

Pulsed Electrical Discharges Assisted by Dielectric Pellets/Catalysts for Diesel Engine Exhaust Treatment

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ABSTRACT

This paper reports the study on gaseous pollutants (NO_x, CO and HC's) using a combination of electric discharge plasma and catalysts. In this study, catalysts being used in conventional catalytic converters of gasoline engine were tried, for the first time, in diesel engine exhaust treatment assisted by electric discharge plasma. Initial studies investigate the effect of packed dielectric materials and catalysts on NO_x removal. Both conventional and non-conventional catalysts were used in the studies. With plasma alone, the removal efficiency of oxides of nitrogen was around 75% and with a suitable combination of catalytic reactor the removal efficiency was as high as 90%. Among the catalysts studied, a new catalyst (CuMnAlO₄) was found to be as effective as the conventional expensive catalyst. The formation of byproducts like N₂O and HNO₃ have been studied and the results are discussed.

1 INTRODUCTION

VEHICULAR pollution is a serious problem today. Due to increased growth in vehicular traffic, the progress achieved through existing control devices are getting offset. The problem is more serious when it comes to diesel engines. The problem with the conventional after treatment technique such as a three-way catalytic converter, which has proved to be very successful in gasoline engines, cannot be applied to lean burn spark ignition engines or diesel engines because these engines burn their fuel with a high excess of air and the oxygen in the exhaust gas stream prevents the catalytic decomposition of oxides of nitrogen. In addition, the precious metals used in the conventional catalytic converters are highly expensive and originate from limited natural sources. This has led the researchers to look for alternative measures for the removal of NO_x resulting in the emergence of non-thermal plasma as a technique for gas treatment. Non-thermal plasma associated with electrical discharges is an excellent technique for the removal of oxides of nitrogen and is proved to be cost effective [1-5]. Non-thermal plasma alone will not be able to remove all the major pollutants present in the automobile exhaust. However, when the discharge plasma is combined with catalysts, there is a scope for removal of these pollutants.

Recently there have been some efforts by researchers in combining catalysts with electric discharge plasma [6-11] but none of these studies was performed using actual

diesel engine exhaust. Since actual exhaust consists of multitude components, the simulated exhaust may provide an incomplete picture of the processes involved. The reactions taking place during the treatment of actual exhaust by pulsed discharges vary largely from that of the simulated exhaust. The investigations of a pulsed corona reactor for treating heavy-duty diesel engine emissions by Grothaus and Fanick [12] resulted in 60% NO_x removal efficiency. Although oxidizing reactions are more pronounced in the case of diesel exhaust (which lead to the formation of NO₂ and HNO₃), there was still a marked decrease in total NO_x. The same authors have also studied the effect of combination of pulsed corona discharges and catalysts and reported NO_x removal efficiency of about 70% [13]. They have not made known the type of catalysts used.

The present work intends to study the feasibility of combining electric discharge plasma with conventional/non-conventional catalysts for treating diesel engine exhaust. The diesel engine was operated under no load condition. Though main emphasis was given to the NO_x removal, the concentrations of CO and HC's were also monitored simultaneously. Initial studies include the effect of packed dielectric materials and catalysts in a plasma reactor on NO_x removal. Studies were conducted at different temperatures. The formation of main byproducts associated with NO_x removal is also discussed briefly.

2 EXPERIMENTAL SETUP

Figure 1 shows the experimental setup. The pulse source consists of a single-phase ac supply, Cockraft-Walton dc

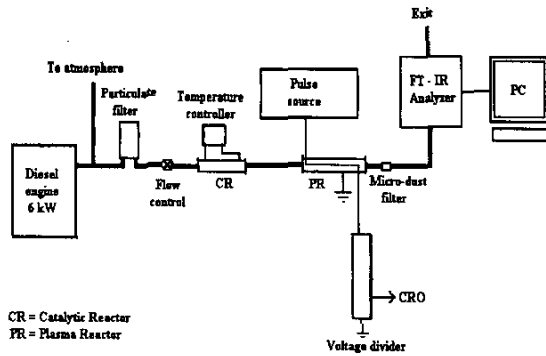


Figure 1. Experimental set up.

voltage multiplier circuit and a rotary spark gap (RSG). The hemispherical rotating electrode of the RSG was connected to a motor through an insulating rod. By changing the speed of the motor, the frequency of the pulses applied to the reactor can be controlled. Throughout the experiments the frequency of the pulses was kept constant at 100 pps (pulses per second). The pulse voltage applied to the reactor was measured by means of a 150 MHz digital oscilloscope (DL1540, 200MS/s Yokogawa) connected through a 2000:1 voltage divider (EP-50K, 50 MHz, Peec, Japan). The power was measured directly from the oscilloscope as the product of voltage and current waveforms. The specific energy density in Joules per liter was then calculated as the ratio of power (W) to the flow rate (liter per minute). A 6 kW diesel engine, under no load conditions, was used for the experiments. A part of the exhaust gas was made to pass through a particulate filter first (PROGARD™, Millipore India Ltd.) to filter out solid particulates down to 4 microns in diameter and then fed to the reactors. A flow meter connected after the particulate filter was adjusted to get a constant gas flow rate of 0.75 liter per minute (lpm). The measurement of NOx from the diesel exhaust was done using an FTIR gas analyzer (DX-4010, Temet Instruments, Finland). Before feeding the exhaust gas into the analyzer, the gas was made to pass through a micro-dust filter to filter out particulates down to 2 μm. The GASMET™ uses the CALCMET™ software to compute the concentrations of the components present in the sample gas from the absorbance spectrum.

During the course of experiments, two different reactors were used, specifically the plasma reactor (PR) and the catalytic reactor (CR). The PR is a dielectric barrier discharge reactor made up of quartz glass tube of diameter (inner diameter = 15 mm and outer diameter = 17 mm). It consists of a stainless steel wire of 0.1 mm diameter as the inner electrode and aluminum foil wrapped over the quartz glass tube as the outer electrode. The studies were conducted by filling the PR successively with dielectric pellets and then with catalysts. Figure 2a shows plasma reactor without pellets and Figure 2b shows the PR filled

