doi:10.14311/ppt.2024.3.50
Plasma Physics and Technology **11**(3):50–53, 2024

SURFACE PLASMA CATALYSED COMPOSITE INDUSTRIAL WASTE FOR NOX ABATEMENT IN DIESEL EXHAUST

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Abstract. A new approach has been proposed by catalyzing composite industry wastes with pulse discharge plasma for reducing oxides of nitrogen (NOx) in diesel exhaust. Solid wastes such as foundry sand and iron tailings were blended to form a new composite waste which is then introduced into a plasma reactor to extract the benefits of catalytic properties. The obtained NOx removal efficiency is 90% at 140 J/L in plasma catalysis as against 36% obtained with plasma alone.

Keywords: Non-thermal plasma, surface discharge, plasma catalysis, industrial wastes, NOx.

1. Introduction

Industrial processes and transportation, that burn fossil fuels, are generating harmful air pollutants calling for external measures that need to be applied for reducing or minimizing the same. Continuous and incremental usage of fossil fuels has led to a highly pollutive environment, particularly concerning the emission of NOx. Diesel engines, in particular, contribute significantly to this problem. The release of hazardous gases from such engines poses severe health issues, including respiratory problems, coughing, and difficulty in breathing. On the environmental front, it is a major contributor to acid rain formation and vegetation destruction. Therefore, urgent attention is required to address the treatment of diesel exhaust. Early attempts to improve engine combustion efficiency involved modifying engine designs, adjusting air-to-fuel ratios, and implementing exhaust gas recirculation techniques. However, engine design modifications are expensive and offer limited improvements in removal efficiency.

To further improve NOx removal efficiency, post-combustion techniques have been introduced, involving the introduction of catalysts into the plasma reactor. The existing catalysis process [1–3] entails filling the plasma reactor with commercial catalyst that may react with polluted gases in the presence of plasma converting them to harmless gases. However, this method requires continuous replacement of catalysts and regeneration leading to expensive running costs and high maintenance, thus posing a major drawback. On the other hand, the usage of industrial wastes in the place of commercial catalysts may offer a cheaper (because of their abundant availability) and efficient (because of presence of metal oxides) technique [4–8].

In the current work, two industrial wastes: iron tailings and foundry sand were blended in equal proportions to form a composite waste (CW). Pellets made out of this composite waste were then exposed to surface discharge plasma associated with a dual metal film reactor. Studies were also conducted with iron tailings and foundry sand getting exposed to plasma individually. Plasma catalysis for NOx removal with composite waste as catalyst perform better than when the reactor is filled with either iron tailings or foundry sand industrial waste. In addition, a distinction was drawn between adsorption and catalytic action to highlight plasma catalysis dominance over cascaded plasma adsorption in NOx removal.

2. Materials and Method

The schematic of the plasma catalysis experimental setup is shown in figure 1. Studies were performed with controlled 3 lpm flow in ambient temperature. In this research work we tried to match with practical conditions by using diesel engine itself as source of NOx. Study was focused on the removal of NOx in dry and dust free conditions. Therefore, filters have been installed for removal of any moisture and soot particle that can interfere with actual readings. NOx has been treated in a reactor made out of quartz cylindrical tube whose inner wall is laced with metal film acting as high voltage electrode and outer wall is wrapped with grounded aluminum foil. Energization for this plasma reactor is through a repetitive nano second pulse voltages at 80 Hz frequency. The rise time of the pulse is about 25 ns.

The purpose of the work is to understand the chemistry of reduction of NOx and therefore, exhaust at controlled flow rate would be sufficient for plasma treatment. A major portion of the exhaust is therefore bypassed to the atmosphere. Exhaust from a 5 kW diesel engine (1500 rpm, single cylinder, air cooled, Prakash Marketing India Pvt. Ltd. India) is passed through dust filters (5 micrometer and 1 micrometer, ultrafilter (India) Pvt. Ltd.) and commercial moisture adsorbent to maintain dry condition. A controlled flow of exhaust at 3 lpm was maintained by a suction pump (0–15 lpm, 1-phase) with a control valve.

