Catalytic Reduction of S.I. Engine Emissions Using Zeolite as Catalyst Synthesized From Coal Fly Ash

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ABSTRACT

The present conventional three way catalytic converter used in gasoline engines controls effectively the levels of CO and HC but it displays poor conversion in harmful NO_x emission. Low cost fly ash based zeolites can be used as catalyst for reduction of engine pollution is gaining new research interests because of their unique properties. In our present work, Na-X zeolite was synthesized from coal fly ash. Two different catalysts(Cu-X zeolite and Fe-X zeolite) using the Na-X zeolite have been prepared by exchanging Na^+ Ions with Copper and Iron metal ions. Then these two zeolites were wash-coated separately on to a cordierite honey comb monolith. The honey comb monoliths were housed properly. Investigations were carried out on the twin cylinder nano engine coupled with eddy current dynamometer. The AVL DI-gas analyzer was used to measure the NO_x, CO, HC, CO_2 and O_2 emissions. Initially the engine was run without catalytic converter and both load and speed tests were conducted at various load (4,7,10,13, and16 kW) and speed (2200, 2400, 2600, 2800, and 3000 rpm).Then the commercial catalytic converter was connected near to the exhaust manifold and the same process was repeated. Similarly the experiments were conducted using Cu-X and Fe-X zeolite converters. The result revealed that the inhouse made Cu zeolite and Fe zeolite catalytic converters reduce emissions better than the conventional catalytic converter.

Keywords: *Synthesis, Zeolite, Emission, Catalyst*

1. INTRODUCTION

Multipoint port-fuel-injected (MPFI) gasoline engines are receiving increasing application because of improved fuel economy, reduced pumping losses and improved thermodynamics of combustion. However, the exhaust from MPFI engines is lean and the three-way catalytic converter used for emission control on stoichiometric vehicles cannot provide sufficient NO_x control to satisfy stringent NO_x standards in a lean environment. Jan Kaspar et al. (1) reviewed the challenges in the development of new automotive catalysts, which can meet future highly demanding pollution abatement requirements. Randip K.Das, et al. (2) developed Iron-exchanged X-zeolite (Fe-13X) catalysts (in pelleted form) and tested in the exhaust of an actual SI engine over a wide range of air-fuel ratio, space velocity and catalyst temperature. Maximum conversion efficiencies of 55.8% and 57.4% were recorded for NO_x and CO respectively. The same group (3,4) investigated with Cu-X, Ni-X and V-X catalyst in S.I engine exhaust and reported that the maximum NOx-conversion efficiencies achieved with Cu-X, Ni-X and V-X are 61.2%, 59.7% and 56% respectively. Souvik Bhattacharyya et al. (5) developed Cu-X, Ni-X and Cu-Ni-X catalysts, and tested in 800 cc S.I engine, and reported that maximum NO_x conversion efficiency achieved with Cu-X catalyst is 59.2% at a space velocity of 31000 h^{-1} and for Ni-X and Cu-Ni-X catalysts the equivalent numbers are 56% and 60.45% respectively at a space velocity of 22000 h^{-1} .Swati Bhimasenrao Wadawadagi (6) conducted experiment with the exhaust of 1089cc, 4 cylinder S.I. engine, with Ag-13X and Cu-13X catalysts in pelleted form, and reported that a maximum reduction of 44% in NO_x, 60% in

CO and 74% in HC was achieved by Ag-13X zeolite catalyst. Ghosh. B et al. (7) developed Cu-ion exchanged ZSM-5 zeolite catalyst and tested in exhaust of S.I. engine, observed that Cu-ZSM-5 Zeolite found to be highly efficient catalyst for the simultaneous reduction of NO_x, CO and HC in the lean air fuel ratio 17.5: 1 . Joseph R Theis [8,9] studied both performance and durability assessment of SCR for treating NO_x emissions from lean-burn gasoline engines. Juan M Zomaro et al. (10), Meille V (11) reported various zeolite wash coating techniques on to the cordierite honey comb monoliths.