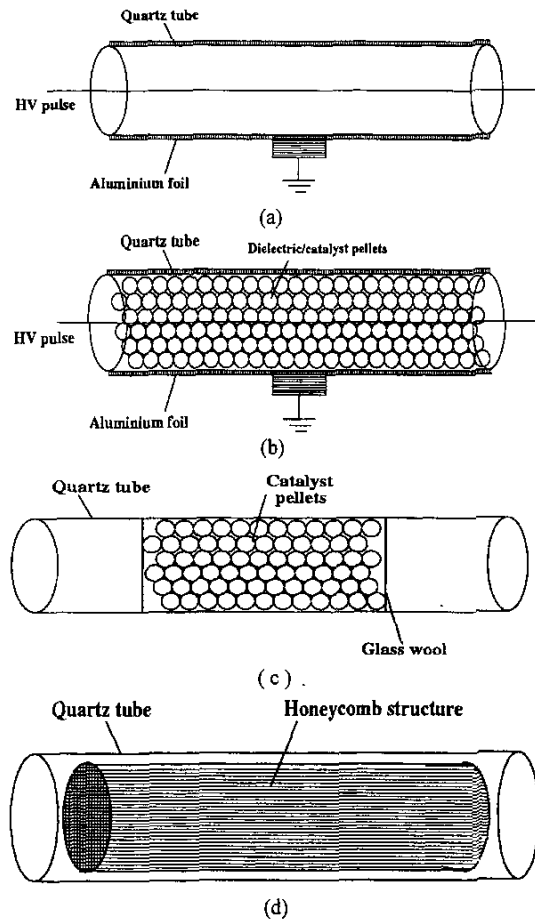


Figure 2. a, reactor without pellets; b, reactor filled with dielectric/catalyst pellets; c, reactor filled with catalyst pellets; d, reactor filled with honeycomb catalyst.

with dielectric pellets/catalysts. In the present experiments dielectric pellets such as BaTiO₃ (ε_r = 3200), Al₂O₃ (ε_r = 10) and glass beads (ε_r = 10) were used. The experiments were then conducted by replacing the dielectric pellets with catalysts such as Pd/Al₂O₃, CuO and Fe₂O₃.

The catalytic reactors consisted of a pellet bed reactor and a honeycomb reactor. Figure 2c shows the catalytic reactor (glass tube of 15 mm diameter and 300 mm length) filled with catalyst pellets such as Pd/Al₂O₃ and Fe₂O₃. The catalysts are packed inside the reactor for a length of about 70 mm and both the ends were held by glass wool. Figure 2d shows the catalytic reactor filled with a honeycomb structure coated with a conventional catalyst (Pt-Rh/CeO₂-Al₂O₃) and a non-conventional catalyst (CuMnAlO₄). The honeycomb for the former is of length 120 mm and diameter 25 mm and was inserted in a glass tube (30 mm diameter, 300 mm long), while for the latter the honeycomb is of length 120 mm and diameter 12 mm and was inserted in a glass tube (15 mm diameter, 300 mm long). In both cases the CR was kept inside an electric

furnace. A brief explanation of the catalysts used in the experiments is given below.

1. Pd/Al₂O₃ (palladium coated over alumina). This is the most commonly used conventional two-way oxidation catalyst for exhaust gas treatment. This was used in the form of pellets (5mm long and 3mm diameter). The catalyst is active at $\leq 200^{\circ}\text{C}$.

2. CuO-ZnO-Al₂O₃ (copper oxide coated over a support of zinc oxide and alumina). This is a base metal catalyst. Before the advent of noble metal catalysts these catalysts were initially used to treat the exhaust gas emissions. Pellets with size of 4 mm long and 6 mm diameter were used in the present studies. This is a good oxidation catalyst for the oxidation reactions of CO and HCs. The catalyst is active in a narrow temperature window of 200–300°C.

3. Fe₂O₃-Cr₂O₃ (Iron oxide doped with chromia). This is also a base metal catalyst that was used in the treatment of exhaust gas before the advent of noble metal catalysts. Pellets with 4 mm long and 6 mm diameter were used in the present studies. The oxidation reactions start around 200°C with this catalyst and the catalyst loses its activity above 500°C.

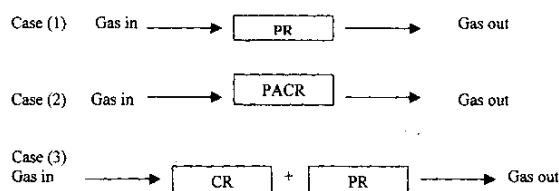
4. Pt-Rh/CeO₂-Al₂O₃ (platinum and rhodium coated over a support of ceria and alumina). This is the most commonly used conventional three-way catalyst for the auto exhaust treatment. This catalyst is coated on a cordierite honeycomb structure of length 120 mm and diameter 25 mm. The catalyst is active at $> 200^{\circ}\text{C}$.

5. CuMnAlO₄. This is a new catalyst prepared in the laboratory. It is a non-conventional catalyst, coated on a cordierite honeycomb structure of length 120 mm and diameter 12 mm. This is a very good oxidation catalyst and works at $> 175^{\circ}\text{C}$.

3 RESULTS AND DISCUSSION

A diesel engine of 6 kW under no load conditions was setup in the laboratory. The experiments were conducted using a filtered exhaust gas. Only a portion of the filtered exhaust gas from the diesel engine was passed through the reactors. Before treating the exhaust gas, either with the PR and/or the CR, the concentrations of CO, THC, NOx, N₂O, H₂O, and CO₂ were measured using a FTIR multi-component gas analyzer. Also, the concentration of oxy-

gen present in the diesel exhaust was measured using a NDIR gas analyzer. Table 1 shows the initial concentrations of these components present in the diesel engine exhaust gas. In the table, "NOx" means the sum of NO and NO₂ concentrations. The concentrations of NO and NO₂ were measured individually and then added to get the NOx concentration. The total hydrocarbons (THC) are the sum of various HC's present in the exhaust. THC in the present study includes methane (CH₄), ethylene (C₂H₄), acetylene (C₂H₂), butane (C₄H₁₀), propene (C₃H₆), benzene (C₆H₆), and toluene (C₇H₈). The experiments were conducted for three arrangements of the plasma reactors as shown below.



PACR refers to plasma-assisted catalytic reactor. In each of the above cases, the relevant exhaust gas component concentrations were measured before and after the plasma/catalytic treatment. In all the experiments, the PR was kept at room temperature and the temperature of the CR alone was varied from room temperature to 300°C.

3.1 STUDIES USING PLASMA REACTOR (PR)

The effect of dielectric pellets on NOx removal has been investigated [14,15] and it was found that the efficiency of the plasma reactor increased by packing it with dielectric pellets. When the plasma reactor was filled with dielectric pellets and pulsed high voltage was applied across the pellet bed, the pellets become polarized and an intense electric field is formed around the contact points of each pellet, causing partial discharges between the pellets. This partial discharge together with the discharge from the wire (referred to as combined discharge) helps in increasing the radical production thereby enhancing the chemical reaction rates leading to more NO removal. However, none of these investigations was conducted on actual diesel engine exhaust. Experiments on NOx removal using dielectric pellets have been conducted to verify the above fact using actual diesel engine exhaust. In these studies the exhaust was treated using a plasma reactor packed with different dielectric materials (BaTiO₃, Al₂O₃ and glass beads). Experiments were also conducted without using any pellets. The study is intended to determine the relative performance of various dielectric pellets. All the experiments were conducted at room temperature. Figure 3a shows the NOx removal efficiency using PR packed with dielectric pellets and PR without pellets as function of specific en-

Table 1. Initial concentrations of diesel engine exhaust gas components.

