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Discharge Based Processing Systems for Nitric Oxide Remediation

(Sistem Pemprosesan Berasaskan Nyahcas untuk Pemulihan Nitrik Oksida)

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ABSTRACT

An electron beam (EB) flue gas test rig and a dielectric barrier discharge (DBD) reactor were tested for the removal of nitric oxide (NO) from gas stream in separate experiments. In both systems, energised electrons were used to produce radicals that reacted with the pollutants. The EB system was a laboratory scale test rig used to treat emission from a diesel run generator. At 1.0 MeV and 10 mA more than 90% NO removal from flue gases flowing at 120 Nm^3/h can be achieved. For higher removal percentage, higher beam current was required. In a related effort, a table top, two tubes DBD reactor was used to process bottled gases containing 106 ppm NO. Total removal (>99%) was achieved when the inlet gas contained only NO and N_2. Additional SO_2 in the in let gas stream lowered the removal rate but was overcame by scaling up the system to 10 DBD tubes. The system was operated with input AC voltage of 35 kV peak to peak. In the EB treatment system, the amount of NO_2 increased at high beam current, showing that the NO was also oxidised in the process. Whereas in the DBD reactor, the amount of NO_2 remained insignificant throughout the process. This leads to the conclusion that the DBD reactor is capable of producing total removal of NO. This is highly desirable as post treatment will not be necessary.

Keywords: Dielectric barrier discharge; electron beam; nitric oxide

ABSTRAK

Kajian terhadap penghapusan nitrik oksida (NO) menggunakan teknik alur elektron (EB) dan nyahcas dielektrik berpenghadang telah dijalankan secara berasingan. Kedua-dua sistem ini menghasilkan elektron bertenaga tinggi untuk menghasilkan radikal yang bertindak balas dengan bahan pencemar. Sistem alur electron tersebut adalah binaan skala makmal yang digunakan untuk merawat gas tercemar yang terhasil daripada sebuah generator disel. Pada 1.0 MeV dan 10 mA, lebih 90% NO berupaya dinyahkan dari gas tercemar yang mengalir dengan kadar 120 Nm_3/j. Arus bim yang lebih tinggi diperlukan untuk mencapai tahap penghapusan yang lebih tinggi. Dalam kajian lain yang berkaitan, sebuah reaktor 2 tiub DBD digunakan untuk memproses gas dari selinder yang mengandungi NO dengan kepekatan 106 ppm. Penghapusan sepenuhnya (>99%) telah dicapai apabila gas masukan mengandungi hanya NO dan N_2. SO_2 tambahan pada gas masukan menyebabkan kadar pengenyahanan susut tetapi ini dapat diatasi dengan menambah bilangan tiub kepada 10. Sistem ini beroperasi pada voltan AC 35 kV puncak ke puncak. Bagi sistem menggunakan EB, didapati kepekatan gas nitrik dioksida (NO_2) meningkat pada arus bim tinggi, menandakan NO telah teroksida semasa proses berlaku. Di dalam sistem DBD bagaimanapun, kepekatan NO_2 tidak menunjukkan peningkatan yang ketara sepanjang proses. Ini menunjukkan bahawa sistem DBD tersebut mampu menyahkan NO secara menyeluruh tanpa keperluan rawatan susulan.

Kata kunci: Alur electron; nitrik oksida; nyahcas dielektrik berpenghadang

INTRODUCTION

Fossil fuel burning from activities such as power generation and transportation had released millions of tonnes of nitrogen oxides (NO_x) into the atmosphere throughout the world. Nitrogen oxide is the generic term to describe mono-nitrogen oxides i.e. nitric oxide (NO) and nitrogen dioxide (NO_2). The Malaysian Department of Environment reported that the NO_2 concentration increased by 6% in 2008 compared to the 2007 level (DOE 2008). With more stringent emission level of NO_x being set, methods of control are also being sought after.

NO_x may be removed by improving combustion process, such as using low NO_x burners, improved gas circulation, and staged combustion. It can also be removed by using post combustion removal techniques such as selective catalytic reduction (SCR). In recent years, discharge based techniques namely electron beam (EB) irradiation (Chmielewsky 1997; Hashim et al. 2001) and dielectric barrier discharge (DBD) are gaining respect as viable technologies for air pollution control, namely to remove NO_x and SO_2 (Kogelschatz et al. 1999; Xu 2001; Mok 2005). This paper reports on work done locally on the utilisation of these two methods of NO remediation.