2. FLY ASH AS CATALYST SUPPORT

Fly ash is the solid waste residue produced from coal, oil and bio-mass combustion. Large quantities of fly ash are produced in electric power plants throughout the world every year. Resource recovery of fly ash generated from coal-fired power plants is one of the most important issues of power plant waste management. Fly ash has a complex chemical composition formed mainly from Silica (SiO_2), Alumina (Al_2O_3), Iron oxides (Fe_2O_3), Calcium Oxide (CaO), Magnesium Oxide (MgO) and small amounts of other oxides. In recent years several new approaches have been taken to utilise fly ashes either to reduce the cost of disposal or to minimise environmental impact. One of the approaches is the conversion of fly ash to zeolites which have many applications such as ion-exchange, molecular sieves, adsorbents and catalysts. Several papers showed that various types of zeolites could be obtained from fly ash by treating it with an aqueous NaOH solution at different curing temperatures. Shih,W-H- et al. (12) Synthesised zeolite A and Zeolite X and examined the ion-exchange capability (IEC)

with Cobalt ion. The author stated that zeolite X has a faster CO^{2+}ion exchange rate than zeolite A. Keka-Ojha et al. (13) converted fly ash to X type zeolite by alkali fusion followed by hydro thermal treatment. The authors compared the synthesised zeolite with commercial 13X zeolite and concluded that the physio-chemical properties of both zeolites are almost same. Anand Srinivasan et al. (14) synthesized zeolite X, Y and Na.PI (90°C) and analcyme and sodalite (150°C) from Class 'F' fly ash using 3 M – Sodium Hydroxide solutions and autogenous pressures. The synthesized zeolites are evaluated for their ability to adsorb sulphur-di-oxide (SiO_2) from a stimulated stack gas containing SO_2. Determinations were made using a UV /VIS spectrophotometer. The authors concluded that the synthesized zeolites adsorb SO_2 gas effectively. Miki Inada et al. (15) investigated the synthesis condition of zeolite from coal fly ash. The author stated that the type and yield of synthesized zeolite strongly depend on alkaline condition and silica-alumina composition of the fly ash source. The author further stated that it is possible to synthesize a specific zeolite from any fly ash by controlling the silica-alumina combination by addition of silica and alumina powders. Dusica Vu Cinic et al. (16) reported that it is possible to form zeolites having greater SiO_2/Al_2O_3 mole ratio by adding SiO_2 in the form of Sodium silicate or other sources such as colloidal silica.

Wojciech Franus (17) synthesized zeolite X by hydrothermal and low temperature methods. The author concluded that hydrothermal reactions gave the zeolite phase rich in Na-X (55 to 60%), whereas in low temperatures reactions the Na-X phase in zeolitic material ranged from 42 to 55%.Xiaping Xuan et al. (18) investigated the selective catalytic reduction (SCR) of NO with NH_3 using metal /fly ash as catalyst. The author changed the original composition of fly ash by mixing small amount of lime, gypsum and Portland cement. Then the new moulded fly ash was treated with concentrated Nitric acid with varying temperature. Finally the treated fly ash was mixed with varying weight% (1.5 and 10%) of active elements (Fe, Cu, V and Ni). By using these prepared samples, SCR activity tests were conducted with NH_3 as reducing agent. The author concluded that fly ash can be used to carry a catalyst to remove NO from flue gas. The author further stated that Cu/FA catalyst gave the highest catalytic NO conversion compared with Fe, Ni and V.M. Chareonpanich et al. (19) synthesized ZSM-5 zeolite from lignite fly ash as main raw material. Sodium Hydroxide, Sodium silicate and Tetra propyl Ammonium Bromide are the other materials which are added with fly ash. The author stated that by adding variable amount of sodium silicate solution into the fly ash solution, it is possible to synthesize ZSM-5 zeolite with different range (20 to 100) of SiO_2/Al_2O_3 mole ratio. Shaobin Wang (20) stated that Fly ash-supported catalysts have shown good catalytic activities for $deSO_x$, $deNO_x$, hydrocarbon oxidation and hydrocracking, which are comparable to commercially used catalysts.

