogram showing peaks (Fig 10.0) and numerical data sheet corresponding to the retention time and peak area (table 6).

Table 6.0 Numerical Data sheet-HPLC

Sr. No.	Retention. Time [min]	Area [milli-Volt-sec]	Height [milli-Volts]	Area [%]	Height [%]	W05 [min]
1	2.823	46.014	7.35	1	1.2	0.11
2	3.01	3899.952	428.713	99	98.8	0.12
	Total	3945.996	433.921	100	100	

The retention time is the characteristic of the compound and the peak area is a direct measure of the concentration.

4.1 Preparation of standards:

The standard solution of Formaldehyde Hydrazone is analyzed using HPLC-UV to get its retention time and concentration. According to the molar equilibrium from the chemical reaction, a standard solution having a concentration of 500µg/ml (w/v) of formaldehyde hydrazone in acetonitrile is prepared and analyzed. The results obtained are of the following nature (refer fig. 10.0):

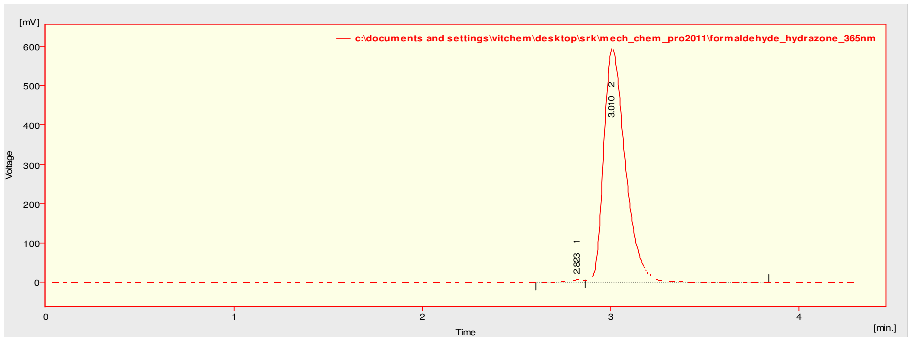

Fig. 10.0 Formaldehyde standard chromatogram

Similarly, peaks were obtained for acetaldehyde and acetone standard solutions.

4.2 Analysis of samples:

The samples collected in the vials after refrigeration are injected in the HPLC-UV apparatus for their analysis. Three iterations of the same sample are carried out to verify the reproducibility of peaks. Arithmetic mean of the corresponding three areas is considered while calculating the concentration. The mean retention time obtained is used to identify the compound.

For the standard solution:

Formaldehyde +	DNPH →	Hydrazone +	Water
1 mole	1 mole	1 mole	1mole
30 gms	198gms	210gms	18gms

The molar mass ratio m_f= 30/210 =1/ 7

Mean area A_m= 3751.6395; Mean retention time T_m= 3.0065 min

For sample:

$$\frac{\text{Area of peak in standard solution chromatogr am}}{\text{Area of peak in sample chromatogr am}} = \frac{\text{concentrat ion of standard solution}}{\text{concentrat ion of hydrazone in sample}}$$

Concentration of formaldehyde in liquid sample is related to the concentration of hydrazone as follows:

$$\text{Concentrat ion of formaldehy de in sample} = \frac{\text{Concentrat ion of hydrazone in sample} * \text{volume of absorbing solution} * \text{mf}}{\text{Volume of exhaust sample collected}}$$

Depending on volume of exhaust sampled, the concentration (weight per liter of exhaust) is calculated.

