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Recent Advancements in Emission Reduction for Diesel Vehicles using Non Thermal Plasma Activation

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Abstract:- Controlling emissions from vehicles has always been a important topic to discuss due to its impact to our environment and it continues to be the same till date .The major constituents of the exhaust gases are improperly burnt hydrocarbons, oxides of nitrogen, carbon monoxide and particulate matter.The non thermal plasma technology could be used to remove the Particulate matter and to lower the emissions because of the NOx.The non heating plasma inside the exhaust set up is produced by a barrier discharge(dielectric).Plasma assisted MnO2 filter could also be used to increase the absorption of Nox which has more efficiency when ozone is added to the exhaust gases.The importance of removal of sulphur dioxide from this is because it affects the catalysts used to reduce Nox.Thus this paper is about the emission control and reduction technique in diesel vehicles.

Keywords:- *Plasma activation,Particulate matter,Nitrogen oxides,Dielectric barrier discharge,Plasma assisted MnO2 filter,Ozone.*

I. INTRODUCTION

Many new technologies and researches are being carried out to reduce the emissions to meet the lastest emission norm BS6. The corona, dielectric and discharges over the surface are produced from the gas.The formation of activated particles with main components results in the electron impact production. The conversion of NO started by discharges in different gas combinations are studied and evaluated. The energy spent for oxidation of nitrogen is reduced by hydrocarbons. The surface reactions are considered generally in plasma selective reduction systems. Plasma produces Carbon Monoxide.They produce aldehydes too.The non heating plasma reactor can affect the oxidation of particulate matter at the exhaust at a very less degree(temperature).

The main goal is to investigate the activation of materials like adsorbent and catalyst by an electrical discharge plasma. This has been used for the diesel engine exhaust treatment. For the purpose of investigation, several configurations are used. The results are discussed and a comprehensive comparison of all the techniques has been made.

II. COMPARISON BETWEEN BS4 AND BS6 NORMS

		BS-IV Norms			BS-VI Norms		
Petrol Vehicles	**Unit**	M & N1 Class I	N1 Class II	N1 Class III	M & N1 Class I	N1 Class II	N1 Class III
CO	g/ km	0.50	0.63	0.74	0.50	0.63	0.74
HC	g/ km	-	-	-	-	-	-
HC+NOx	g/ km	0.30	0.39	0.46	0.17	0.195	0.215
NOx	g/ km	0.25	0.33	0.39	0.08	0.105	0.125
PM	g/ km	0.025	0.04	0.06	0.0045	0.0045	0.0045
Diesel Vehicles	**Unit**	M & N1 Class I	N1 Class II	N1 Class III	M & N1 Class I	N1 Class II	N1 Class III
CO	g/ km	1.00	1.81	2.27	1.00	1.81	2.27
HC	g/ km	0.10	0.13	0.16	0.10	0.13	0.16
HC+NOx	g/ km	-	-	-	-	-	-
NOx	g/ km	0.08	0.10	0.11	0.060	0.075	0.082
PM	g/ km	-	-	-	0.0045	0.0045	0.0045

M category include motor vehicles having at least four wheels and for the carriage of passengers
N1 Class I include Power-driven vehicles having at least four wheels and for the carriage of goods (< 3.5 tonnes)

Fig 1

Basically the idea behind our selection of topic is to reduce the emission coming out of the vehicle to satisfy the upcoming BS6 emission norms.

III. THE AUTOMOTIVE INDUSTRY OF INDIA AND THE BHARAT STAGE-VI NORMS

- The quicker enhancements of the automotive industry in India has paved way for obstacles such as causing pollution to the surrounding environment.
- The Government of India has decided to introduce and implement Bharat Stage VI norms from April 2020 in 15 major cities of the country to reduce the emission levels.
- Since we are bypassing BS-V, Indian original equipment manufacturers (OEMs) are now looking at a very big task ahead of themselves. Fine tuning in existing engine manufacturing techniques and technology of fuel helps in sustainable mobility.
- This paper explains in brief about various means of implementing sustainability in automotives namely, engine size reduction, onboard diagnostics, use of after treatment devices, using alternate fuels,advanced combustion methods,electric and hybrid vehicles.
- Using hydrogen as an alternate fuel may serve as an excellent remedy but it cannot be implemented since hydrogen is inflammable and is to be stored properly. So, advanced techniques are to be adopted to satisfy the norms..