Significant contribution by various researchers employed this process by varying the hydrothermal temperature (21-28). Based on the literature survey, it can be concluded that alkali fusion followed by hydrothermal treatment is the most reliable method of obtaining X, Y and ZSM-5 type zeolites selectively from fly ash of different compositions. It was,

therefore, thought desirable to convert fly ashes from some of the Indian thermal power plants to zeolites, which could be used as catalysts for some industrially important reactions. In our earlier work (29), zeolite –X like material was synthesised from lignite fly ash and transition metals (Cu, Ni and Fe) are ion exchanged in the zeolite. Similarly 13-X zeolite were purchased from market and the same metals (Cu, Ni and Fe)are ion exchanged in 13-X zeolite. Then all the metal doped zeolites are separately made as pellets (average diameter of 3mm). The prepared pellets were housed separately into a cylindrical pipe (with inlet and outlet cones). The test were performed on the catalyst with 800 cc ,three cylinder petrol engine and a maximum reduction of around 60% in NO_x, 85% in CO and 80% in HC was achieved by synthesised zeolite catalysts.

In this work fly ash samples collected from Mettur thermal power plant Tamilnadu, India were used to convert zeolite. Scanning electron microscopy (SEM), X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis were carried out on ray fly ash. The XRD pattern obtained was shown in Fig-1.
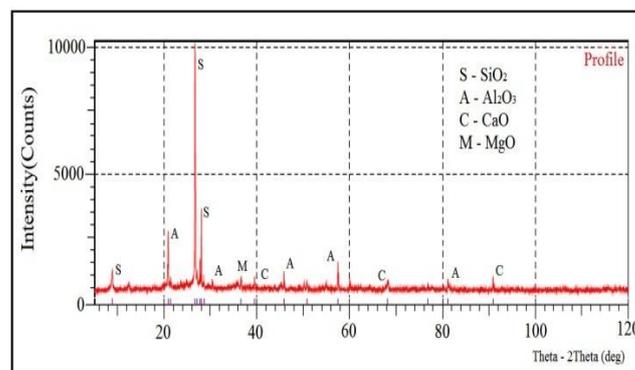

Fig 1 XRD pattern of fly ash

The obtained XRD data of the sample was compared with the JCPDS for the XRD data of SiO_2, Al_2O_3, CaO and MgO. The major portion of 2θvalues were matched with the JCPDS patterns for SiO_2 (JCPDS card no 89-1668) and Al_2O_3 (JCPDS card no 88-0107). Few peaks of the samples matched with the JCPDS pattern of CaO (JCPDS card no 82-1690) and MgO (JCPDS card no 89-7746). The comparison data is shown in Table 1. From the XRD results, it is concluded that the fly ash material used in this study has the predominant oxides such as SiO_2, Al_2O_3, CaO and MgO.

Table 1Comparison of XRD data obtained on fly ash material with standard JCPDS data

Standard XRD data for SiO_2 (JCPDS. No. 89-1668) (2θ values)	Standard XRD data for Al_2O_3 (JCPDS No. 88-0107) (2θ values)	Standard XRD data for CaO (JCPDS No. 82-1690) (2θ values)	Standard XRD data for MgO (JCPDS No. 89-7746) (2θ values)	Powder XRD data for fly ash material	
				(2θ values)	I/Io
9.109	--	--	--	8.8738	7
20.456	21.201	--	--	20.9116	18
--	21.315	--	--	21.4366	3
26.773	--	--	--	26.6957	100
27.365	--	--	--	27.1553	5
27.756	--	--	--	27.7921	8
--	28.235	--	--	28.0500	28
28.141	--	--	--	28.6111	4
36.696	36.953	37.401	36.863	36.6172	6
39.517	40.023	--	--	39.5304	5
45.756	45.988	--	--	45.8548	7
--	51.026	--	--	50.8024	4
--	57.139	--	--	57.4901	12
--	60.686	--	--	60.0364	5
--	67.910	67.467	--	68.2064	4
--	76.293	--	--	76.8941	3
--	81.136	--	--	81.1921	5
--	--	88.659	--	90.8898	5

