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Electrical Discharge Plasma for Activation of Adsorbent and Catalytic Materials for Diesel Engine Exhaust Treatment

R. Rajagopala*, N. Jagadisha, A. D. Srinivasan

Department of Electrical & Electronics Engineering, Sri Jayachamarajendra College of Engineering, Mysore - 570 006, Karnataka, India.

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ABSTRACT

A detailed investigation on the activation of materials like adsorbent and catalyst by electrical discharge plasma is carried out. This property has been used for the treatment of diesel engine exhaust. For the purpose of investigation, several configurations are used. The results are discussed and a comprehensive comparison of all the techniques has been made. The effectiveness of the technique with regard to pollutants control and byproduct reduction is discussed. A high NOx removal efficiency is achieved when double step electrical discharge plasma activates red mud catalyst and double step electrical discharge plasma activates MS13X adsorbent. In double step electrical discharge plasma activated catalyst technique, the red mud catalyst was operated without any additional HC or ammonia at 400°C, whereas the double step electrical discharge plasma activated adsorbent technique was operated at low temperature (<200°C).

Key words: *Electrical discharge plasma, Diesel engine exhaust, Pollutants control, MS13X adsorbent, Red mud catalyst, Double step, NOx removal, and byproduct reduction.*

1. INTRODUCTION

Controlling emissions from combustion engines particularly from diesel driven ones is a challenge to the researchers across the globe. In the case of diesel engines, despite the modifications in engine design and improvement in after treatment technologies, a large amount of NOx and CO continue to emit and attempts to develop new catalysts to reduce these pollutants have been so far less successful. The electrical discharge plasma (non-thermal plasma) is a prominent non-conventional technique, which can produce chemically active species that can facilitate the removal of NOx and other pollutants within diesel exhaust [1-3].

Further, electrical discharge plasma activates catalysis and adsorption when it is combined with a catalyst and an adsorbent. Plasma associated catalysis and adsorption are gaining lot of importance [4-9].

The objective of the study is to investigate the activation of materials like adsorbent and catalyst by an electrical discharge plasma. This property has been used for the treatment of diesel engine exhaust. For the purpose of investigation, several configurations are used. The results are discussed and a comprehensive comparison of all the techniques has been made. The effectiveness of the technique with regard to pollutants removal and byproduct reduction is discussed. The plasma and adsorbent reactors are operated at room temperature while catalyst reactors are operated at high temperature.

2. EXPERIMENTAL

In this section, experimental setup and materials used in this work are discussed in detail.

2.1. Experimental Setup

The schematic of the diesel engine exhaust treatment is shown in Figure 1 using double step electrical discharge plasma activated adsorbent/catalytic technique.

A 3.3 kW diesel engine was used as the exhaust source. The whole of the exhaust from the engine was not treated in view of infrastructure limitation in the laboratory.

Further, as our objective is to examine the underlying principle involved in the exhaust treatment, only a part of the main exhaust from the engine was treated.

A 30 kV pulse source was used in the studies. Throughout the experiments, the frequency of the

*Corresponding Author:
E-mail: rajagopala_73@yahoo.com
Phone: +91-9343312865

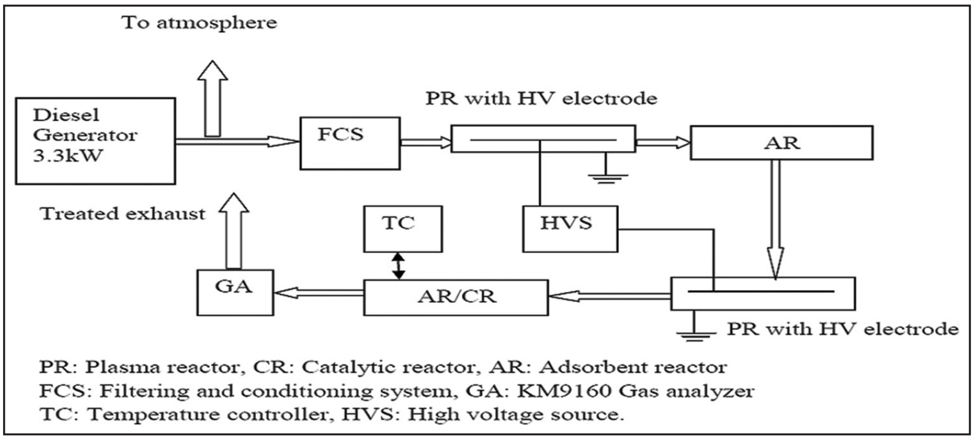

Figure 1: Diesel engine filtered exhaust treatment using double step electrical discharge plasma activated adsorbent/catalytic technique.