IV. INFORMATION ABOUT THE METHODOLOGY

References have been taken from similar journals to arrive at the experimental set up .The experimental setup comprises of a two cylinder, four-stroke, indirect diesel injection engine. This experiment is to be conducted under stable conditions at 2kW engine load which remains to be constant. The rate of flow of exhaust gas passing through the flow reactor was kept constant at 3.2 L/min for all experiments.These values are standardised based on successful experiments from other journals. The cooling process of the reactor is done via a water trap. Risk of electrocution is avoided by removing condensate water using a water trap.The plasma is created inside the reactor using a device called dielectric barrier discharge (DBD). The barrier discharge is found to be an excellent source of energized electrons . The setup consists of two tubes of quartz material which is placed one inside another i.e concentric structure, each with thicknesses of walls about 2 to 3 mm. The outer diameter of the internal tube is taken to be 11.5 mm and inner diameter is designed to be 7.5 mm. In a similar way for the outer tube, the internal and external diameters are 18 and 22 mm, respectively. Exhaust passes through the gap between these two quartz tubes.The discharge gap is 3 mm. Heat resistors are added at the two ends of the reactor tubes . The centre electrode is of diameter 6mm , which is passed through the central axis of the inner tube. The external boundary of the outer tube is grounded by using aluminium foil. The barrier discharge device length is found to be 250 mm. By boosting a neon yellow transformer at 50 Hz is applied between the electrodes to form the plasma and the AC voltage source is obtained. In between the ground and the outer edge electrodes a capacitor is used. The experiment is proceeded by applying a range of voltages from 7 kV to 13 kV at a constant frequency of 50 Hz. Filter papers were used to collect samples of particulate matter at the reactor exit. Different samples have been collected for each voltage level ranging from 7 to 13kV, and a combustion-type PM analyser which measures soot particles, organic fraction of soluble components and sulphate. For the purpose of finding the rate of particle deposition within the reactor setup, size distribution of particulate matter was measured at reactor entry and reactor exit at no voltage condition. Thereafter, the plasma was introduced inside the DBD reactor . The distribution of size and composition of particulate matter results have been analysed to obtain a better understanding of plasma effects over proportion of particulate matter. Moreover, the effect of non heating plasma on different oxides of nitrogen has been taken into consideration. They are measured by a technique called fourier transform infrared in the entry and exit of the reactor at various levels of voltage.

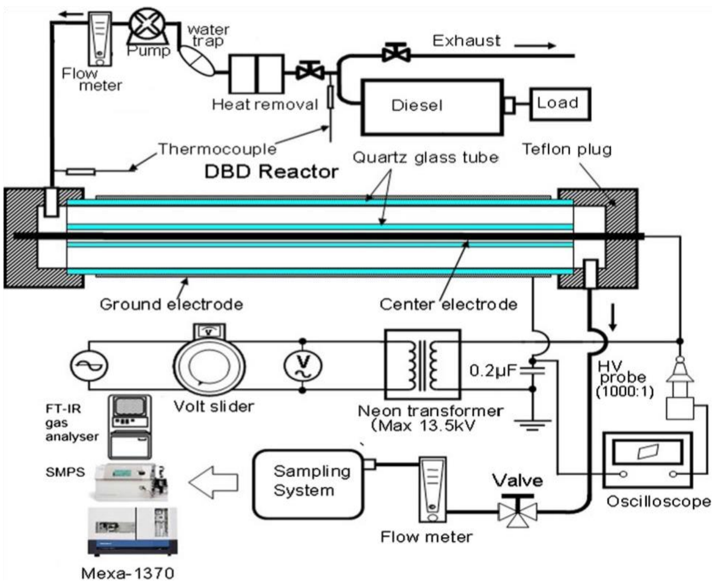

Fig 2:- DBD reactor setup

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➢ *Specifications of discharge power :*