Plasma reactor is energized with repetitive pulse supply by connecting a rotary spark gap (RSG) switch to a transformer-rectifier (25 kV, 50 Hz) (T-R) and

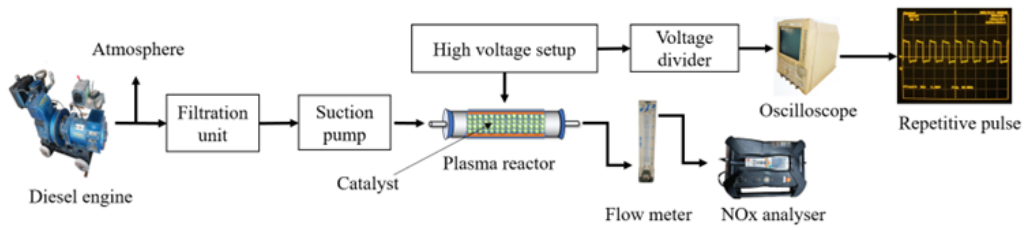

Figure 1. Experimental setup for NOx reduction.

a filter capacitor (0.5 microfarad, 50 kV) setup. The RSG has four rotating electrodes situated around a centrally placed rotating electrode connected to a motor shaft through an insulating rod. DC voltage from T-R set gets chopped repetitively by RSG at specific frequency which can be varied by changing the speed of motor. In the current study the voltage pulse is at 80 Hz with a rise time of 28 ns. The plasma reactor is made of cylindrical quartz glass tube having an outer diameter of 28 mm, inner diameter of 24 mm and length of 29 cm. Two metal films were pasted at equidistant on the inner surface of the glass tube along the central axis of the cylinder and the films were energized with high voltage to facilitate mainly surface discharges. An aluminum foil was wrapped on the outer surface of the reactor forming the ground electrode. The two ends of the reactor are closed with silicon stoppers to arrest any leakage of the gas. Additionally, in the context of plasma catalysis studies, stoppers facilitate the holding the industrial waste pellets tightly packed inside the reactor. Industry wastes such as iron tailings (from iron ore industry) and foundry sand (metal casting industry) were procured, grounded and pelletized by mixing with binder solution consisting of Na_2SiO_3:H_2O taken at 1:5. The soft pellets so prepared were sintered for 2–3 hours at 200 °C to make hard and porous pellets.

The exhaust composition was measured using a NOx analyser (testo-350, Germany). Analyser has capability to measure oxygen, oxides of nitrogen and carbon. Treated exhaust sometimes contains excessive ozone which can be detrimental to the sensor of the analyser. For solving this issue, an ozone destructor was introduced strategically between pathway of the plasma chamber and analyser. This arrangement helps to decompose surplus ozone thus protecting the sensors. Though the studies were mainly on plasma catalysis, comparative analysis was carried out with plasma adsorption and with plasma alone cases so as to highlight the enhanced efficiency NOx removal efficiency due to plasma catalysis. The results are further discussed in detail from the point of reaction pathways.

3. Result and discussion

In this study, efforts have been made to assess the possibility of industrial wastes to exhibit catalytic property in the presence of plasma for mitigation of gaseous pollutants. Diesel exhaust was used at 3 lpm fixed flowrate at room temperature. The initial exhaust concentration contains O_2 (16.46%), NO (184 ppm), NO2 (17 ppm), NOx (201 ppm), CO (1098 ppm) and CO_2 (3.28%).

Application of voltage created oxidative environment which leads to formation of the radicals, ions, excited electrons react to the gaseous pollutants and forms higher oxides. Initially, exhaust contains high concentration of NO compared with NO_2. In the presence of air, O radical will react to NO and results in NO_2. NO is continuously decreasing and NO_2 is increasing as seen in figure 2. In addition to NO_2 formation, some amount of NO may convert to higher oxides such as N_2O_4, N_2O_5 etc.

Reactions involving O/N radicals and ozone (O_3) molecules with oxides of nitrogen towards formation of NO_2 and other higher oxides in plasma environment have been mentioned in the authors' earlier paper [7].

The composite waste-based pellets consisting of iron tailings and foundry sand was compactly filled in the plasma reactor and exhaust is made to pass through them. It was observed that for low values of specific energy (around 40 J/L) itself the NOx removal efficiency was significantly high (83%) and remained almost constant for higher values of specific energy. Specific energy is defined as the ratio of power input to the reactor in watt and gas flow rate in liters per second. At about 140 J/L the efficiency was about 90%, an increase of 7%. Plasma catalysis with individual industry wastes exhibited different trend where there was almost proportional increase of NOx removal efficiency with respect to the specific energy. The possible reaction pathway can be attributed to the presence of mineral oxides such as Fe_2O_3, Al_2O_3, CaO etc., in the industrial wastes that have directly and indirectly affecting the NOx removal. The reactions are summarized as shown below:

$$12CO + 4Fe_2O_3 \rightarrow 12CO + 8Fe \quad (1)$$

$$8Fe + 12NO \rightarrow 6N_2 + 4Fe_2O_3 \quad (2)$$

$$8Fe + 6NO_2 \rightarrow 3N_2 + 4Fe_2O_3 \quad (3)$$

Aluminium oxide may promote formation of methoxide which further react with NO/NO_2 resulting in methyl nitrate or methyl nitrite as shown by equations (4–7). On the other hand, the CaO though present in low proportions may react with NO forming