pulses was kept constant at 100 pps. The pulse voltage applied to the plasma reactor (PR) was measured using a 150 MHz digital oscilloscope (DL1540, 200 MS/s, Yokogawa) connected through a 2000:1 voltage divider (EP-50K, 50MHz, PEEC, Japan). The current was measured using a current probe (P6021, Tektronix).

A dielectric barrier electric discharge reactor (referred to as PR) was employed in the present studies. The PR was a cylindrical glass tube (inner diameter: 15 mm and outer diameter: 17 mm) consisting of a stainless steel rod of thickness 1 mm as the inner electrode and aluminum foil wrapped over the glass tube as the outer electrode. The effective length of the reactor where discharge took place was 30 cm. The experiments involving PR were carried out at room temperature.

The catalytic reactor was made of quartz glass tube of 15 mm diameter and effective length of 38 cm and whole reactor was filled with red mud catalytic material in the form of pellets. The adsorbent reactor was made of quartz glass tube of 15 mm diameter and the effective length of 38 cm and whole reactor was filled with MS13X adsorbent material in the form of pellets.

In the experiments filtered exhaust, filtering of the exhaust was done first using filtering and conditioning system (FCS). The filtered exhaust was then allowed to enter the treatment zone.

The exhaust gas was made to pass through a tube containing steel wool, to filter out oil mist and macro-sized particulate matter. The exhaust was then passed through FCS. The FCS consists of three filters and a moisture separator. The function of the FCS is to filter out the carbonaceous soot, any coarse particles, oil mists, and water from the exhaust gas. Proper care has been taken in the development of this conditioning system so as not to affect the sample gas components. The measurement of NOx and other gaseous pollutants present in the diesel engine exhaust gas was carried out accurately using a QUINTOX KM 9160, Kane International UK gas analyzer.

2.2. Materials

In this section, detailed discussion about the two types of materials used in the present work, i.e., catalysts and adsorbents are made.

2.2.1. Catalyst materials

The catalyst material used in the present work is red mud catalyst.

Red mud is solid waste product of Bayer process (refining of bauxite to produce alumina), a typical Bayer process plant produces two times red mud as alumina. It is a mixture of solid and metallic oxide bearing impurities; it is one of the most important disposal problems for aluminum industry. In general, ferric oxide (Fe_2O_3) is the major constituent of red mud and gives it its characteristic brick red color. The surface area of red mud powder lies between 20-30 m^2/g. Red mud has a fine particle size distribution with 90% by volume below size of 75 μ, and high surface area. The use of noble metals as catalyst suffers from problems like a high price, low stability, volatilization and poisoning, whereas metal oxides from industrial waste are more resistance to poisoning and less active compared to noble metal, however, their low cost makes them desirable.

Thus, the use of industrial waste or naturally occurring solids containing catalytically active metals such as Fe, Ni, and V as a substitute to commercial catalysts can help reduce the cost associated with the use of catalyst. Red mud which mainly contains a mixture of oxides of Fe, Al, Ti and smaller amounts of Si, Ca and Na is a potential alternative catalyst at the commercial scale. Even after minor treatments, it is still cheaper than both noble metals and metal oxides. For the destruction of certain air emissions, red mud has been studied for the selective catalytic reduction of nitric oxide.

2.2.2. Adsorbent materials

We are considering only physical adsorption since the pollutant removal has been effectively accomplished by physical adsorption. Physical adsorption is caused mainly by Vander wall's forces and electrostatic forces between adsorbate molecules and the atoms that compose the adsorbent surface. Thus, adsorbents are characterized first by surface properties such as surface area and polarity.