In order to introduce the plasma inside the exhaust , AC voltage obtained from boosting the transformer using neon ,at 50 Hz was applied between the electrodes of the barrier discharge reactor. The primary input voltage is measured using a slider voltage device and transformer with less number of turns. The transformer with more number of turns is used to convert the input voltage into high voltage upto 15 kV. The load on the oscilloscope is minimised by inserting a high-voltage probe into the circuit. The charge which is stored in the barrier discharge reactor is defined by introducing a capacitor between the ground and marginal electrode.

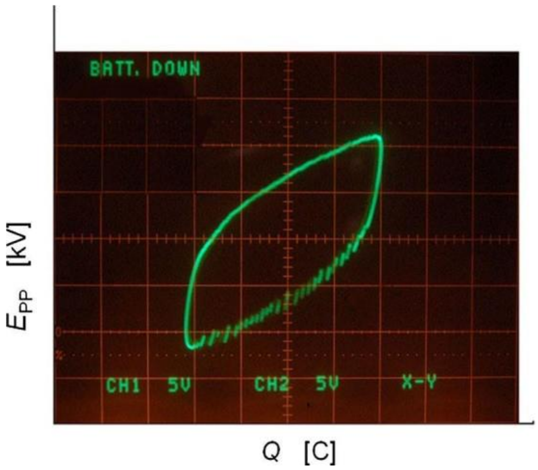

Fig 3:- E–Q Lissajous on oscilloscope

The power of discharge inside the reactor is measured using the charge–voltage Lissajous technique. This represents the amount of charge in the capacitor and the input voltage between the electrodes obtained from an oscilloscope. The above figure area indicates the energy of electrical discharge per cycle , and the average power of discharge can be premeditated by multiplying frequency and the energy per cycle. The voltage ranges from 7 kV to 13 kV and for all voltages the Lissajous figures have been secured by taking photographs from the oscilloscope. The image processor is used to calculate the discharge power at varying levels of voltage. From the experiment it was found that the condition of non heating plasma is very infirm inside the exhaust . When there is an increase in voltage , the discharge power increases. This is experimentally seen, wherein the discharge power jumps to about 1.5 W at 13kV. This spot is the juncture at which the plasma is quite strong and it can be expected that a large amount of ions and free moving radicals react inside the exhaust.

➢ *Plasma assisted MnO2 filter:*

This is a technology that combines the sulphur reduction properties of MnO_2 with the working of ozone from a desirable pressure with plasma technology. The desulfurization and denitration reactions are promoted by plasma activated chemical species.

The reaction of MnO_2 with sulfur and oxides of nitrogen produces sulfates and nitrates respectively. The SO_2 and NO_2 interactions reduct the efficiency of MnO_2 catalysts by removing both the species. By analysing the MnO_2 catalyst material after exposure to exhaust gas containing both SO_2 and NO2, it instills the production of both manganese nitrate and manganese sulfate .

The evaluation was based on the reaction of ozone on the performance of MnO_2 catalyst for SO_2 and NO_2 reduction. The dielectric barrier discharge method generates an atmospheric-pressure non-equilibrium plasma. From this study it is understood that, by introducing ozone at a low concentration the performance of the catalyst in reduction of both SO_2 and NO_2 was improved. The improvement in NO_2 reduction was effective.The ozone introduction seems to give a reaction which helps in reducing nitrogen oxides to nitrogen. Initially 99% of SO_2 and NO_2 were eliminated from the stream of exhaust . Some experiments were conducted by researchers that have even proved that there are completely nil emissions of NO_x while using plasma assisted MnO2 filters in the presence of oxides of sulphur. The plasma-assisted filter seems to instill the reduction of SO_2 because of SO_3 generation and also it will reduce oxides of nitrogen to nitrogen.