V. RESULTS AND DISCUSSION:

The results of the Raw Sample from the HPLC analysis are as are shown in Fig 11.0

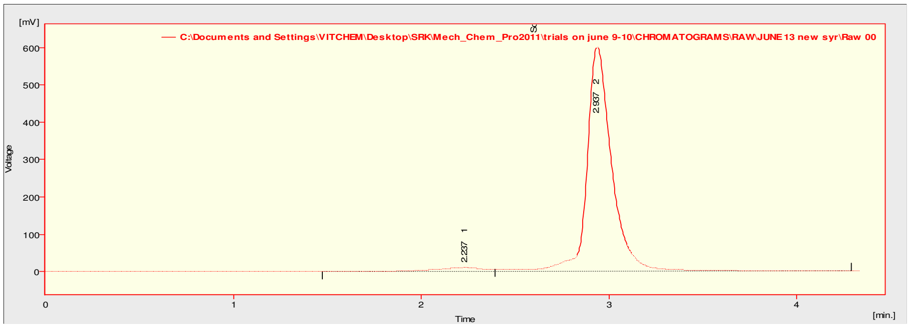

Fig. 11.0 Raw sample chromatogram

The retention time of this peak is comparable to the retention time of formaldehyde standard solution. Minor deviation is due to the slight variation in back pressure. Solitary formaldehyde peak is obtained. Peaks of acetaldehyde and acetone are not obtained due to their lower concentrations than the limit of detection, at the given loading condition. The data is sufficient to understand the qualitative change in carbonyl concentration with the use of several catalytic converter arrangements.
Exhaust samples with different catalytic converter arrangements are collected and analyzed. Retention time of each arrangement is close to that of formaldehyde standard. Sample chromatograms for two arrangements are given in figures 12.0 and 13.0.

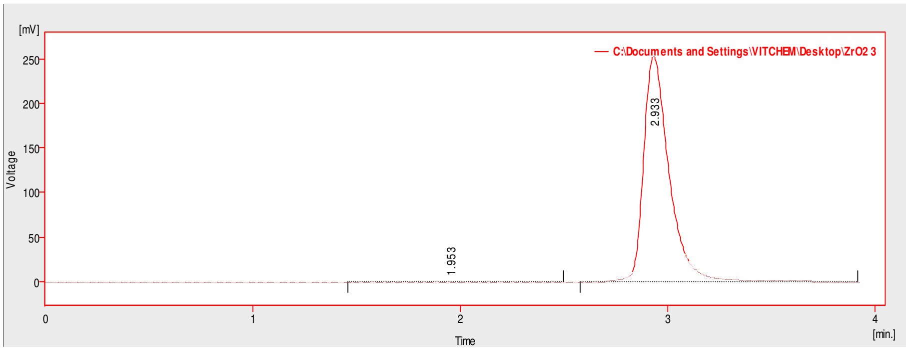

Fig. 12.0 Chromatogram-One ZrO_2 catalytic converter sample

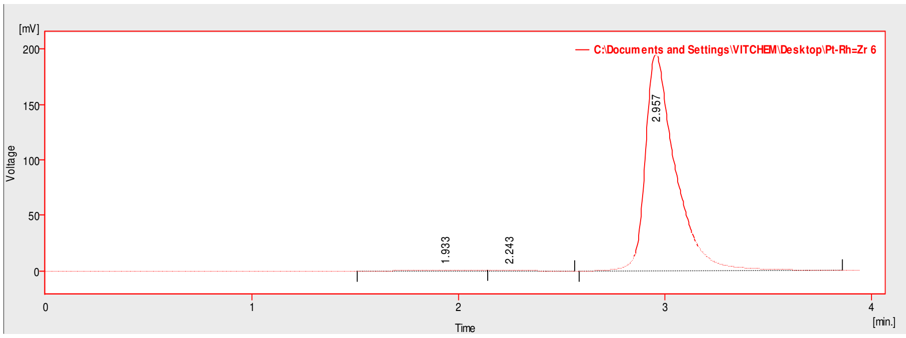

Fig. 13.0 Chromatogram-ZrO_2 CATCON in series with Pt-Rh catalytic converter

Chromatograms for seven different arrangements are obtained and formaldehyde concentrations are examined (Table 7.0 and Fig 14.0). Percentage reduction for each of the arrangements is then analyzed (Refer fig. 15.0). CO, HC and NO_x conversion efficiencies for conventional three way catalyst (Pt-Rh and Pd-Rh) are determined (refer fig. 16.0). It is observed that their efficiencies remained constant irrespective of combination with specially designed ZrO_2 catalyst.