Component	Concentration
CO	700 ppm
THC	90 ppm
NOx (NO + NO ₂)	150 (115 + 35) ppm
N ₂ O	2.5 ppm
H ₂ O	2.5 vol%
CO ₂	2 vol%
O ₂	11.2 vol%

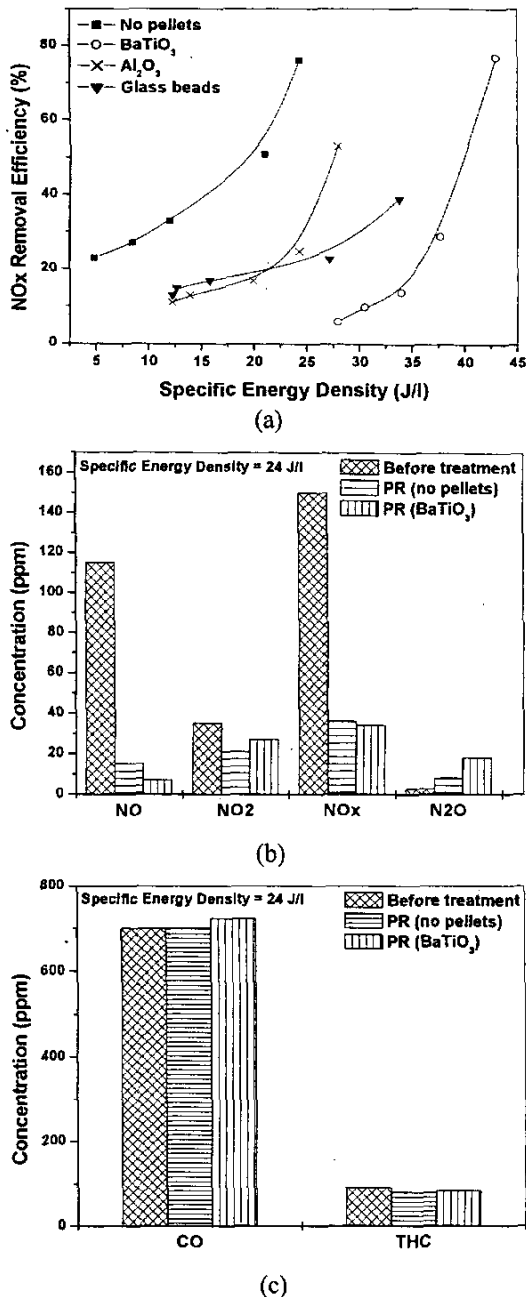
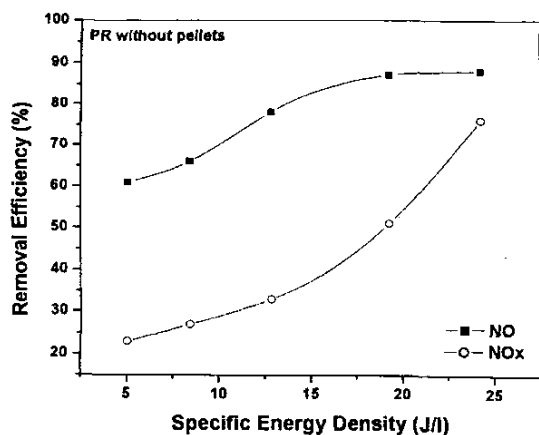


Figure 3. a, NO_x removal efficiency for PR packed with and without dielectric pellets as a function of specific energy density; b, comparison of concentrations of NO, NO₂, NO_x and N₂O for PR packed with BaTiO₃ and PR without pellets; c, comparison of concentrations of CO and THC for PR packed with BaTiO₃ and PR without pellets.

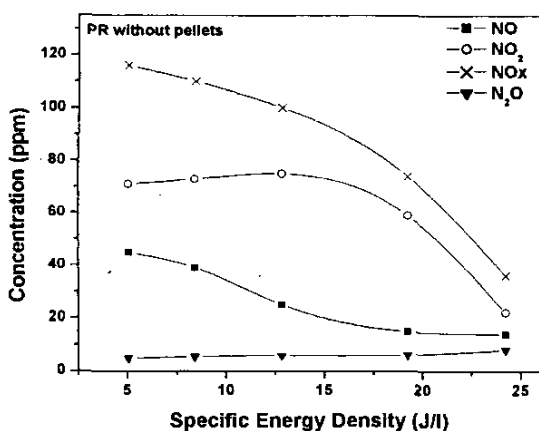
ergy density. Both BaTiO₃ packed PR and PR without pellets show maximum NO_x removal efficiency. PR packed with Al₂O₃ and glass beads exhibited high NO removal but not NO_x removal. Also, it should be noted that the PR without pellets exhibited the least energy consump-

tion. Figure 3b compares the concentrations of NO, NO₂, NO_x and N₂O for PR packed with BaTiO₃ and PR without pellets, before and after treatment, at the maximum specific energy density. It is observed that the reduction in NO_x is almost the same for both cases. With BaTiO₃ packed PR, the NO₂ production is higher compared to PR without pellets, which indicates that BaTiO₃ generates maximum quantity of oxygen species. Consequently, BaTiO₃ packed PR generated maximum amount of N₂O as compared to PR without pellets. At maximum specific energy density (24 J/l) the concentration of N₂O increased to 18 ppm from an initial value of 2.5 ppm for BaTiO₃ packed PR. For PR without pellets the concentration of N₂O was increased to 8 ppm from an initial value of 2.5 ppm. Figure 3c compares the concentrations of CO and THC for BaTiO₃ packed PR and PR without pellets before and after treatment at the maximum specific energy density. For BaTiO₃ packed PR the concentration of CO was found to increase from the initial value. At maximum specific energy density, the CO concentration was increased to 725 ppm from an initial value of 700 ppm whereas for PR without pellets there was no change in initial CO concentration. There is a slight reduction (10%) in the concentration of THC using BaTiO₃ packed PR and PR without pellets. From the above discussion, it is observed that PR without pellets is a better choice compared to PR filled with dielectric pellets. A detailed study of NO_x removal using PR without pellets is explained in the following paragraph.