➢ *Experimental setup and methodology*

The amorphous citric acid method is used to prepare energized manganese dioxide with several defined areas and commercialised MnO_2.

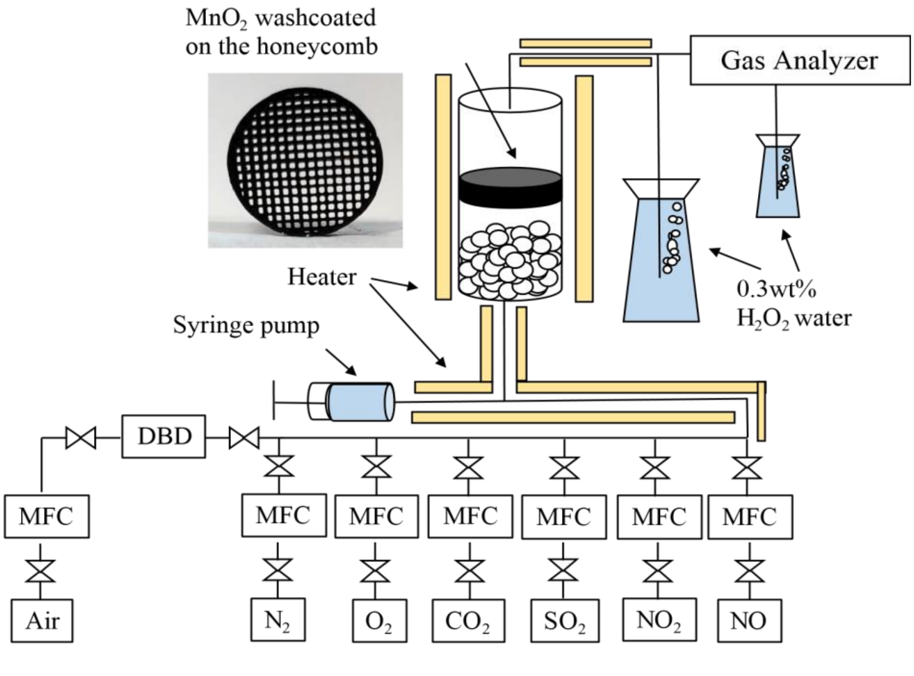

Fig 4:- Mass flow controller

The defined area of surfaces is managed by varying the concentration of tricarboxylic acid.The absorption performance result of sulphur dioxide is measured using a thermogravimetry device.It is found from the experiment that the absorption performance of SO_2 is increased by increasing the surface area. With an expanse area of 320 m^2/g,other experiments were conducted since it is found to be a standard value. The results obtained from the experiments showed that high specific surface area manganese dioxide comprises an average pore diameter of 52 Å and a particle diameter of 3.0μm.

The production of a counterfeit diesel gas is controlled by a gas controlling unit c i.e. a high specific surface area manganese dioxide filter and the concentration after passing through the high specific surface area manganese dioxide filter is measured by using an electrically actuated chemical gas analyser. The NO, SO_2 and NO_2 proportions were analysed using this electrically actuated chemical gas analyzer .The ozone is generated by using a dielectric barrier discharge unit. The concentration of ozone was measured by using KI reduction titration method involving $Na_2S_2O_3$. The neutralization of outflowing gas is done and the H_2O_2 solution is used to collect them.

➢ *High Specific Surface Area(HSSA) MnO_2 filter :*

The gas purification performance is analysed by using an MnO_2 honeycomb filter in the setup under large space velocity conditions by assuming practical onboard usage for transports. Al_2O_3 honeycomb filter is augmented with HSSA MnO_2 filter . The diameter of this filter is taken to be 30 mm, thickness of the filter as 835mm, and the surface thickness of Al_2O_3 was 0.45 mm in a square shaped duct. The base of Al_2O_3 filter was immersed into the damp solution of high specific surface area manganese dioxide and Al_2O_3 as the binding component. At 473 K ,the calcination of HSSA MnO_2 filter is accomplished by using a furnace. The quantity of supported high specific surface area manganese dioxide was limited to approximately 45 to 50 g/L to remove the impact of surface dispersal defiance on the performance of gas refining .