The EB process consisted of a large scale laboratory set up to treat emission from a diesel generator flowing between 120 – 200 Nm^3/h. The DBD reactor had a much

smaller processing flow rate that varies from 1 to 10 SCFH. The treated gases are industrially prepared in cylinders. Both studies are designed as proof of concept where experiments were carried out to demonstrate the feasibility of using these techniques to remove NO.

EXPERIMENTAL SETUP

EXPERIMENTAL SETUP USING HIGH ENERGY ELECTRON BEAM GENERATOR

The schematic diagram of the experimental test rig which was built at the Malaysian Nuclear Agency (MNA), Kajangis shown in Figure 1. A diesel generator set was used as the source of flue gas that contained high NO_x (ranging between 150 and 220 ppm) and almost zero SO_2. The flue gas flow through a static mixture chamber and a spray cooler before entering the process vessel inside the irradiation room. The main function of the spray cooler was to reduce the flue gas temperature and increase the moisture content by spraying fine water droplets into the gas flow. In our earlier work, (Hashim et al. 2001) it was found that the gas temperature dropped significantly, from 110°C to around 40°C after passing the spray cooler. When the water spray was turned off, the temperature only dropped to around 60°C. This is not the ideal process temperature as suggested by Chemilewsky et al. (1997). Thus, during the latest experiments, a steam generator was installed next to the static mixture to provide heat and moisture in the gas. The flue gases was still required to pass through the spray cooler since there was no alternate route. The water spray was turned off. The measured temperature was within the required 70°C to 75°C range at the process vessel (Chmielewsky et al. 1997). The gas composition was monitored continuously at the inlet (i.e. before the irradiation vessel) and at the outlet (after the irradiation vessel) using a chemilumine scence type NO_x analysers, model 42C, manufactured by Thermo Environmental Instruments Inc. (TEI). This is a USEPA accepted standard method. The SO_2 was measured directly using the Thermo Environmental Industries SO_2 analyser, model number 43°C.

The electron beam machine used in this experiment is the EPS 3000, a Cockcroft-Walton type machine manufactured by Nissin High Voltage, Japan having maximum energy of 3.0 MeV and beam current of 30 mA. It generates electrons by heating a tungsten filament and accelerates the electrons through high electric field. A multi staged divider in between the high voltage potentials, allows the electron to gain energy as it passes through the electric field in high vacuum. The high energy electron passed through a thin titanium window to escape the vacuum condition. It then penetrates a second titanium window to enter the experimental condition, at an almost atmospheric pressure inside the processing vessel.

EXPERIMENTAL SETUP USING DIELECTRIC BARRIER DISCHARGE REACTOR

The dielectric barrier discharge (DBD) reactor was developed at the Plasma Research Laboratory, Physics Department, University of Malaya. Originally it was used to produce ozone for treating waste water from textile industry (Rajeswari et al. 2001). Industrial gas was fed into the inlet to produce the ozone. The same reactor was

