Removing NOx indoor air by combining pulsed dielectric barrier discharges with CUO-MNO2/TiO2 catalyst

REMOVING NO_X IN INDOOR AIR BY COMBINING PULSED DIELECTRIC BARRIER DISCHARGES WITH CuO-MnO_2/TiO_2 CATALYST

V.R. Chirumamilla[1], W.F.L.M. Hoeben [1], F.J.C.M. Beckers[1],
E.J.M. van Heesch[1], A.J.M. Pemen[1]

[1] *Technische Universiteit Eindhoven, Department of Electrical Engineering, Electrical Energy Systems Group, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands*
V.R.Chirumamilla@tue.nl

In this paper, an experimental study on NO_X removal using synergy between plasma and catalyst in a packed bed pulsed DBD reactor is carried out. FTIR is used as diagnostic tool to study NO, NO_2 and other by-products formation. Operating characteristics such as pulse repetition rate, initial NO_X concentration, and specific energy input have been studied. Pulse frequency is varied to change the energy densities. A comparison between the plasma alone and in-plasma catalytic system is made with respect to the removal efficiencies, by-products formation and energy densities.

1 Introduction

Indoor air quality (IAQ) is gaining in importance due to health and safety concerns. People spend substantial amounts of time indoors and thus IAQ affects people's well-being. With poor IAQ, people often report symptoms such as irritation of Eyes, Nose, and Throat (ENT), fatigue, headaches, allergies, nausea and dizziness. Therefore, maintaining IAQ is very important. One of the important inorganic pollutants encountered indoors is NO_X, a generic term used to summarize NO and NO_2. Non thermal plasma techniques have been widely studied for NO_x removal[1- 3]. High energy electrons produced in non-thermal plasma by electrical discharges collide with the gas molecules to produce radicals such as $N^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, $O_3^{\cdot}$, and excited species such as N_2^*, O_2^* and so on by the electron-impact dissociation and ionization reactions. These chemically active radicals are very effective for NO_x conversion. Combining a plasma reactor with a catalytic reactor might help to back convert nitrogen oxides to molecular nitrogen with minimum by-products formation if the plasma operating conditions are selected carefully.

Different types of electrical discharges have been used to produce non-thermal plasma to reduce the pollutants, VOCs and NO_X. In this study, a pulsed DBD reactor is combined with CuO-MnO_2/TiO_2 catalyst. To combine the plasma reactor with a catalytic reactor, there have been various arrangements proposed in the literature such as one-stage configuration or in-plasma catalysis and two-stage configuration or post-plasma catalysis[6]. However, there has been no specific plasma catalyst configuration or a catalyst for a specific application. Only few literatures are found on low-level indoor NO_X. Hence, this paper is focussed on low-level NO_X removal in indoors by exploiting the synergy between the plasma and CuO-MnO_2/TiO_2 catalysts.

2 Experimental Details

The schematic representation of the experimental setup is shown in fig 1. The reactor consists of a quartz tube of ≈10mm diameter with a stainless steel electrode in the centre. There is a steel mesh over the reactor which acts as ground electrode. Working gas in all the experiments is Airproducts Airzero 4.8 synthetic air at atmospheric pressure. Mass flow controllers were used to control the flow of synthetic air and NO into the reaction chamber. Bruker Tensor27 FTIR with variable path gas cell is used as diagnostic tool to study NO, NO_2 and other by-products spectrum. The plasma is energized by adjustable 0-35 kV, 0-1000 pps HV-pulses of µs duration. High voltage probe and current probe are used to measure the discharge voltage and current from the power source. These two probes were connected to Lecroy Wavesurfer oscilloscope. Plasma energy density is varied by changing the pulse repetition rate (f). Pulse counter is used to read the pulse repetition rate. Energy per pulse (E_p, J) and energy densities (ε, J/L) are calculated by using equation 1 and 2 respectively. F is the volumetric gas flow through the reactor (L/s). To study in-plasma catalytic configuration, the reactor chamber is filled with CuO-MnO_2/TiO_2 catalyst (3% CuO, 6.8% MnO_2 from Heraeus, Hanau, Germany). This catalyst was chosen mainly due to its effectiveness for ozone decomposition. It was reported by Van Durme et al [5] that the toluene degradation efficiency using CuO-MnO_2/TiO_2 with post plasma configuration in a pin-to-mesh corona reactor yielded 35 times higher energy efficiency compared to plasma alone process. In this paper, the same will be tested for NO_X removal with in-plasma configuration.