Molecular sieves are synthetically produces zeolite (metal alumina silicates) characterized by pores and crystalline cavities of uniform dimensions. Molecular sieves have pore size 3-10 Å, which are uniquely determined by the unit structure of the crystal. These pores will completely exclude molecules, which are larger than their pore diameters. The effective surface area of molecular sieves is in the range of 400-800 m^2/g. Type 3A, 4A and 13X are the commonly available adsorbents which show NOx adsorption. Among them, the best NOx adsorption is given by the type 13X. It is a modified form of the sodium Zeolite with pore diameter of 100 nm. Aromatic and branched chain hydrocarbons can also be adsorbed on type 13X molecular sieves. These are available in the form of pellets, beads, and powders.

3. RESULTS AND DISCUSSION

Before treating the exhaust gas, the concentrations of CO, CO_2, NO, NO_2, NOx, O_2, and aldehydes were measured. Table 1 shows the typical concentrations of the pollutants under 0% load and 27.27% load conditions.

In Table 1, NOx means sum of concentrations of NO and NO_2. The concentrations of NO and NO_2 were measured individually and then added to get the NOx concentration. In this work, the pollutant removal results were presented in terms of energy density (ED). The ED was calculated as the ratio of average discharge power to the gas flow rate and is expressed in joules per liter J/L. The ED and removal efficiency are given by Equations (1) and (2), respectively.

Table 1: Initial concentration of main pollutants in the diesel engine exhaust.

Main pollutants	0% load (No load)	27.27% load
CO_2	0.10%	0.60%
CO	323 ppm	229 ppm
NO	110 ppm	257 ppm
NO_2	30 ppm	69 ppm
NOx	140 ppm	326 ppm
O_2	20.70%	20.50%

ED = Discharge power (W)/Gas flow rate (L/s), J/L (1)

Removal efficiency = [Initial concentration (I) − Concentration after treatment (F)]/Initial concentration (I) (2)

3.1. NOx Removal by Catalyst Process

A nonconventional catalyst, red mud, in the form of pellet was been used. The catalyst was operated in the temperature range of 200-400°C to facilitate decomposition reaction.

The reduction of oxides of nitrogen to N_2 in the presence of iron and its oxides by CO is investigated by Hayhurst and Lawrence [10]. The metallic iron was far superior to its oxides in decomposition of NO to NO_2. NO reduction by CO over Fe_2O_3 takes place via the following reactions:

$$12CO + 4Fe_2O_3 \longrightarrow 12CO_2 + 8Fe \quad (3)$$

$$8Fe + 12NO \longrightarrow 6N_2 + 4Fe_2O_3 \quad (4)$$

$$CO + NO \longrightarrow CO_2 + 1/2\ N_2 \quad (5)$$

The reaction favoring NO_2 removal is

$$8Fe + 6NO \longrightarrow 3N_2 + 4Fe_2O_3 \quad (6)$$

Similarly, Al_2O_3 in red mud favors the reduction of NOx in the presence of formaldehydes which are present in the diesel exhaust. The favorable reaction pathways for NO and NO_2 are:

$$CH_3O + NO \longrightarrow CH_3ONO \quad (7)$$

$$CH_3O + NO_2 \longrightarrow CH_3ONO_2 \quad (8)$$

Figure 2 shows NOx removal efficiency in red mud catalyst material under no load and load condition. It is observed that NOx removal efficiency is less under load condition compared to no load condition for a given temperature. This can be attributed to the high pollutant concentration at load condition which reduces the activity of the catalyst in turn resulting in reduced NOx removal under load condition [8].

3.2. NOx Removal by Electrical Discharge Plasma Process

Figure 3 shows NOx removal efficiency of electrical discharge plasma process. It is observed that, with increase in ED, NOx removal efficiency also increases. The removal may be due to the variety of reactive species formed in electrical discharge plasma, resulting in a wide spectrum of reaction path ways. The NOx removal efficiency depends on reduction of NO. The NO to NO_2 conversion reactions involving O/O_3 radicals are shown below:

$$O_2 + e \longrightarrow O + O \quad (9)$$

$$NO + O \longrightarrow NO_2 \quad (10)$$

$$O_2 + O \longrightarrow O_3 \quad (11)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (12)$$

3.3. NOx Removal by Electrical Discharge Plasma Activated Catalyst Process

In this section, single step and double step electrical discharge plasma activated catalyst material process with regard to NOx removal is presented.