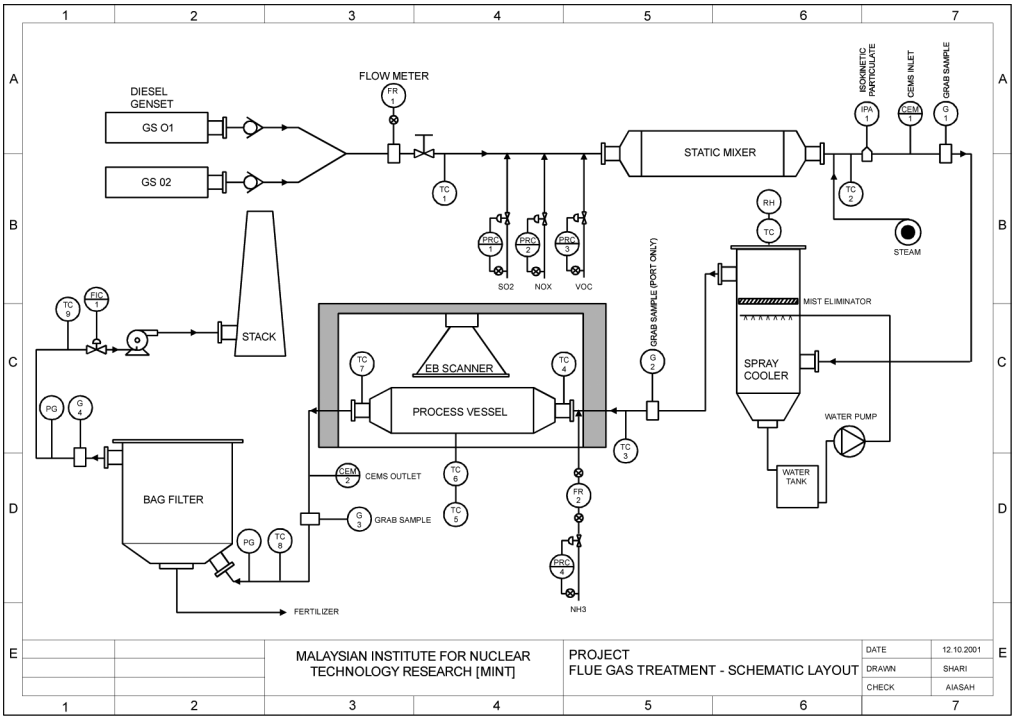

FIGURE 1. Schematic diagram of the EB Flue gas test rig at the Malaysian Nuclear Agency

later used in the earlier experiments to treat NO as reported by Hashim et al. (2007). It consisted of a number of DBD tubes with coaxial electrodes and a Pyrex test tube used as the dielectric material. Gas stream flows through the narrow space between the surface of the dielectric and the outer (earthed) electrode. When a 50 Hz AC high voltage was applied across the electrodes, micro-discharges will occur randomly between the surface of the Pyrex tube and the outer electrode across the narrow space. It was the micro-discharges which supply energy to the continuous stream of gas through the energetic electrons and hence inducing the reaction. The high voltage had to be set at a suitable threshold voltage for the desired reaction to occur. In this case, for the removal of NO, the threshold voltage was found to be > 30 kV (peak-to-peak). The crossed sectional diagram of a DBD tube is shown in Figure 2 and the schematic diagram of the experimental arrangement for the gas treatment is as shown in Figure 3.

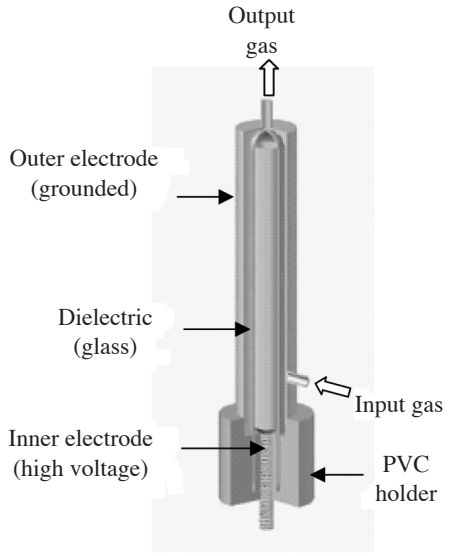

FIGURE 2. Crossed sectional diagram of a DBD tube

In these experiments, a known concentration of NO from a bottled source was used. The initial concentration was around 100 ppm added with sulphur dioxide (300 ppm) and nitrogen gas as the balance. The flow rate was controlled by a Dwyer flow meter. The flow meters used were either with a range of between 0 – 5 SCFH or 0-200 SCFH depending on the flow rate required in the particular experiment. The gas flowed directly into the DBD tubes where the reaction took place. The dielectric discharge produced energetic electrons that produce radicals to react with the gas. A chemilumine scence's type NO analyser (TEI Corporation, model 42C) was used to continuously analyse the output throughout the process.

Throughout the experiments, the voltage was set between 32 and 35 kV based on the earlier work done (Hashim et al. 2007). Unless stated otherwise, only two tubes connected in series were used in the experiments. Connecting the tubes in series provides longer discharge length hence producing more radicals to increase the removal efficiency (Gentile et al. 1995).