Figure 4a shows the removal efficiencies of NO and NO_x for PR without pellets. When the specific energy density is around 5 J/l, the concentration of NO was decreased to 45 ppm from an initial value of 115 ppm. This reduction corresponds to about 60% removal of NO. This is because of strong oxidation reaction in high oxygen atmosphere leading to the formation of NO₂. The concentration of NO₂ was increased to 70 ppm from an initial value of 35 ppm at this specific energy density. So, there is a decrease in NO_x concentration by 34 ppm (from initial 150 ppm to 116 ppm). But up to specific energy density of 13 J/l, the oxidation reactions were dominant resulting in NO removal efficiency of nearly 80% and NO_x removal efficiency of only around 35%. However, beyond 20 J/l, the concentration of NO₂ started decreasing thereby increasing the removal efficiency of NO_x. The reason for NO₂ drop is that the NO₂ reacts with hydrocarbons and water to release various other HC by-products, HNO₃, N₂O etc. The rate coefficients for these reactions are more favorable at higher radical energies than that at lower radical energies. At 24 J/l the NO_x removal efficiency became 76%. This is well represented in Figure 4b, which shows the concentrations of NO, NO₂, NO_x and N₂O as a function of specific energy density. It has been reported that without any additives the reduction of NO into N₂ in high oxygen atmosphere is not possible [14,17]. In the present studies, since an actual diesel exhaust was treated, it is



(a)



(b)

Figure 4. a, NO and NOx removal efficiencies for PR without pellets; b, concentrations of NO, NO₂, NOx and N₂O as function of specific energy density for PR without pellets.

possible that the presence of HCs in the exhaust has played the role of additives in the decrease of NO concentration [12]. To correlate this we observed decrease in the concentration of hydrocarbons. At the same time the NOx removal was also associated with the formation of HNO₃ and N₂O. The concentration of N₂O was found to increase from initial 2.5 ppm to 8 ppm at the maximum specific energy density (24 J/l). Though HNO₃ was not measured quantitatively, its presence was confirmed by qualitative analysis. For this, the treated exhaust gas was made to pass through distilled water for about 10 minutes and this water was tested for its acidity using a pH meter. The results confirmed the presence of HNO₃. The formation of HNO₃ is desirable as it could easily be neutralized to a salt by simple chemical methods.

3.2 STUDIES USING PLASMA-ASSISTED CATALYTIC REACTOR (PACR)

The efficiency of NO removal achieved by a catalyst assisted with electric discharge plasma at room temperature

has been reported [15] and found to be quite comparable with that achieved by conventional catalytic converters operated at $\leq 300^\circ\text{C}$. However, the above study was not conducted by using actual diesel exhaust gas. Also, NOx removal was not discussed. Hence, the focus of this paper is placed on the NOx removal by catalysts assisted by electrical discharges using actual diesel engine exhaust gases and comparison of performances of conventional and non-conventional catalysts assisted by electrical discharges. The experiments were conducted by packing the catalysts (in pellet form) in a plasma reactor at room temperature using actual diesel engine exhaust. A reactor configured in this manner is referred to as a plasma-assisted catalytic reactor (PACR). The studies were limited to room temperature because of the practical difficulties. The catalysts used in the study were Pd/Al₂O₃, (a conventional catalyst) and Fe₂O₃ and CuO (both non-conventional catalysts). Figure 5a shows the NOx removal efficiencies as function of specific energy density for PACR packed with different catalysts. It is observed that the NOx removal efficiency is above 60% for low specific energy densities in all cases. The NOx removal is dominated by catalytic adsorption rather than by pulsed discharges in these cases. Fe₂O₃ and CuO showed very high adsorption characteristics when compared to Pd/Al₂O₃ catalysts. The NOx concentration was decreased from 150 ppm to 105 ppm with Pd/Al₂O₃ catalysts. This amounts to 30% removal of NOx. However, when the specific energy density is around 5 J/l the NOx removal efficiency became 63%. For higher specific energy densities, the removal was linear and reached a maximum of 88%. With the CuO packed PACR, the NOx removal efficiency was almost saturated beyond a specific energy density of 5 J/l. CuO alone adsorbed nearly 70 ppm NOx out of initial 150 ppm. The maximum NOx removal efficiency obtained with the CuO packed PACR was 94%. For the Fe₂O₃ packed PACR, the NOx removal efficiency was 90% for a specific energy density of only 5 J/l. This is because Fe₂O₃ catalysts adsorbed 116 ppm of NOx (77% adsorption). Beyond this specific energy density, there was no significant increase in removal efficiency. Figure 5b compares the concentrations of NO, NO₂, NOx and N₂O before and after treatment for PACR packed with catalyst pellets. Though the NOx removal was higher for CuO and Fe₂O₃ packed PACR, the N₂O production was higher for these two when compared to Pd/Al₂O₃ catalysts.

Figure 5c compares the concentrations of CO and THC before and after treatment for PACR packed with catalyst pellets at maximum specific energy density (24 J/l). The Fe₂O₃ packed PACR showed maximum removal of CO followed by the Pd/Al₂O₃ and CuO cases. The readings were taken by passing the exhaust gas through the catalyst until steady readings were obtained. Once the readings were stabilized (i.e. no more adsorption is possible by the catalysts) the discharges were produced inside the reactor by applying the pulses. It was found that the presence of

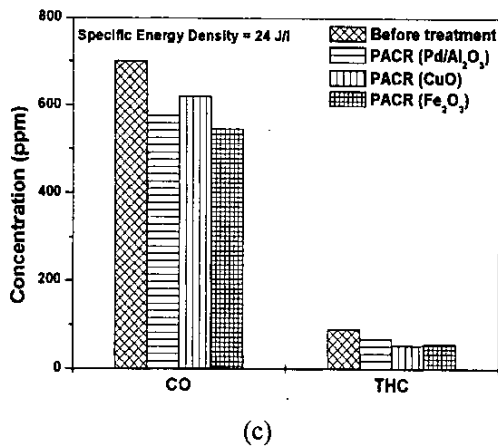
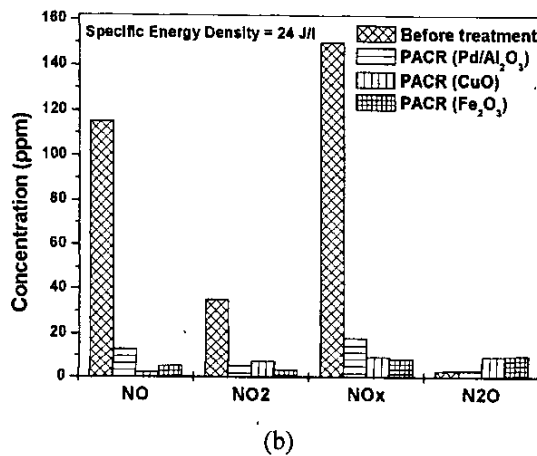
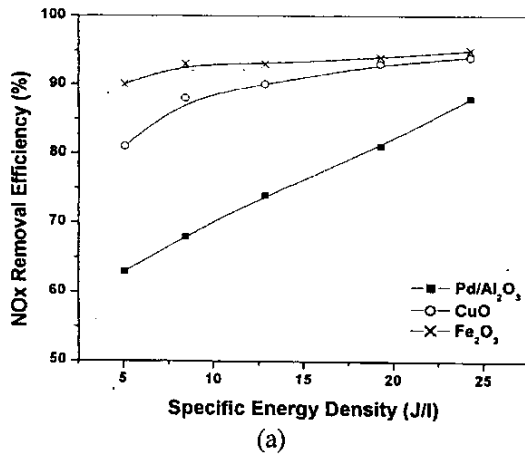