3. CATALYST PREPARATION

The as- received fly ash sample was screened by a sieve (180 micron) which eliminates larger particles. Then the fly ash was treated with Hydrochloric acid to increase the activity in zeolite formation. Then the HCl-treated fly ash was mixed with NaOH solid powder and Sodium silicate pentahydrate ($Na_2SiO_25H_2O$) powder. The weight ratio of fly ash to NaOH powder and Sodium silicate powder was 1:0.5:1. After grinding, the powders were poured into an aluminium tray and heated at 550° C in a furnace for 1hr. The fused fly ash powders were ground and poured into a glass flask followed by the addition of distilled water (10g /100ml). The mixture was aged 1 day with stirring at room temperature and ambient pressure. Then the mixture was cured at 90° Cat ambient pressure. All precipitated solids were washed two times with distilled water followed by vacuum filtration to remove the excess sodium hydroxide and soluble impurities. The solid powder (Zeolite-X like material) was dried at 80°C in air for 12 hours. The synthesis process is shown in Fig 2.
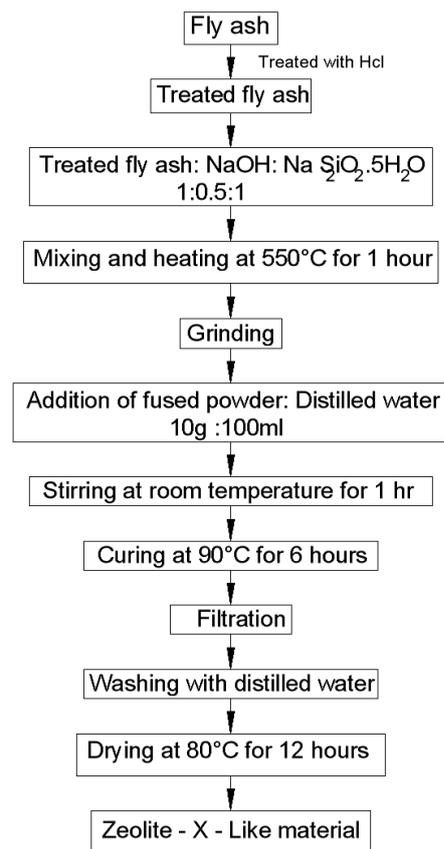
Fig 2 Flow diagram of Synthesis Process

Table 2 Chemical composition of fly ash and zeolite [determined by XRF (Mass %)]

	Raw fly ash	Zeolite
SiO_2	44.54	58.09
Al_2O_3	35.76	20.26
Fe_2O_3	7.58	5.21
CaO	2.38	1.58
Na_2O_3	0.47	8.25
K_2O	1.82	1.21
TiO_2	1.57	1.25
MgO	0.87	0.87
P_2O_5	1.53	0.51
SO_3	1.70	0.86
L.O.I	1.78	1.91

XRD, XRF and SEM analysis were conducted on synthesized zeolite. The results of XRF analysis of both raw fly ash and synthesised zeolite (Table 2) were compared and it was found that the weight percentage of SiO_2 and Na_2O_3 in synthesized zeolite is significantly increased. It was found through SEM investigations (Fig.3 and Fig.4) that the microstructure of catalyst surface was changed. The particle sizes on the treated catalyst surface were smaller than they were for the raw fly ash.
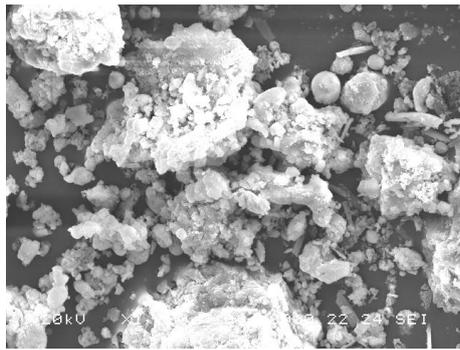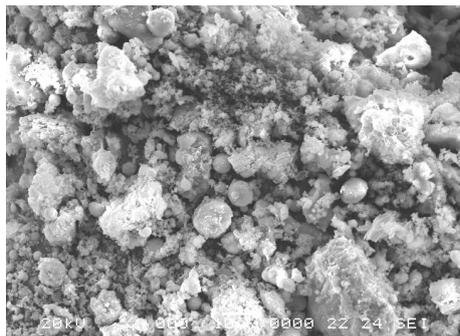
Fig 3SEM- image of raw fly ash

Fig4 SEM image of synthesis of fly ash

A. Na+ -ion EXCHANGE METHOD

10 gram of X-zeolite like powder was mixed with1000 ml of 0.05 M $CuCl_2$ (fisher scientific) solution. The mixture was continuously stirred at warm temperature for 24 hours .After ion exchange the mixture was vacuum filtered and washed with copious amount of distilled water until no free ions were present in the filtrate. The resulting slurry was oven dried and then activated by heating at 500°C for 6 hours. Fe-Zeolite catalyst was also prepared by the same way as explained above. For preparing Fe-Zeolite catalyst $FeCl_3$ (Fisher scientific) was used.