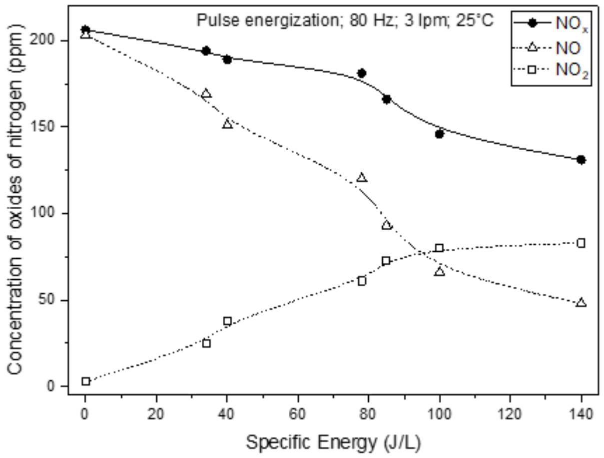

Figure 2. Variation of oxides of nitrogen in pulse energization

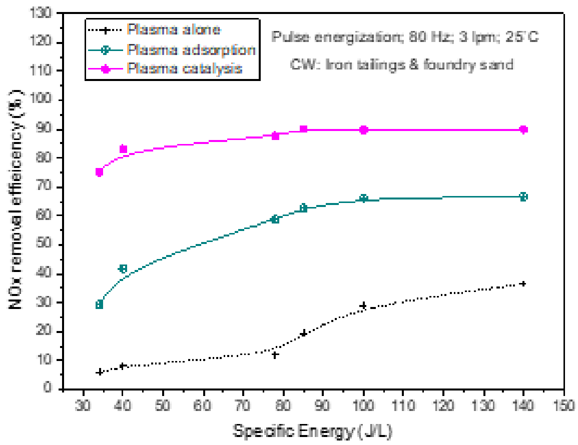

Figure 3. NOx removal efficiency with composite wastes under different plasma techniques

calcium nitrate shown by equations (8–10). Finally, to remove the ambiguity of adsorption of NO_2 in industrial wastes and to ascertain the role of plasma catalysis, a separate set of experiments was carried out by allowing the exhaust to go through the plasma reactor followed by an adsorbent reactor filled with the newly prepared CW based catalyst. Figure 3 presents a comparative analysis of the three cleaning processes namely plasma alone, plasma catalysis and plasma + adsorption. The plasma catalytic effects are significant throughout the applied voltage range as observed from the figure. At about 140 J/L the DeNOx efficiency was 90% with plasma catalysis, 67% with plasma adsorption and 36% with plasma alone. The 23% increased DeNOx efficiency with plasma catalysis when compared to plasma adsorption can be solely attributed can be catalytic reactions activated by the plasma owing to presence of metal oxides in industrial wastes.

$$CH_3CHO + O \rightarrow CH_3CO + OH \tag{4}$$

$$CH_3CO + O \rightarrow CH_3CO + CO \tag{5}$$

$$CH_3O + NO \rightarrow CH_3NO_2 \tag{6}$$

$$CH_3O + NO_2 \rightarrow CH_3NO_3 \tag{7}$$

$$3CaO + 6NO + 3O \rightarrow 3Ca(NO_2)_2 \tag{8}$$

$$2CaO + 4NO_2 \rightarrow Ca(NO_2)_2 + Ca(NO_3)_2 \tag{9}$$

$$Ca(NO_2) + NO_2 \rightarrow Ca(NO_3)_2 + 1/2N_2 \tag{10}$$

At this juncture, it is appropriate to mention that plasma catalysis with composite wastes exhibited higher DeNOx efficiency when compared to plasma catalysis with individual industry wastes be it foundry sand or iron tailings as shown in figure 4. At about 140 J/L, there was 90% DeNOx efficiency observed with composite wastes as against 67%/64% associated with foundry sand/iron tailings respectively. The blending of the two individual wastes has resulted in increased concentration of Fe_2O_3, CaO and Al_2O_3