$$E_P = \int V_{Pulse}(t) I(t) dt \qquad (1)$$

$$\varepsilon = \frac{f E_P}{F} \qquad (2)$$

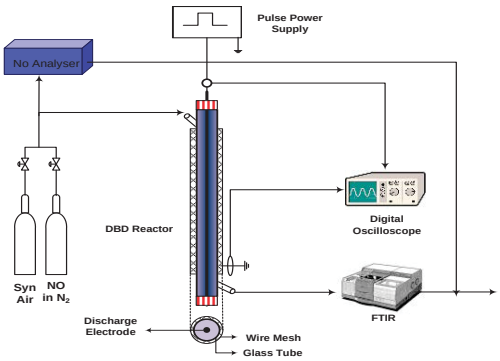

Figure 1: Schematic representation of experimental setup

3 Results and Discussions

The Experiments were carried out with plasma alone reactor and plasma combined with CuO-MnO_2/TiO_2 catalyst. Pulse repetition rate was used as operating parameter to vary energy densities.

3.1 NO conversion in plasma alone reactor

Experiments with plasma alone are carried out for 5 different initial NO concentrations (2ppm, 3ppm, 5ppm, 6ppm and 9ppm). Effect of initial NO concentration on energy densities and by-products such as N_2O and O_3 formation were studied. Concentrations of N_2O and O_3 are expressed in absorption units. Fig.2 shows NO conversion with respect to ε. It was observed that NO is converted completely regardless of initial concentrations but dependent on the energy densities. With increase in energy densities, production of O radicals is higher than the production of N radicals because of the low dissociation energy requirement for O_2 than N_2 [2]. Thus produced O radicals combine with O_2 to form O_3 which helps in oxidizing NO to NO_2 as described in the reactions 1 to 4. An increase of 2J/L of ε is observed for every ppm increase in NO initial concentration. It was also observed that at high energy densities there is a synthesis of NO which can be due to the counter reaction of excited N (^2D) with oxygen to form NO and O as given in reaction 5.

$$O_2 + e \rightarrow O + O \quad (1)$$

$$O + O_2 \rightarrow O_3 \quad (2)$$

$$O + NO \rightarrow NO_2 \quad (3)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$

$$N + O_2 \rightarrow NO + O \quad (5)$$

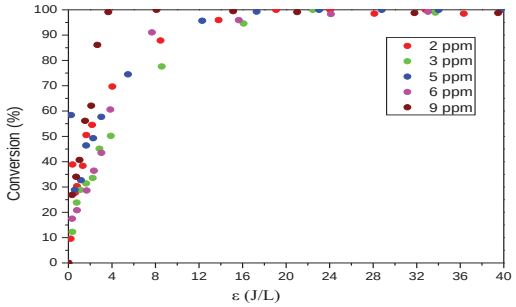

Figure 2: NO conversion as a function of energy density in plasma alone reactor

Along with increase in conversion as a function of ε, it was also observed that the by-products formation also increases as seen in Fig.3. It may be due to the fact that at high energy densities, production of N radical's probability increases and these radicals may combine with NO_2 to form N_2O and O radicals. The generated O radicals combine with O_2 to form ozone as mentioned in reaction 2.

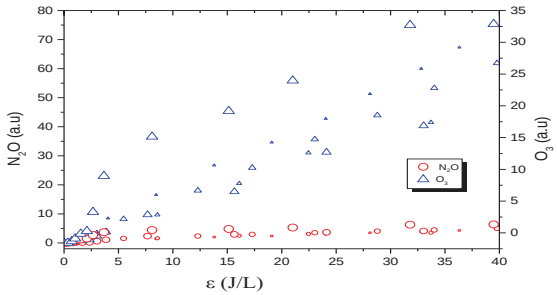

Figure 3: N_2O and O_3 formation as a function of energy density in plasma alone reactor

$$NO_2 + N \rightarrow N_2O + O \quad (6)$$

3.2 NO conversion in plasma catalytic reactor

Fig.4 shows NO conversion as a function of energy density for both plasma reactor and plasma catalytic reactor at an initial NO concentration of 6 ppm. It was observed that with increasing ε, conversion of NO increases significantly in both the reactors. More than 70% of NO conversion happens at ε approximately 4J/L with reactor operating with plasma alone whereas plasma combined with catalyst requires approximately 2 J/L. It was also noticed that the complete NO conversion requires 33J/L for Plasma reactor and 22J/L for plasma catalytic reactor.