B. CORDIERITE MONOLITHS

Cordierite monoliths with cell density of 400 CPSI, 0.17 mm wall thickness and dimensions of 90 mm diameter and 90 mm length were purchased from Bocent Advanced Ceramics Co Ltd, China.

C. MONOLITH WASHCOATING

A Slurry was prepared using a mixture of 20 weight % zeolite, 2weight % colloidal silica and the remaining weight % of water. The monolith piece was dipped in the slurry for one minute and excess slurry was removed by flowing compressed air through the monolith channels for a fixed time of 5 seconds from both the ends. The wash coated monolith catalyst was then dried at 120°C for two hours. This stepwise dipping and drying process was repeated until the desired quantity (15% weight of monolith) of wash coat was deposited on the monolith support. Finally the monolith was calcined at 500°C for 5 hours. The deliberate calcinations reduced the likelihood of crack formation in the wash coat layer. The adherence of the washcoat was determined by the so-called adherence test, which consists in determining the weight loss of the coated monoliths in an ultrasonic bath.

D. FABRICATION OF CATALYTIC CONVERTER

The wash coated monoliths are housed separately in a steel casing with inlet and outlet cones. The zeolite catalytic converters are fabricated as same as commercial catalytic converter. Fig 5 shows photographic view of all the three catalytic converter.

Fig 5 Catalytic converters

4. EXPERIMENTAL STUDY

Table 3 Engine specification

Engine	Nano Engine
Type	2-cylinder, 624 cc, MPFI
Bore diameter	73.5 mm
Stroke	73.5
Maximum power	37 bhp @ 5000 rpm
Maximum torque	51 Nm @ 3000 rpm
Dynamometer constant	9549.5
Compression ratio	9.5:1

1. Nano Engine
2. Eddy current dynamometer
3. Spark Plug
4. Weighing balance
5. Fuel tank
6. Fuel pump
7. Air filter
8. AVL Di-gas analyser
9. Pressure transducer
10. Crank angle encoder
11. Charge amplifier
12. Indimeter
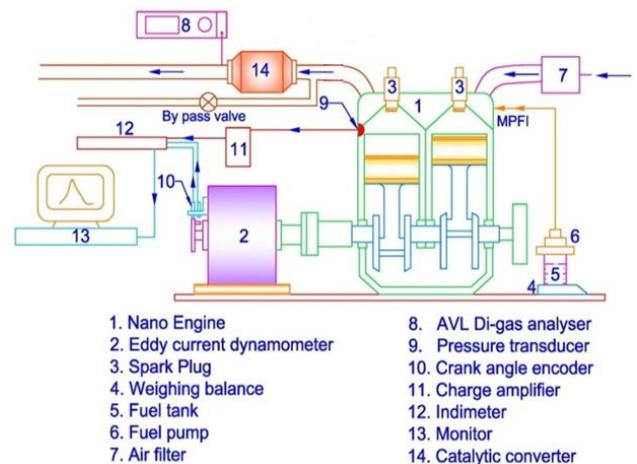13. Monitor
14. Catalytic converter

Fig 6 Experimental Setup

The experimental study was conducted with exhaust of a stationary, four stroke, twin cylinder, water cooled SI engine with a displacement volume of 624cc. Figure 6 illustrates the test facility for this study whose specification is given in

Table. 3. The Nano engine is mounted on the test bed. The engine was directly coupled to an eddy current dynamometer, with suitable switching and control facility for loading the engine. The AVL-Di gas analyzer was used to measure CO, HC, CO_2, O_2 and NO_x. The temperatures of the Exhaust gas was measured by Chromel-Alumel thermocouple fixed at three different points of the convertor. Without catalytic converter, the engine was run at different loads (4,7,10,13 and 16kW) at a rated speed of 2500 rpm and at different speed levels (2200, 2400, 2600, 2800, 3000 rpm) at a rated load of 8 kW. In each case, the concentration of HC, CO, CO_2, O_2 and NO_x were measured. Then the commercial catalytic converter was fitted to the engine exhaust manifold such that the exhaust gas enters the convertor axially. Then the engine was run at the same load and speed conditions as it was when run without catalytic converter and the concentration of CO, HC, CO_2, O_2 and NO_x were measured in each case. Then, the above process was repeated using Fe-zeolite and Cu-zeolite convertors.