Figure 5. a, NO_x removal efficiency for PACR packed with catalyst pellets; b, comparison of concentrations of NO, NO₂, NO_x and N₂O for PACR packed with catalyst pellets; c, comparison of concentrations of CO and THC for PACR packed with catalyst pellets.

discharges enhanced the CO removal by catalyst. The catalyst Fe₂O₃ alone removed 125 ppm of CO (by adsorption process) and the combination of discharges and catalyst removed 155 ppm of CO. Hence 30 ppm of CO was re-

Table 2. CO and THC removal efficiencies using different catalysts for PACR at 27°C.

Pollutants	Removal Efficiencies (%)		
	Pd/Al ₂ O ₃	CuO	Fe ₂ O ₃
CO	18	11	22
THC	26	42	39

moved by the catalysts in presence of pulsed discharges. There was about 50 ppm of CO adsorption using Pd/Al₂O₃ catalysts. The PACR packed with Pd/Al₂O₃ catalysts removed 125 ppm of CO. So, there was a decrease in CO concentration by 75 ppm in the presence of pulsed discharges. Adsorption of CO by CuO was much less (10 ppm). However, the presence of discharges assisted the catalysts in removing 80 ppm of CO. Maximum removal of THC was achieved by CuO packed PACR followed by Fe₂O₃ and Pd/Al₂O₃ packed PACR. In this case too, the pulsed discharges assisted the catalysts in removing the hydrocarbons.

The above results show that even at room temperature some reactions were taking place on the surface of the catalyst in presence of pulsed discharges, which resulted in the removal of NO_x, CO and THC. Though the removal efficiencies of CO and THC are low in these studies (Table 2), it is still quite interesting considering the fact that the catalysts are not active at room temperature.

3.3 STUDIES USING A COMBINATION OF PLASMA/CATALYTIC REACTORS

In this study, the exhaust gas from the diesel engine is made to pass through a combination of catalytic and plasma reactors connected in series. This is an attempt to study the feasibility of placing a plasma reactor along the exhaust channel in a vehicle without disturbing the existing catalytic converters. Both conventional and non-conventional catalysts were used in the form of pellets as well as a honeycomb structure. Initial studies were focused on selecting a suitable combination of PR and CR. For this, catalytic reactor packed with Pd/Al₂O₃ pellets was tested for two combinations with PR. In the first case, CR was put after PR (this combination is referred as PR+CR) and in the next case CR was put before PR (this combination is referred as CR+PR). The studies were carried out at different temperatures of CR. It should be noted that in all these experiments the PR was kept at room temperature and only the temperature of the CR was raised. Preliminary results in regard to this were presented in [16]. Fig. 6a shows the NO_x removal efficiencies for PR+CR combination at different temperatures. At room temperature and at 100°C, the catalytic adsorption is high resulting in the high NO_x removal efficiencies. The NO_x removal efficiency decreases with increase in the temperature of the catalytic reactor. The NO_x removal efficiency was as low as 35% when the temperature of CR is raised

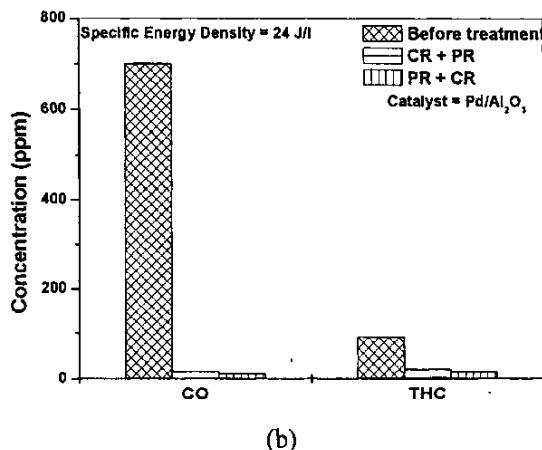
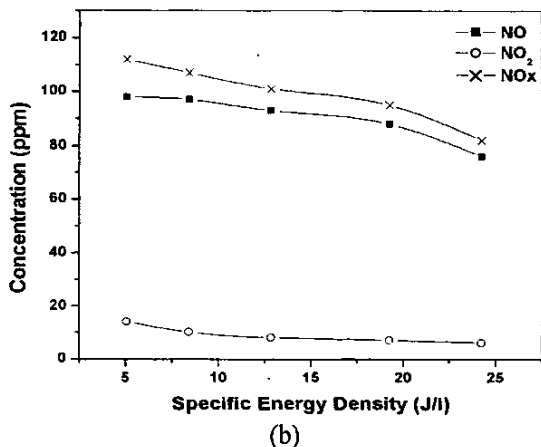
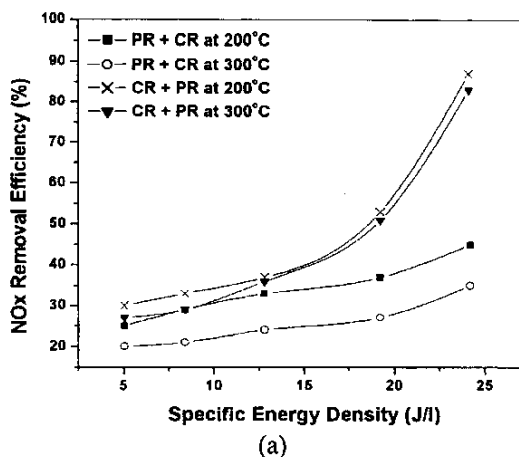
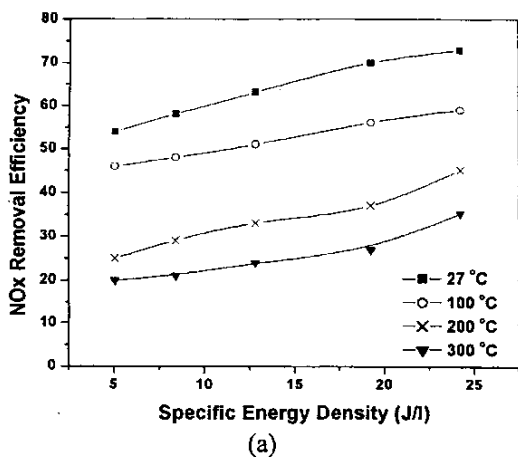