V. RESULTS OBTAINED FROM THE EXPERIMENT

The quality of air is maintained by desulfurization by using $DeSO_x$ filters . The $DeSO_x$ filter is investigated and also it captures sulphur at minimal temperature. To establish this, high specific surface area manganese dioxide was mainly focussed . The effectiveness of sulphur dioxide in capturing solo particles and the sulphur reduction advanced attributes of high specific surface area manganese dioxide in a stuffed package under large space velocity and minimal conditions of temperature were studied. The following is the understanding obtained from this study:

The high space surface area manganese dioxide filter is excellent at capturing sulphur dioxide. SO_2 is captured at a rate of 1.2 10^3 lg_{SO2}/ (g_{MnO2} min) at 270 C is found in a thermogravimetry experiment. At minimal temperature conditions, it is understood that rate of reaction of sulphur dioxide depends on reaction inside the element.Under large space velocity condition 99% percent of SO_2 is captured. For deep sulphur reduction the process has enough reaction rate of sulphur dioxide. This material has a maximum absorption rate of enough sulphur dioxide in order to encapsulate higher quantities of sulphur dioxide gas. In order to achieve deep sulphur reduction at minimal temperature and under large space velocity conditions, the reaction rate of the component needs to be enhanced.

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- *Effect of plasma activation on particle composition of diesel:*

The efficiency of heat resistant plasma on minute carbon particles, soluble organic fraction and particles of sulphate were analysed. Samples of particulate matter were collected on filters of silica material at the exit end of the reactor and then analysed.With respect to the efficient compilation , most of the collected particulate matter on the filters are presumed to form a mode of collection.There was no plasma formed inside the exhaust ,at no voltage mode. So,it is inferred from the test that soluble organic fraction is considerably more when compared to other contents. When being measured at the reactor exit, the fraction of sulphate was found to be very low from which it can be inferred that the plasma technology does not affect the sulphate content.

When the input voltage is increased, a continuous decrease in proportion of particulate matter can be achieved. The concentration of carbon particles at the reactor exit when there is no plasma is found to be 0.0011 mg/L, and it decreases to 0.0002 mg/L when there is an increase in voltage up to 13kV. This in equivalence to 74% of removal of particulate carbon mass using plasma technology . This happens because of the property oxidation present in plasma technology.Nitrogen dioxide , ozone and other effective oxidizing components available in plasma technology helps in the removal of carbon soot. These results infer that plasma is effective in removing carbon particulate matter. The main reactions for oxycarbon based particles in state of plasma can be inferred as below:

$C + 2NO_2 \rightarrow CO_2 + 2NO$
$C + NO_2 \rightarrow CO + NO$
$C + O_3 \rightarrow CO_2 + (½)O_2$

At a voltage of 10.6kV there was a great drop down in the concentration of soluble organic fraction about 38%.Eventually there was an increase in concentration when the applied voltage was 11 to 13kV . This outcome is with agreement to the results. While at these voltages levels the number of particles at mode of nucleation uprises, with a significant decline in particulate matter numbers in collective mode. When these voltages are applied there is a significant drop down in the particulate matter number and so it can be presumed that some soluble organic fraction constitutes reduced particles clinging on to the surface and forming some more damp particles. This assumption is to be studied in a detailed manner in future.

- *Effect of energy density on Particulate Matter removal :*

Consumption of energy need to be accessed correctly as it is an integral obstacle in the plasma applications for the reduction and removal of Particulate Matter. Energy density is used for calculating the discharge energy and defined as the ratio of power discharged to the exhaust flow rate. The removal rate of the plasma applications are affected by the magnitude of energy density The impact of energy density on removal rate of total particulate matter is also studied as a reference to conclude the results . The PM numbers are to be increased in nucleation mode particles at 12kV and 13.6 kV, so the PM removal has been considered for particles not less than 30 nm.