Figure 4 gives NOx removal by electrical discharge plasma activated catalyst process for both single step and double step arrangements. The single step plasma activated catalyst with red mud as catalyst, gives a NOx removal of around 80% at ED of 15 J/L, under no load condition. The NOx removal efficiency of red mud catalyst alone at 400°C is around 30% and by plasma at 15 J/L alone is around 40%. Thus, it is seen that the plasma activated catalyst performs better showing synergy characteristics. This can be explained as below: When catalyst alone treats diesel engine exhaust, the catalytic action is not significant, as the aldehydes concentration is low. The plasma being oxidizing environment, produces more NO_2 and aldehydes. In the plasma activated catalyst process, exhaust entering the catalyst contains more NO_2 and aldehydes and as said earlier, Al_2O_3 in red mud favors the NOx removal in red mud in the presence of aldehydes (refer reactions [7] and [8]). As a result, plasma activates catalyst and combined process brings in synergy. Similarly in the double step arrangement, a high NOx removal close to 84% is achieved.

3.4. NOx Removal by Adsorbent Process

In this section, the NOx removal using nonconventional adsorbent, MS13X, in the form of pellet has been discussed. The adsorbent was operated at room temperature. From the Figure 5, it is observed that NOx removal is not much affected by engine loading in the adsorbent. The exhaust has more NO molecules than NO_2. Hence, NOx removal efficiency is less with MS-13X owing to its pore size and internal surface area [5].

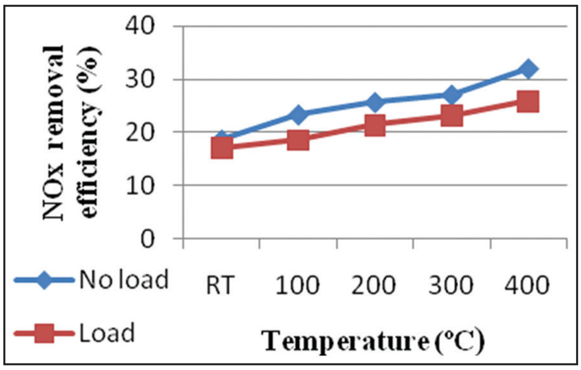

Figure 2: NOx removal efficiency in red mud catalyst material under no load and load condition.

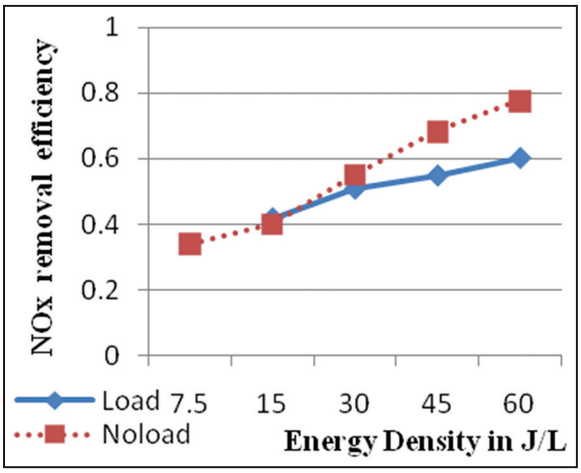

Figure 3: NOx removal efficiency of electrical discharge plasma process.

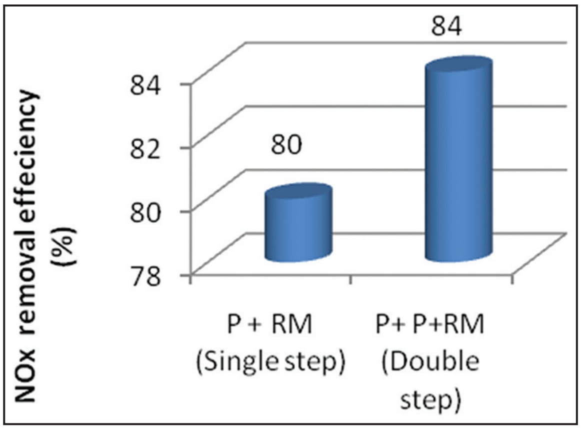

Figure 4: NOx removal by electrical discharge plasma activated catalyst process.