Table 7.0 HCHO concentrations for various catalytic converter arrangements

Sr. No.	**Catalytic converter arrangement corresponding to the injected sample**	**Mean retention time of the injected sample in sec**	**Mean peak area of the injected sample in Milli-Volt-sec**	**Concentration of formaldehyde in the sample in µg/l of exhaust**
1	Raw (No CATCON)	2.9434	5333.993	580.3169
2	Pd-Rh	2.93	2897.93	315.2831
3	Pt-Rh	2.9266	2645.003	287.7656
4	Pd-Rh/ZrO_2	2.9543	2350.9683	255.7758
5	ZrO_2	2.931	2283.46	248.4312
6	2*ZrO_2	2.932	2272.859	247.2779
7	Pt-Rh/ZrO_2	2.9276	2166.016	235.6538

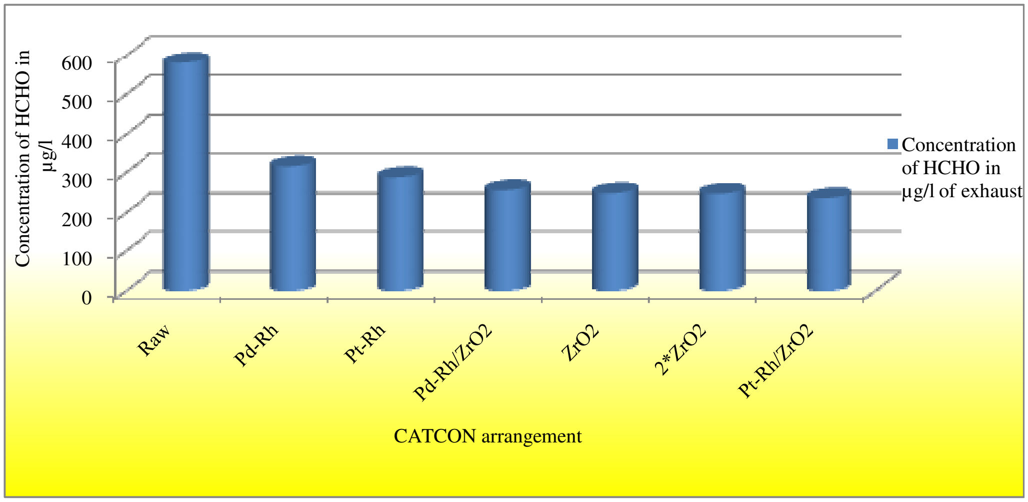

Fig. 14.0 Concentration of formaldehyde for different CATCON arrangements

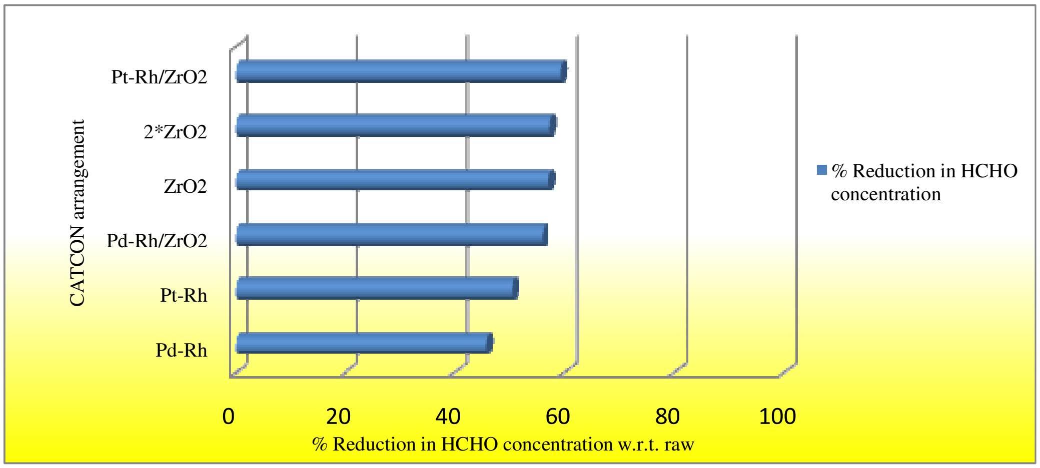

Fig. 15.0 Percentage reduction of formaldehyde in the exhaust