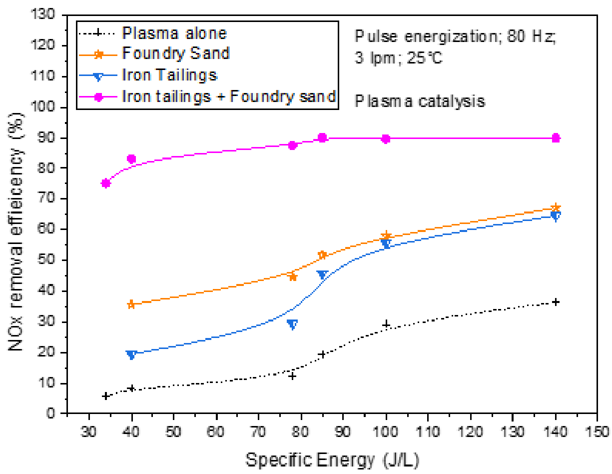

Figure 4. Performance comparison of plasma catalysis with individual/composite waste-based pellets

which have played a crucial role in causing the catalytic reactions in the presence of plasma leading to the enhanced DeNOx efficiency. Figure 5 presents the SEM images of the composite and waste-based pellets where the less bright portion indicate in the composite waste (CW) indicates the increased composition of metal oxides. This justifies that blending of two industry wastes may contributes towards higher metal oxide concentration when compared to that with individuals. Table 1 shows the mineral composition of the composite as well as individual waste pellets. It can be seen that there is a marked increase in the Fe_2O_3, CaO and Al_2O_3 in the composite wastes when compared to that with individual iron tailings/foundry sand wastes. Finally, for a given specific energy the DeNOx removal was compared between the composite and individual waste in terms of the three treatment processes as shown in the bar graph in figure 6. Composite wastes exhibited maximum removal efficiency of NOx (90%) during plasma catalysis when compared to other individual wastes (64–67%) or other treatment processes.

Metal oxides	Composite waste (%)	Iron tailings (%)	Foundry sand (%)
Fe_2O_3	20.17	3.81	0.66
Al_2O_3	12.47	1.8	0.855
CaO	2.38	1.68	0.32
MgO	11.91	0.08	0.01

Table 1. Composition of major mineral oxides

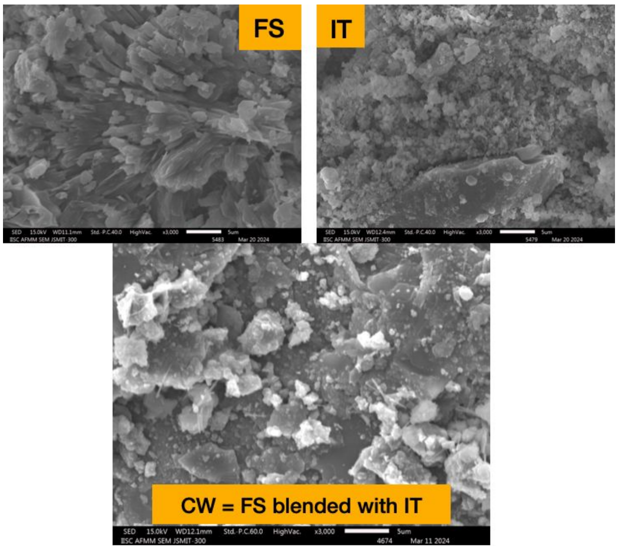

Figure 5. Scanning Electron Microscope images of individual/composite waste pellets

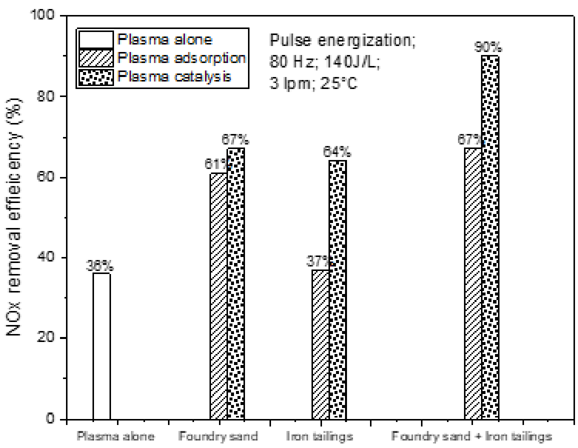

Figure 6. Comparison of NOx removal efficiency for the studied industrial wastes under different plasma techniques

4. Conclusion

Through this work we have demonstrated a new concept of blending two industrial wastes to form a composite waste which in turn was used as a catalytic medium in presence of plasma. The major inferences can be itemized as below:

- Blending of multiple industrial wastes enhances the composition of mineral oxides in the composite waste.
- The DeNOx efficiency in plasma catalysis with composite wastes far exceeds that with individual wastes at a given specific energy. At about 140 J/L the DeNOx efficiency was 90% when compared to about 65% that observed with individual wastes.
- The composite wastes can be an economically viable alternative (due to abundant presence of industrial wastes) to commercial DeNOx catalysts.

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