Figure 6. a, NO_x removal efficiencies for PR+CR (Pd/Al₂O₃) combination at different temperatures; b, concentrations of NO, NO₂ and NO_x for PR+CR (Pd/Al₂O₃) combination at 200°C.

Figure 7. a, comparison of NO_x removal efficiencies of PR+CR and CR+PR combinations (catalyst—Pd/Al₂O₃) at 200°C and 300°C; b, comparison of concentrations of CO and THC before and after treatment for both PR+CR and CR+PR combinations at 300°C.

to 300°C. This was because the NO₂ generated by PR was adsorbed on the catalyst surface initially and slowly dissociated back into NO. This was evident as high concentration of NO was still left after the treatment with PR+CR combination. Figure 6b shows the concentrations of NO, NO₂ and NO_x as function of specific energy density at 200°C with PR+CR combination. It is observed that the concentration of NO₂ was very low indicating the adsorption by catalyst whereas that of NO was high. This clearly showed that some of the NO₂ adsorbed on the catalyst was slowly dissociated into NO.

For CR+PR combination, it is found that at all temperatures the NO_x removal efficiency is very high when compared to that of PR+CR combination. For example, Fig. 7a compares the removal efficiencies of NO_x, for both the combinations, at 200°C and at 300°C. At 200°C, NO_x removal efficiency for CR+PR combination was about 40% higher than that of PR+CR combination and at

300°C, the difference was about 50%. The N₂O concentrations were monitored for both the combinations. There was only negligible increase in the concentration of N₂O in both the combinations.

Figure 7b compares the concentrations of CO and THC before and after treatment for both the combinations at 300°C. The performance of both the combinations was equally good with respect to CO and THC removal and there is only a negligible difference between the two.

It should be noted here that the above set of experiments were conducted with only one catalyst (Pd/Al₂O₃) in the CR but for two combinations, CR+PR and PR+CR. It is inferred that the CR+PR combination performs better in NO_x removal and henceforth the studies were reported for CR+PR combination. The advantages of using CR+PR combination include preventing the deposition of HNO₃ formed by PR on the catalysts (as observed

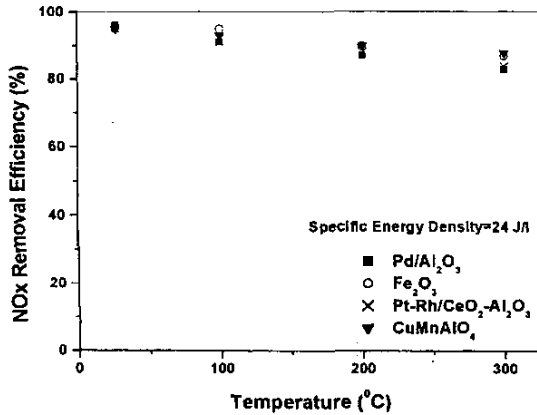


Figure 8. NOx removal efficiency for CR+PR combination using different catalysts as a function of temperature.

under PR+CR case) and achieving maximum NOx removal efficiency for a given temperature of the CR. Further experiments were carried out using the CR+PR combination.

Figure 8 shows the NOx removal efficiencies as a function of temperature of CR for CR+PR combination employing all the four catalysts. It can be observed that as temperature increases the removal efficiency decreases. At room temperature the NOx removal was 96% and at 300°C, it was 83% for Pd/Al₂O₃ catalysts. This is because at room temperature the catalytic adsorption aids the NOx removal. At 300°C, most of the NO was oxidized to NO₂ and reduction in total NOx concentration was reduced. However, this decrease is not very high and NOx removal efficiency is always above 80%. Hence, NOx can be removed effectively irrespective of the temperature of the catalytic reactor. All the catalysts showed maximum removal of CO and THC at 200°C and 300°C. This is because the catalysts become active only above a temperature of 200°C.

3.3.1 STUDIES WITH CR+PR COMBINATION (CR CONSISTS OF CATALYSTS IN THE FORM OF PELLETS)

Two kinds of catalysts were used here, Pd/Al₂O₃ (conventional) and Fe₂O₃ (non-conventional) in the pellet form. The performances of both the catalysts were studied in combination with PR. Figure 9a shows the NOx removal efficiencies achieved using these catalysts in CR+PR combination when CR is maintained at 300°C. The catalysts alone did not remove much NOx. For example, Pd/Al₂O₃ could remove only 35 ppm of NOx (about 20%) and Fe₂O₃ could remove only 15 ppm of NOx (about 10%) even at 300°C in the absence of discharge plasma. This is because at high oxygen atmosphere like diesel exhausts the catalysts oxidize most of the NO into NO₂ keeping NOx constant. But when CR is combined with PR, the