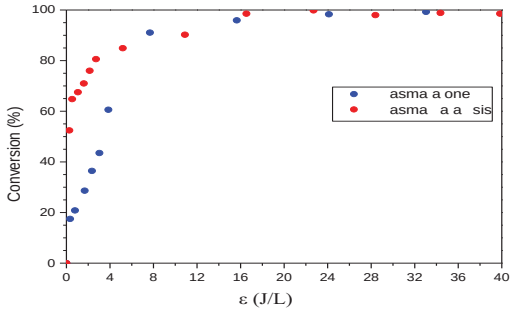

Figure 4: NO conversion as a function of energy density for both plasma and plasma catalytic configuration for 6 ppm initial concentration

Fig.5 shows the formation of N_2O and O_3 as a formation of ε in both the scenarios of plasma reactor and plasma catalytic reactor. For the same conversion, N_2O formation using plasma catalytic reactor has been reduced by 4 times while the ozone formation has been reduced by 32 times thus establishing the synergy between plasma and catalyst combination. No intercomparision of N_2O and O_3 conversion ratios can be done without futher calibration of absorption units. Plasma generated O_3 and O might have been used by the catalyst reactive surface to react with adsorbed NO to form NO_2 thus reducing the formation of O_3.

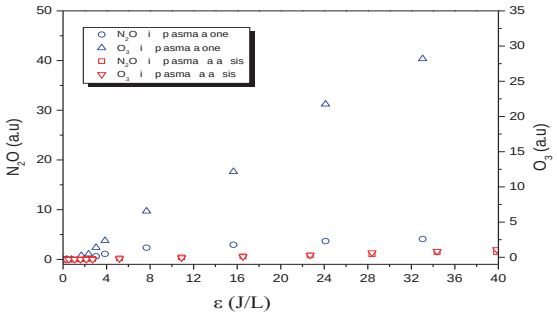

Figure 5: N_2O and O_3 formation as a function of energy density for both plasma and plasma catalytic configuration for 6 ppm initial concentration

With increase in conversion of NO, there is an increase in formation of N_2O and O_3 (Fig.6). As NO is completely oxidized to NO_2, produced O radicals react with O_2 to form ozone and N radicals reacts with NO_2 to from N_2O as described in reaction 6. In the case of plasma combined with CuO-MnO_2/TiO_2 catalyst, ozone was decomposed to a greater extent.

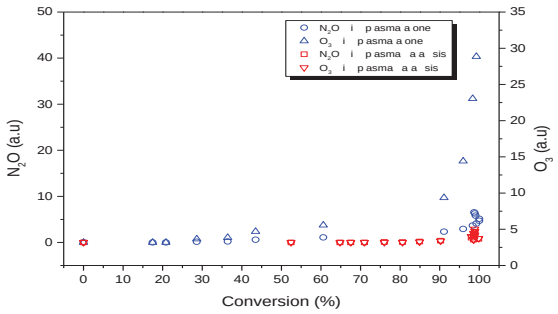

Figure 6: N_2O and O_3 formation as a function of NO conversion for both plasma and plasma catalytic configuration

4 Conclusions

Experimental investigations were carried out for NO_x removal at low concentrations. Two types of configurations i.e, plasma reactor and plasma catalytic reactor have been used. In this pulsed DBD plasma reactor, energy density of 4 J/L is required to remove 70% of NO which is somewhat better than the reported values by using corona discharges. CuO-MnO_2/TiO_2 is used as a catalyst and this catalyst was chosen mainly due to its effectiveness for ozone decomposition. It was observed that the NO removal efficiency is dependent of energy density in both the configurations. CuO-MnO_2/TiO_2 found to be effective in reducing N_2O and O_3 formation by 4 times and 32 times respectively. Further investigation to quantify N_2O and O_3 will be carried out. Also, performance of CuO-MnO_2/TiO_2 with post-plasma configuration will be investigated.

Acknowledgements

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