RESULTS

REMEDIATION OF NO USING ACCELERATED ELECTRON

Changes in the concentration of nitric oxide was observed within minutes after exposure to the electron beam radiation. In order to observe the effect of the beam intensity to the removal efficiency, the current was varied between 1 mA to 12 mA at every 10 minutes interval. The data was logged automatically every 1 min. The results were analysed in two ways. Firstly, the average final concentration over a period of 10 min for each intensity level was calculated and plotted against the beam current value as shown in Figure 4. The NO concentration reduces at an inverse exponential trend. However, the NO_2 was observed to increase especially at higher current. This shows that the NO is oxidised into NO_2 and hence leads to

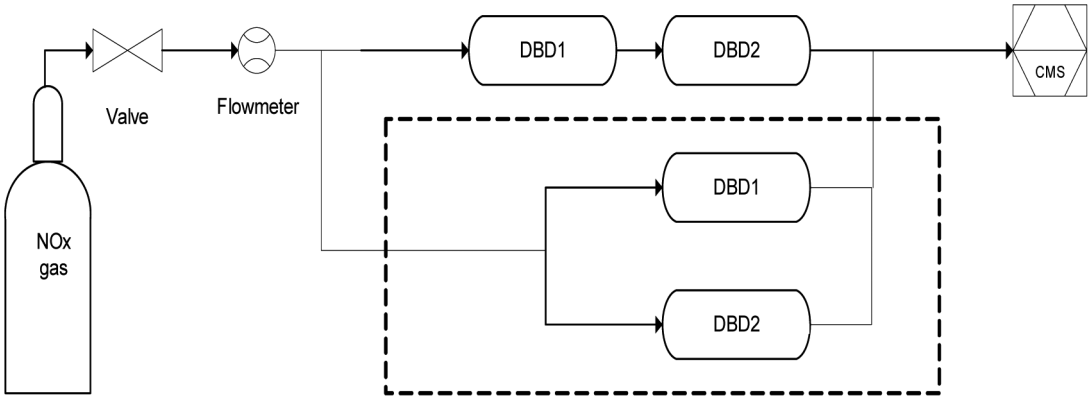

FIGURE 3. Schematic diagram of the NO_x removal experimental setup. The DBD cells were connected either in series or in parallel (as shown in dotted-line box)

the formation of HNO_3 since water molecule is available in the partially humid inlet gas. Thus the end emission may contain acidic gases that requires further treatment.

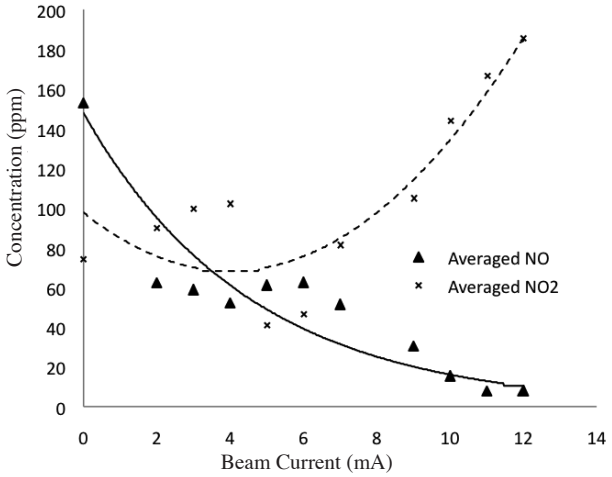

FIGURE 4. Average concentration of NO and NO_2 at different level of beam current

Secondly, the results can also be presented as calculated removal efficiency as in Figure 5. The result shows a linear relation between the beam current and removal efficiency. The removal efficiency (%) was calculated using the formula:

$$\eta(\%) = \frac{[NO(in)] - [NO(out)]}{NO(in)} \times 100.$$

This formula was also used to calculate the removal efficiency when using the dielectric barrier discharge system.