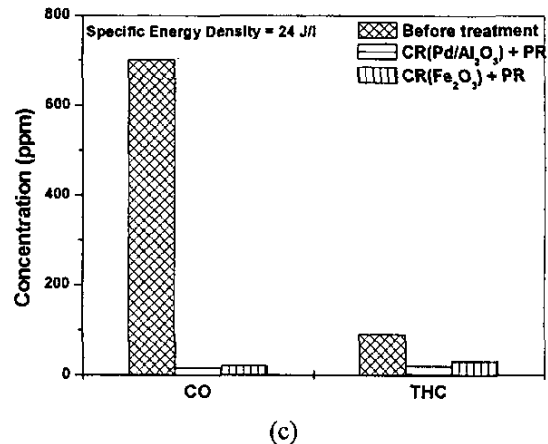
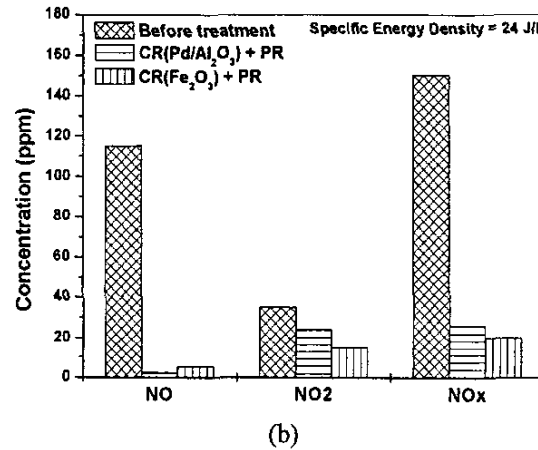
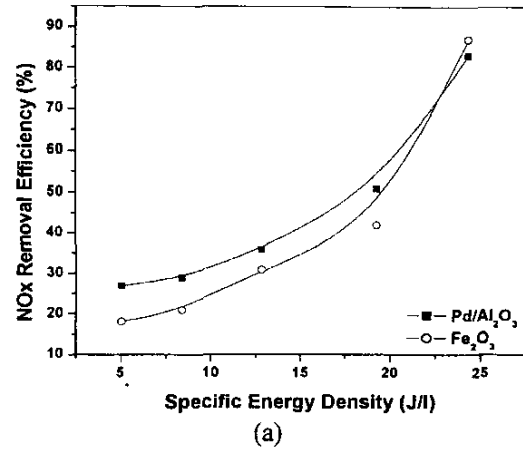


Figure 9. a, NOx removal efficiencies for CR+PR combination at 300°C (catalysts in the form of pellets); b, comparison of concentrations of NO, NO₂ and NOx before and after treatment for CR+PR combination at 300°C (catalysts in the form of pellets); c, comparison of concentrations of CO and THC before and after treatment for CR+PR combination at 300°C (catalysts in the form of pellets).

NOx removal efficiencies increased to 83%. Here the NOx removal was because of the presence of PR, the processes of which have already been explained. With Fe₂O₃ pellets

inside the CR the NO_x removal efficiency was slightly higher than that with Pd/Al₂O₃. However, at lower specific energy densities Pd/Al₂O₃ showed better performance. The N₂O production was very low with both the catalysts. Figure 9b shows the concentrations of NO, NO₂ and NO_x before and after treatment using Pd/Al₂O₃ and Fe₂O₃ catalysts in CR+PR combination when CR is maintained at 300°C.

Figure 9c shows the concentrations of CO and THC before and after treatment using Pd/Al₂O₃ and Fe₂O₃ catalysts in CR+PR combination when CR is maintained at 300°C. With catalysts alone, CO was almost completely removed for Pd/Al₂O₃ but when PR is placed after CR the CO concentration was slightly increased. This is because of CO₂ being reduced to CO and O₂ in presence of pulsed discharges in the PR. It is also true that partial oxidation of HC species will result in CO production. However, this increase is very negligible (15–20 ppm) and since diesel engines emit lesser CO concentration this increase should not be a problem. The same is observed with Fe₂O₃ catalyst also. Both the catalysts were found to be equally good in removing CO and THC when combined with a plasma reactor. It is inferred from these experiments that the catalyst Fe₂O₃ was found to be as good as conventional catalyst Pd/Al₂O₃ in the removal of CO and THC.

3.3.2 STUDIES WITH CR+PR COMBINATION (CR CONSISTS OF CATALYSTS IN HONEYCOMB STRUCTURE)

Current catalytic converters employ catalysts coated on a honeycomb structure for treating auto exhausts. We have conducted experiments with a section of one such honeycomb structure (Bharat Heavy Electricals Limited, India make) and coating the same with a conventional as well as a non-conventional catalyst. The honeycomb structure was then placed inside a glass tube forming a catalytic reactor. The plasma reactor was placed after this catalytic reactor and the details of the studies are as reported below. A commonly used conventional catalyst such as Pt-Rh/CeO₂-Al₂O₃ and a new, laboratory made non-conventional catalyst CuMnAlO₄ were used for coating on the cordierite honeycomb structure. Fig. 10a shows the NO_x removal efficiencies with these catalysts in CR+PR combination when CR is maintained at 300°C. The catalysts alone could not remove significant amount of NO_x. Both the catalysts removed only 30 ppm of NO_x out of total 150 ppm in the absence of pulsed discharges, which amounts to 20% of NO_x removal. However, when PR is placed after CR more than 85% of the NO_x was removed in the combined process with both the catalysts. Fig. 10b shows the concentrations of NO, NO₂ and NO_x before and after treatment for CR+PR combination when CR is maintained at 300°C. The N₂O production was low in both the cases.

Figure 10c shows the concentrations of CO and THC before and after treatment using these two catalysts in CR+PR combination when CR is maintained at 300°C. Catalysts alone oxidized CO to CO₂ to a maximum extent (nearly 100%) and the increase in CO (due to dissociation of CO₂) concentration because of PR was negligible. THC was also removed effectively by both the catalysts. It is observed from the above set of experiments that the new, laboratory made catalyst CuMnAlO₄ performed equally effective when compared to the conventional expensive catalyst. The new catalyst is also inexpensive though the exact cost per gram is yet to be evaluated. This laboratory made catalyst appears to be a promising alternative to the conventional catalyst.

3.4 RELATIVE PERFORMANCE OF THE REACTORS USED IN CURRENT STUDY

In this section, the results obtained by using different reactors are compared. In each kind of reactor, the best one was selected. Since not all the reactors were studied under different temperature conditions, only room temperature studies are compared. In the first reactor i.e. PR, PR without pellets was found to be better as compared to PR packed with dielectric pellets. In the second kind of reactor i.e. PACR, Fe₂O₃ catalyst showed better performance than CuO and Fe₂O₃. In the third reactor configuration, CR+PR, Pd/Al₂O₃ (pellets) and CuMnAlO₄ (coated on honeycomb structure) catalysts were proved to be better. All the above reactors were selected by taking into account the removal efficiencies of NO_x, CO and THC. Fig. 11a shows NO_x removal efficiencies for all these reactors at room temperature. PACR packed with Fe₂O₃ and CR+PR employing Pd/Al₂O₃ catalyst showed maximum removal efficiencies even at lower specific energy densities. This is because of high adsorption characteristic nature of these catalyst pellets at room temperature. CuMnAlO₄ also exhibited adsorption characteristics at room temperature but it was not as high as that of Fe₂O₃ as the catalyst is coated onto a honeycomb structure. The NO_x removal efficiency was 76% for PR without pellets and is less than that of the other reactors at room temperature.