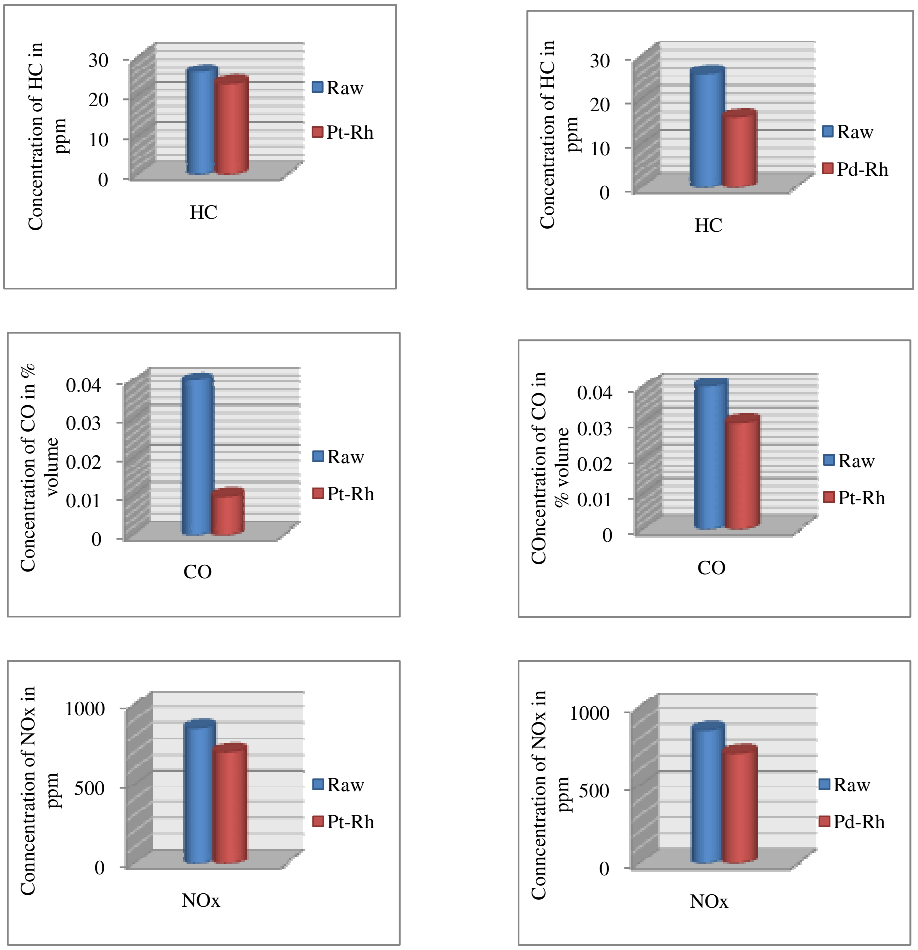

Fig 16.0: Pt-Rh and Pd-Rh HC,CO and NO_x reduction.

Formaldehyde concentration obtained for one ZrO_2 catalyst sample is significantly lower than raw emissions. The effect is attributed to the selective nature of ZrO_2 catalyst in oxidation of carbonyls. Added ZrO_2 catalyst showed further reduction. Thus with optimum loading and surface area improvement methods, better results are achievable.

Pt-Rh catalyst shows better carbonyl reduction than Pd-Rh catalyst. However, each of the three way catalysts is less efficient than ZrO_2 catalyst. This could be due to non-selective oxidative nature of these catalysts where-in alcohol vapors in exhaust are partially oxidized to carbonyls thereby increasing their concentration.