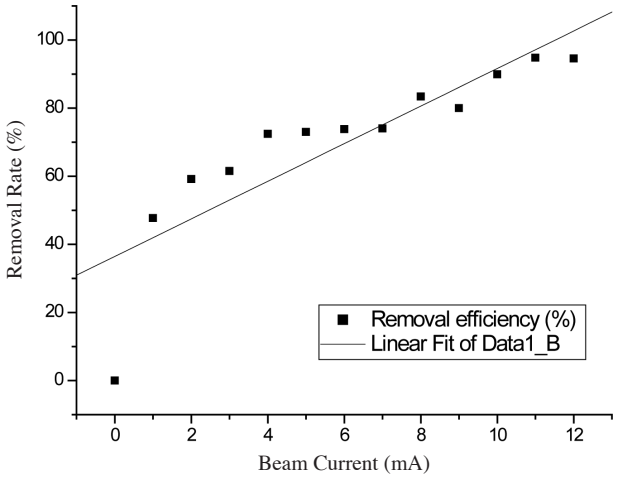

FIGURE 5. NO removal efficiency (%) for different beam current

REMEDIATION OF NO USINGDIELECTRIC BARRIER DISCHARGE

The reduction of the NO from a gas stream with nitrogen as the background gas by using the DBD is shown in Figure 6. In this case, the gas was flowing at 2 standard cubic feet per hour (SCFH) through two DBD tubes connected in series. The input high voltage was set at 32 kV (peak-to-peak). Almost complete removal was achieved, since there was no other active species in the gas stream to react with the N and O. This is an ideal situation where NO remediation is achieved totally via the reduction pathway (Gentile et al. 1995).

Summary of the experiments carried out using two DBD tubes, with input high voltage fixed at 32 kV (peak-to-peak) while varying the flow rate is shown in Table 2. Complete removal rate (more than 99%) was observed for flow rate of up to 5 SCFH. For flow rate of above 5 SCFH the efficiency of NO removal was observed to decrease until as low as 30% (at a flow rate of 15 SCFH). This shows that the reactor has limited processing capability at high flow rate. If we set the requirement at a minimum of 80% removal, the rector is usable for flow rate of just under 10 SCFH.

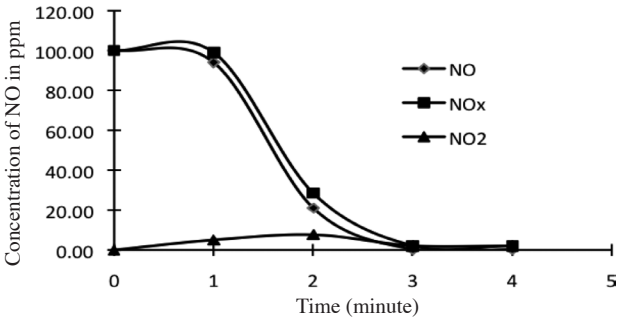

FIGURE 6. Removal of NO from gas stream with N_2 as background using two DBD tubes in series at 32kV (peak-to-peak) and flow rate of 2 SCFH

TABLE 1. Removal rate of NO from gas stream with N_2 as background, at different flow rate

Flow rate (SCFH)	Removal rate (%)
1	99.99
2	99.84
3	99.04
4	99.99
5	99.99
6	97.37
7	94.56
8	90.90
9	86.29
10	72.64
15	30.36

When the inlet gas composition is modified to contain SO_2 (300 ppm) as well as N_2 in the background the NO removal rate was found to be significantly affected (Figure 7). In this case, the input high voltage of 32 kV (peak-to-peak) and flow rate of 2 SCFH were used.

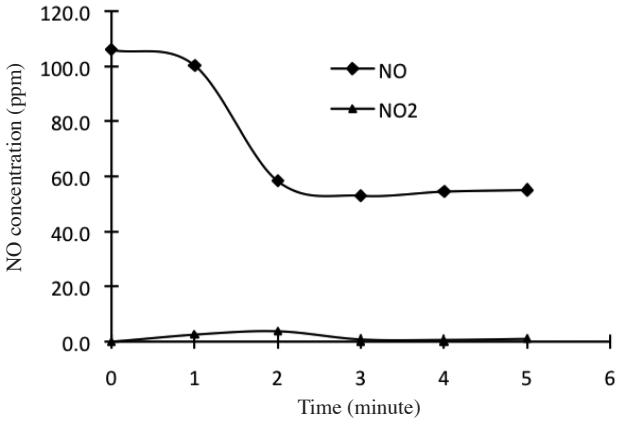

FIGURE 7. Removal of NO from gas stream containing SO_2 and $N_2$by using two DBD tubes at 32kV (peak-to-peak) and flow rate of 2 SCFH

The final removal rate was calculated to be only 48.02% as compared to 99.84% when the background consists of only N_2. Interestingly, the amount of NO_2 remained very low showing that the rate of oxidation did not increase.