Figure 11b shows the concentrations of CO and THC before and after treatment for all the reactors at room temperature. There was no change in initial concentration of CO for PR without pellets and CR (CuMnAlO₄)+PR reactors after the treatment. PACR packed with Fe₂O₃ could remove about 150 ppm of CO at room temperature itself. This is an important result as catalysts seldom work at room temperatures. With the reactor CR (Pd/Al₂O₃)+PR, there was a small increase in the CO (10 ppm) concentration from initial concentration. Though the catalyst adsorbed about 10 ppm of CO the PR placed after CR reduced CO₂ into CO. However, the increase is very small and can be ignored. The removal of THC is more with

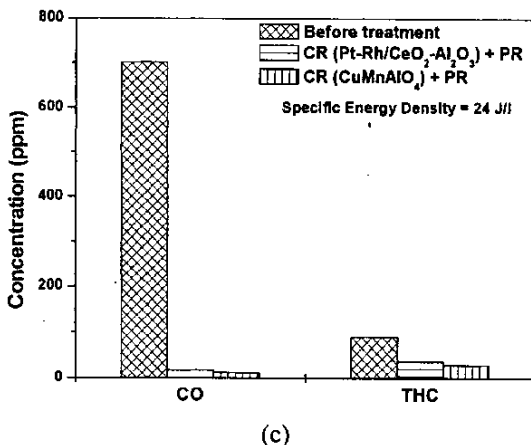
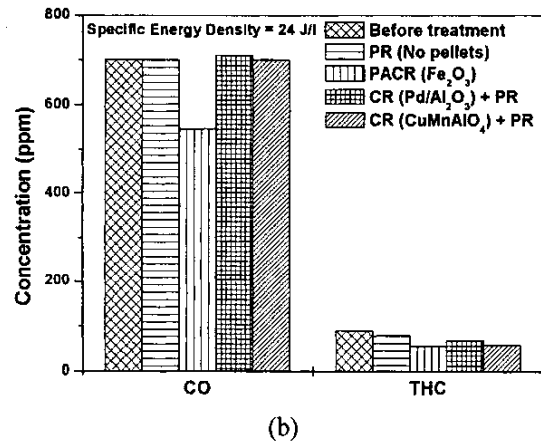
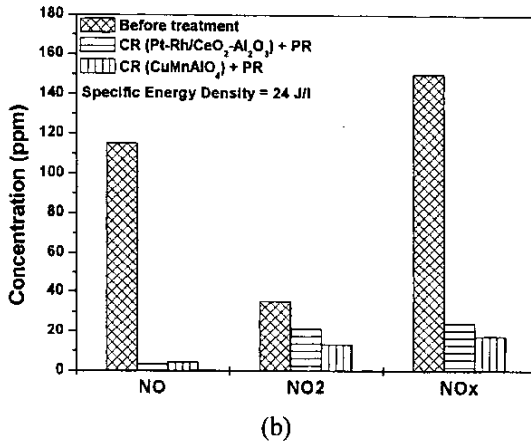
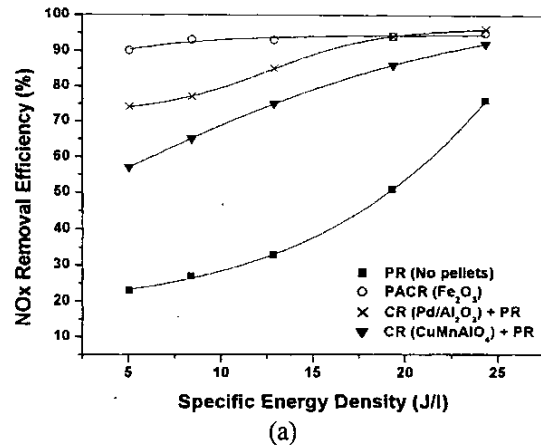
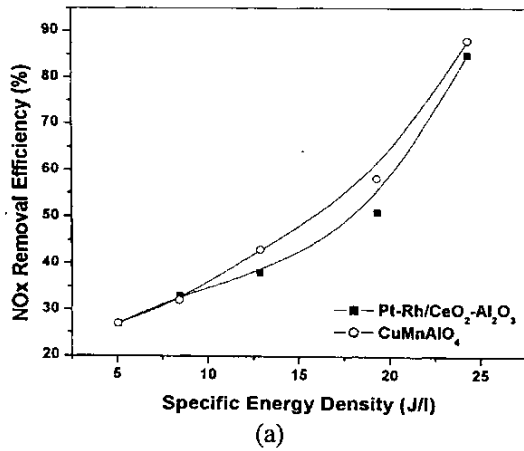


Figure 10. a, NOx removal efficiencies for CR + PR combination at 300°C (catalysts in the form of honeycomb); b, comparison of concentrations of NO, NO₂ and NOx before and after treatment for CR + PR combination at 300°C (catalysts in the form of honeycomb); c, comparison of concentrations of CO and THC before and after treatment for CR + PR combination at 300°C (catalysts in the form of honeycomb).

Figure 11. a, NOx removal efficiencies for different reactors at room temperature as a function of specific energy density; b, concentrations of CO and THC before and after treatment for different reactors at room temperature.

PACR packed with Fe₂O₃ and other reactors showed moderate performance. PR without pellets showed the least removal of THC.

4 CONCLUSIONS

THE major conclusions drawn from the present studies are,

1. The room temperature studies of plasma reactor (PR) packed with and without dielectric pellets showed that the NOx removal efficiency is higher for PR without pellets. Furthermore, when the exhaust gas was treated with a PR packed with BaTiO₃ pellets, an increase in CO was observed as well as the formation of higher levels of N₂O.
2. The performance of plasma-assisted catalytic reactor (PACR), where plasma and catalyst are in the same reactor, showed that even at room temperature some reactions were taking place on the surface of the catalyst in presence of pulsed discharges resulting in the removal of

NO_x, CO and THC. Though the removal efficiencies of CO and THC are not high in these studies, it is still quite interesting considering the fact that the catalysts are not active at room temperature.

3. CR + PR combination was found to be better than PR + CR combination. For CR + PR combination the NO_x removal efficiency was always high irrespective of the temperature of the CR.

4. In the absence of plasma the catalyst could remove NO_x only up to about 15–20% even at 300°C. However, in presence of plasma the NO_x removal efficiency was always higher than 80% for temperatures up to 300°C.

5. The studies conducted using a new, lab-made, less expensive catalyst (CuMnAlO₄) used in conjunction with pulsed discharge showed promising results. Interestingly, the new catalyst performed equally well in the removal of NO_x, CO and THC from the diesel engine exhaust when compared to that with conventional three-way catalyst.

ACKNOWLEDGMENTS

We thank the Department of Solid State and Structural Chemistry Unit, IISc and Bharat Heavy Electricals Limited, Bangalore, for providing some of the catalysts during the course of our experiments.

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