ZrO_2 catalyst used in series with Pt-Rh catalyst shows the highest percentage reduction in formaldehyde concentration. Pt-Rh is effective in CO mitigation than Pd-Rh. The percentage reduction for HC and NO_x is comparable for both. Pt-Rh also depicts better carbonyl reduction ability. The better overall catalytic properties of Pt-Rh than Pd-Rh may be due to contamination of palladium catalyst by some elements in exhaust of BE-diesel fuelled engine (Johnson Matthey website, 2011) [13]. The unaffected carbonyls are selectively taken care of by the ZrO_2 catalyst downstream.

Increasing Platinum loading in conventional catalyst could give better results for carbonyl mitigation. However, ZrO_2 is a better choice than noble metals in terms of availability and cost. Moreover it features a selective nature towards oxidation of aldehydes. Thus, Pt-Rh in combination with ZrO_2 becomes technologically effective and economically viable choice.

VI. CONCLUSIONS

All the significant contributions listed in section 2 were experimentally verified and results are reported. Formaldehyde was the most dominant carbonyl at the given loading conditions. Other aldehydes and ketones could be detected using HPLC equipment with better limit of detection or collecting higher volume of exhaust. Zirconium oxide shows effective catalytic activity towards carbonyl mitigation, better than conventional three way catalysts. Combination of Platinum Rhodium and Zirconium Oxide catalyst enables significant reduction of carbon monoxide, hydrocarbons, nitrogen oxides together with aldehydes and ketones. Platinum-Rhodium catalyst plays a role in mitigation of CO, HC, NO_x while aldehydes are taken care of by ZrO_2 downstream. The said catalyst combination is an important development in catalytic converter technology, both due to its technological and economic features, especially in case of alcohol fuelled engines. It promotes the use of renewable fuels such as BE-diesel, methanol-diesel, methanol, gasoline and so on. Improved catalyst efficiencies are achievable with optimum catalytic converter design. ZrO_2 catalyst used in series with Pt-Rh catalyst shows the highest percentage reduction in formaldehyde concentration. The future work is to be carried out with different arrangements of catalytic converter modules of lengths (currently used in series) in series and parallel. The problem of insulation of the converter and leakages at joints while making series units of standard lengths of converters currently available for 2 wheelers for use in 4 wheelers needs to be further investigated. The selection of parameters in identifying different percentage is done from existing test methods and preparation of catalyst combinations by experience, during this work and procedure for selection needs to be investigated.

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Author's Biographies:

Abhishek Balkrishna Sahasrabudhe: Bachelor of Mechanical Engineering, University of Pune. (Vishwakarma Institute of Technology). Departmental academic topper. Now, pursuing Graduate studies in Mechanical Engineering at Stanford University, California. Graduate Research Assistant at High temperature Gas dynamics (HTGL) Laboratory-Stanford University. Research Interests: Engines and energy systems, Pollution mitigation, Alternative and renewable energy, combustion and kinetics, Computational fluid flow and heat transfer, mechatronics / design.

Sahil Shankar Notani: Bachelor of Mechanical Engineering, University of Pune (Vishwakarma Institute of Technology). Presently working at Emerson Innovation Center as an R&D Engineer, Keeps interest in learning computational domains for design and optimization of mechanical systems, Aspires to pursue Masters in Engineering from a renowned university in the said domain.

Tejaswini Milind Purohit: Bachelor in Mechanical Engineering, University of Pune. (Vishwakarma Institute of Technology). Presently working as a Graduate Engineering Trainee at Mahindra & Mahindra Ltd, Wishes to pursue Masters in the field of mechanical engineering.

Tushar Patil: B. E. Mechanical from the University of Pune (Vishwakarma Institute of Technology). Current occupation: Working as an Engineering services person at Jubilant life sciences, Aims to pursue Masters in Business Administration from the best university.

Satishchandra V. Joshi: Satishchandra V. Joshi is working as professor of Mechanical Engineering at Vishwakarma Institute of Technology, Pune in Maharashtra, India. He earned his Ph. D. from Indian Institute of Technology Bombay at Mumbai, India. Professor Joshi has vast experience in Industry, teaching and research. He has published papers in International, National journals and conferences numbering 15. Professor Joshi has worked on projects of World Bank and Government of India on energy aspects.