Discharge power and removal efficiency are(Okubo et al. 2004): directly proportional to each other. At first, the removal rate for the particles not less than 30 nm is about 60 %.It increases to about 76 % at an energy density of 10.1 J/L. Almost all particles not less than 31 nm can be removed when the power discharged is in the closest to 27-28 J/L.

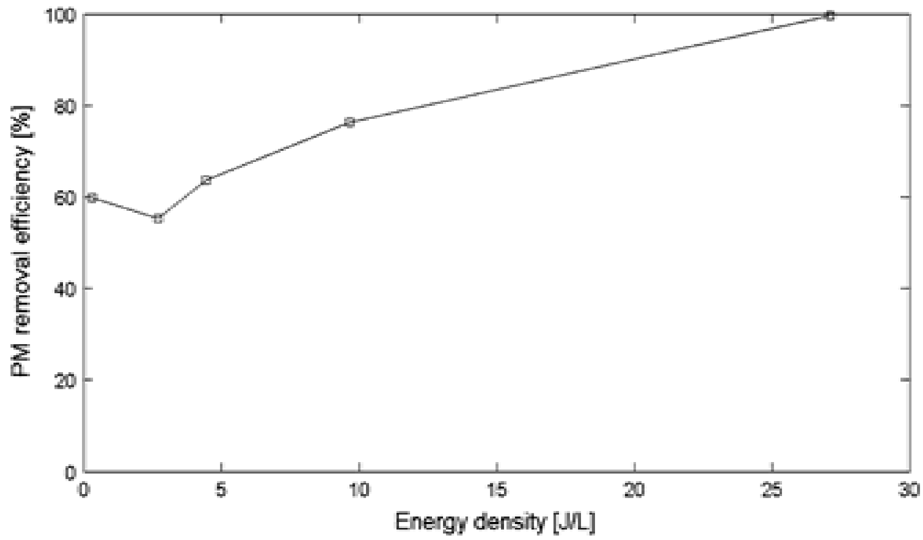

Fig 5

- *Effect of NTP on Box:*

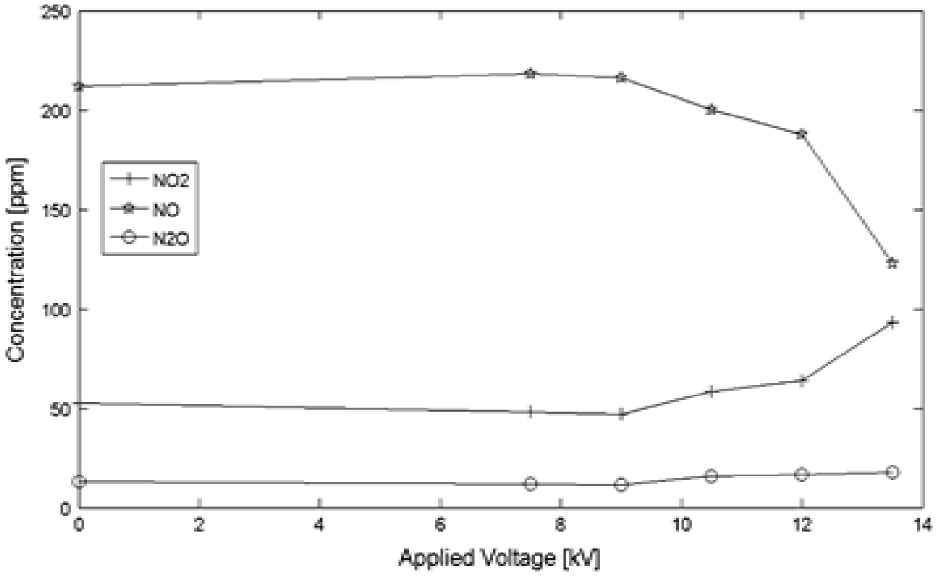

Fig 6

The NOx reduction reactions by involving Plasma technology can be considered in couple of main divisions .Here NOx molecules can be changed to N2 and O2 molecules under plasma state through the following reactions:

$N_2 + e \rightarrow N + N + e$
$NO + N \rightarrow N_2 + O$
$O_2 + O \rightarrow O_3$
$N_2 + e \rightarrow N_2(A) + e$
$N_2(A) + NO \rightarrow N_2 + N + O$
$N_2(A) + N_2O \rightarrow 2N_2 + O$
$NO_2 + N \rightarrow N_2 + O_2$

where $N_2(A)$ denotes that N_2 is in a excited state.

In the second category, the dominant reaction is oxidation of NO to NO2 by the following reactions:

$O_2 + e \rightarrow O + O + e$
$NO + O \rightarrow NO_2$
$O_2 + O \rightarrow O_3$
$NO + O_3 \rightarrow NO_2 + O_2$

References and experimental setups are taken from different literatures and combined to express our views in it .

The impact of NTP on NOx has been noted down and understood during the experiments. A Fourier transform infrared spectroscopy gas analyser is used to analyse the samples.

The range of the applied voltages have been changed from 7.6 to 13.6 kV and NO, NO_2, N_2O and entire NOx concentration have been taken into account. The change in the concentration can be seen to be started after 9.1 kV. Therefore, until this point plasma has not been strong enough to make any drastic change in concentrations of nitrogen oxide. NO is oxidised to NO_2 because of the presence of different active oxygen species and ozone . A more detailed study on this topic could result in more advanced usage of ozone. NO concentration is reduced by 73 to 75% and NO_2 concentration is raised by 76 to 78 % by applying the highest possible voltage at 13.6 kV while conducting the experiments. On the other hand, a small raise in N_2O concentration has been found during the experiments. The initial concentration of N_2O was about 13 parts per million when there is nothing inside the exhaust, and this concentration was raised to about 18 to 19 ppm when applied voltage was 13.6 kV. This raise is happening because of the reaction of NO_2 with the produced N radicals during the procedure of plasma process by the following reaction .
$NO_2 + N \rightarrow N_2O + O$

- *Plasma activation on reduction of NOx (Non thermal plasma):*

The effect of NTP on NOx emission reduction is studied. The maximum energy density is restricted by the voltage applied at 13.4 kV to 14 kV. If the energy density is increased a steady increase in NOx removal rate can be noted. NOx removal rate is less, while the energy density is changing up to 9 to 10 J/L. However, a significant increase in NOx removal rate has been observed when energy density has been raised to 26-27 J/L. For the given configuration, the maximum NOx removal efficiency is about 20 % approximately .The total NOx reduction cannot be achieved fully from considering the use of plasma alone on NO, NO_2 and N_2O only. Other nitrogen oxides such as NO_3 and N_2O_5 can be formed, and they should be considered in the upcoming usages as these compounds could be used for various other reasons and applications .

VI. CONCLUSION

The plasma (NTP) discharges method in found as to be a convincing method to reduce NOx and Particulate Matter emissions in diesel exhaust and NOx and starting hydrocarbons at low temperatures in petrol vehicle exhaust.The diesel and petrol undergo some changes chemically,when exposed to plasma.The presence of oxygen is dominated by the oxidation process. Reduction of NOx effectively is the primary purpose of the plasma method used in exhaust gases. Plasma combined with catalysts, which are often referred as the "plasma-assisted catalysts", can be used in the reduction of Nitrogen Oxides. Plasma by nature has the capacity to improve catalyst selectivity and and also has good removal rate. Plasma catalysts have shown their effectiveness by removing about 48-50% of NOx at an economic fuel penalty of less than 4-5%.Therefore, this could serve as the most suitable method adapted in emission reduction systems.

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