5. RESULT AND DISCUSSION

Figure 7 shows the variation of NO_x conversion efficiency with brake power of the engine

NO_x conversion efficiency is calculated by using the formula below;

$$NOx \; conversion \; efficiency = \frac{Inlet\;NOx - Outlet\;NOx}{Inlet\;NOx} \times 100$$

It is seen from the figure that the in house made Cu-zeolite and Fe-zeolite monolith reduce NO_x emission significantly high when compared to commercial monolith. It is also seen that at 13 kW load condition a maximum of 59% of NO_x conversion was achieved by Fe-zeolite monolith and at lower load condition (3kW) Cu-zeolite monolith performs better than Fe-zeolite monolith. Same trend of results were obtained in speed test also (not shown). More percentage reduction in NO_x in the presence of oxygen is attributed to the presence of CO and HC in the exhaust gas which acts as reducing agents, reducing NO_x into N_2 and O_2 and oxidizing CO and HC into CO_2 by using produced O_2 and O_2 available in the exhaust gas.
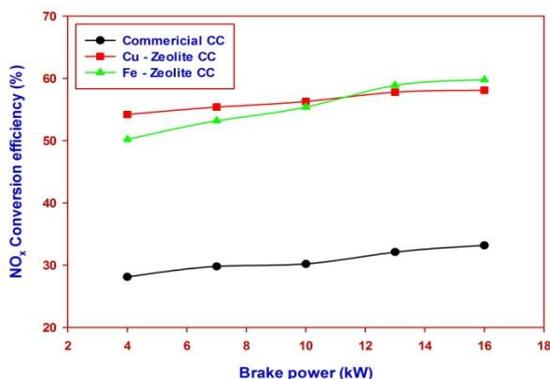

Fig 7 Percentage reduction of NO_x Vs load

Fig 8 shows the NO_x conversion efficiency with the exhaust gas temperature.It is seen from the figure that the Cu and Fe zeolite catalysts behave differently at low temperatures and at high temperatures the difference is minimum. Cu-zeolite catalyst reduce NO_x emission by around 40% at 160°C and around 57% at 300°C and after 400°c the convertion

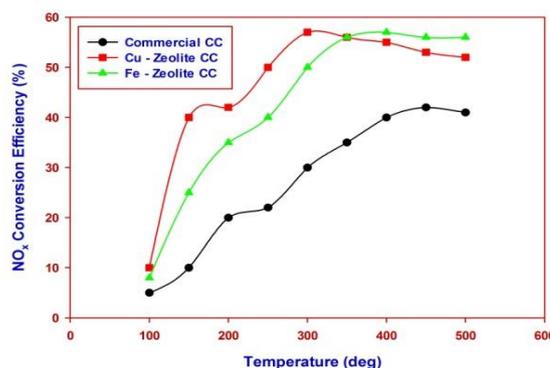efficiency starts decreases.Fe-zeolite catalyst performs better in the temperature range of 350°C and 450°C.