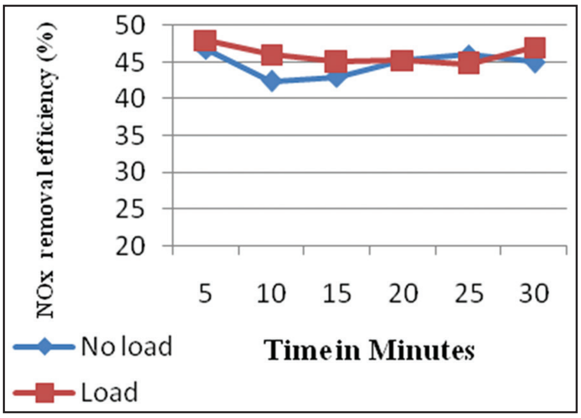

Figure 5: NOx removal efficiency in MS13X adsorbent under no load and load conditions.

3.5. NOx Removal by Electrical Discharge Plasma Activated Adsorbent Process

In this section, single step and double step electrical discharge plasma activated adsorbent hybrid process with regard to NOx removal is presented.

Figure 6 gives NOx removal by electrical discharge plasma activated adsorbent process for both single step and double step arrangements. The single step plasma activated adsorbent with MS13X as adsorbent, gives a NOx removal of around 85% at ED of 15 J/L, under no load condition. The NOx removal efficiency of MS13X adsorbent alone at low temperature (<200°C) is around 45% and by plasma at 15 J/L alone is around 40%. Thus, it is seen that the plasma activated adsorbent performs better showing synergy characteristics. This can be explained as below:

When adsorbent alone treats diesel engine exhaust, the adsorption is not significant as the exhaust has more NO molecules than NO_2. In the plasma activated adsorbent process, the exhaust entering adsorbent reactor has more NO_2 molecules due to oxidizing nature of plasma. MS13X pore size and surface area are suitable for NO_2 adsorption. As a result, electrical discharge plasma activates adsorbent and combined process brings in synergy. Similarly in the double step arrangement, a high NOx removal close to 90% is achieved.

4. CONCLUSION

The conclusions drawn from this study are as follows. The NOx removal performance of red mud catalyst and MS13X adsorbent improves when they are cascaded with electrical discharge plasma. A high NOx removal efficiency of 84% is achieved when double step electrical discharge plasma activates red mud catalyst at 400°C. A NOx removal efficiency of 90% is achieved when double step electrical discharge plasma activates MS13X adsorbent at low temperature (<200°C).

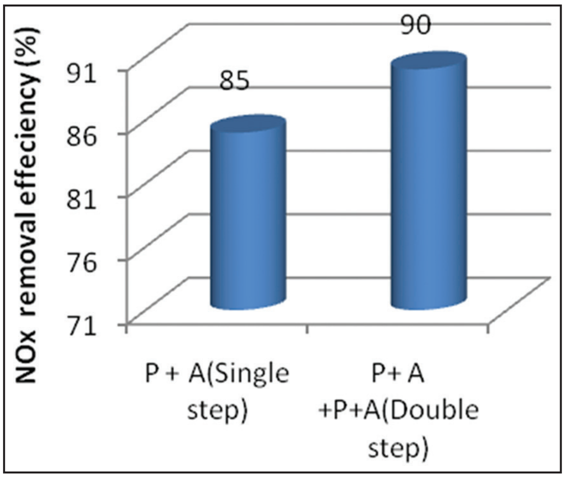

Figure 6: NOx removal efficiency by electrical discharge plasma activated adsorbent process.

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***Bibliographical Sketch**

Rajagopala. R was born in Mysuru, India, on 4th December, 1973. He received the B.E & ME degree in Electrical Engineering and Power Electronics from Bangalore University in 1996 & 1998, respectively. Currently, pursuing Ph.D. in hHigh voltage engineering under VTU. He worked as lecturer in JNNCE, Shimoga from 1998 to 2006. He is currently Associate Professor and HoD in the department of E&EE, GSSSIETW, Mysuru. He is mainly working on the application of electrical discharge plasma techniques for diesel exhaust cleaning.