Fig 8 NO_x Emission against temperature

Figure 9 and 10 shows the variation of HC and CO conversion efficiency with brake power of the engine. In agreement with the result of many other researchers, the commercial monolith also controls effectively the levels of HC and CO emissions. It is seen from the figure that there is no much difference between commercial and inhouse made zeolite monoliths. It is also observed that a maximum of 88% of CO conversion was achieved by Fe-zeolite monolith. This is because the catalyst aids the reaction of CO to CO_2 with the remaining oxygen in the exhaust gas. Similarly a maximum of 85% of HC emission reduction was achieved by Fe-zeolite monolith. It appears that reduction of the unsaturated HC can be depicted as a NO_x dissociation reaction accruing the catalyst where the unsaturated HC is responsible for the removal of the adsorbed oxygen generated by the NO_x dissociation.
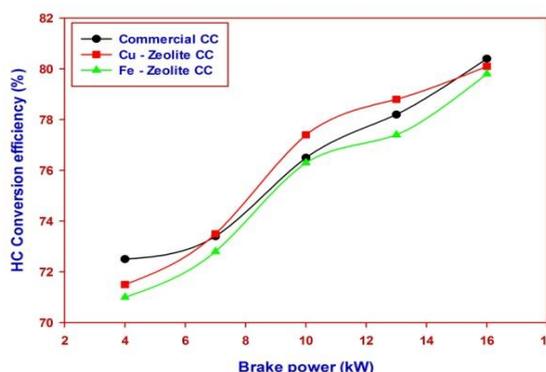

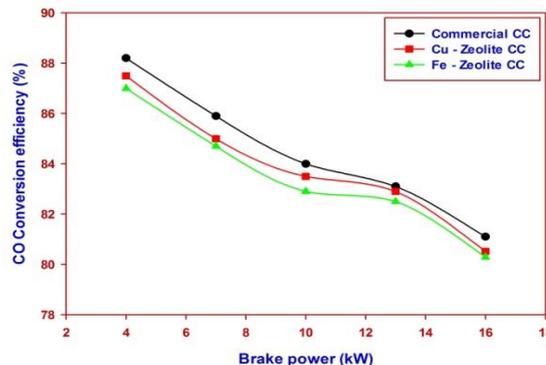**Fig 9 Hydrocarbon against Brake Power**

Fig 10 Carbon Monoxide against Brake Power

Figure 11 shows the variation of O_2 emission with brake power. It is seen from the figure that the volume of O_2 emission is considerably decreased in all levels of load conditions. It is evident that apart from the oxygen produced from the NO_x dissociation reaction, the engine-out oxygen is effectively utilized to convert CO to CO_2.
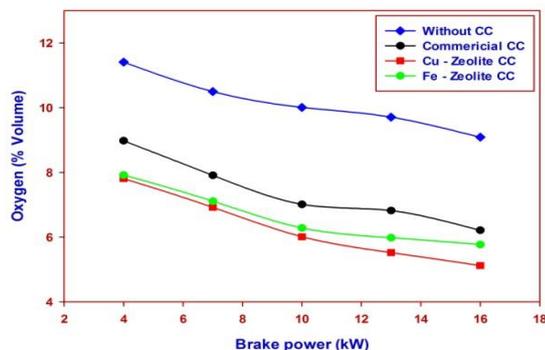

Fig 11 Oxygen against brake power

Figure 12 shows the thermal efficiency of catalytic convertor of the engine. It is seen from the graph that there is a small decrease in the brake thermal efficiency compared to commercial catalytic convertor. The reason may be of the washcoating of a thin zeolite layer in to the monolith channels.
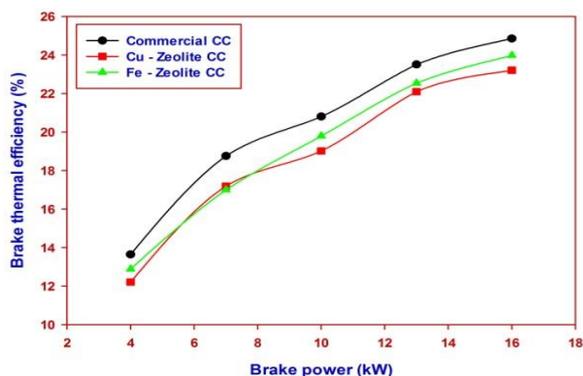

Fig 12 Brake thermal efficiency against brake power

6. CONCLUSION

- The In-house made metal doped zeolite converter performs better than that of commercial converter.
- The Cu-Zeolite monolith showed the best low temperature NO_x reduction performance, while the Fe-zeolite monolith provided the best high temperature NO_x conversion.
- CO and HC emissions were significantly reduced at all levels of load conditions. It is also observed that the trends for percent reduction in HC and CO are almost similar in speed test.
- Back pressure developed across the catalyst bed is well within the acceptable limits.
- During 50 hours of experimental evaluation of Catalytic Convertor, no appreciable deactivation of convertor was observed.

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