In order to treat gas stream at higher flow rate, the reactor was scaled up by using more DBD tubes connected in series. Up to 10 tubes were used to find the most suitable combinations to totally remove the NO from the gas mixture with N_2 and SO_2 as background gases. Figure 8 shows the results where the discharge voltage and the flow rate were fixed at 32 kV (peak-to-peak) and 2 SCFH respectively. As expected, the efficiency improved with the number of tubes connected in series. It was observed that the removal efficiency saturated when seven tubes were used. The saturation in the NO removal efficiency was caused by the limitation of the current that can be supplied by the power supply, which was only 3 mA. As the number of DBD tubes was increased, the total capacitance of the reactor increased and correspondingly more current was drawn to sustain the micro discharges inside the tubes. Hence in order to power the discharge of more than seven tubes connected in series, a power supply with higher current should be used.

DISCUSSION

High energy electrons are the main ingredient in both processes. The common removal mechanism is the reduction process where nitric oxides are reduced to nitrogen and oxygen gases as stated by the equation below:

$$NO + N \rightarrow N_2 + O. \quad (1)$$

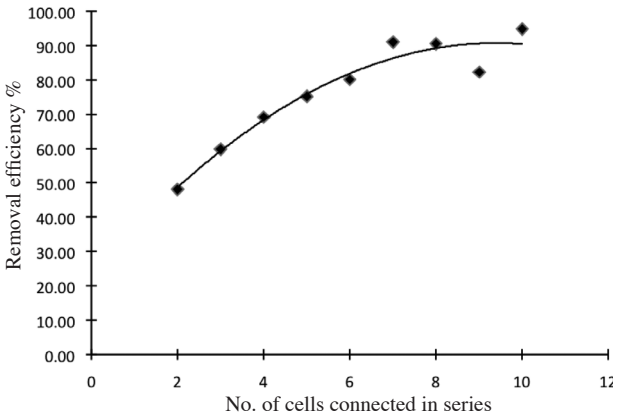

FIGURE 8. Relationship between the removal efficiency and the number of cells connected in series

Electron energy is consumed in the ionisation, excitation and dissociation of the molecules and finally in the formation of active free radicals *OH, HO_2*, O, N and H. These radicals oxidise NO to NO_2 which in reaction with water vapour, normally present in the stack gas, form HNO_3 (Calinescu 2008).

NO is an unstable gas thus this process can be easily induced when there is sufficient energy to break the N-O bond. However, oxidation can also occur during the process, where NO_2 is formed as the end product.

$$NO + O \rightarrow NO_2 \quad (2a)$$

$$NO_2 + OH \rightarrow HNO_3. \quad (2b)$$

In the EB process ,humidity or air molecules plays an important role as it enhances oxidation and formation of acids as in 2a and 2b. Thus, the end product consists of NO_2 and HNO_3 that needs further treatment. Post irradiation treatment include addition of NH_3 or $Ca(OH)_2$ to neutralise the acidic air, resulting either NH_4NO_3 or $Ca(NO_3)_2$ as by product (Namba 1992; Paur et al. 1992). Such post treatment may not be necessary for the DBD processing. In fact, oxidations enhanced by the water molecules are much preferred to be avoided. In the DBD system, it was observed that oxidation process can be minimised by manipulating the arrangement and the number of tubes in the reactor, thus improving the efficiency of the system. All experimental results show that significant oxidation occurs only within the first 3 minutes of the process (Figures 6 and 7). After that period, reduction process overtakes the oxidation and hence no increase in the NO_2 is observed. This is one clear advantage of the modular type DBD reactor over the static EB system.

Interestingly, the serial configuration in the DBD reactor is in agreement with the double staged EB irradiation of flue gases as suggested by researchers elsewhere (Chmielewsky et al. 1997; Namba 1992; Paur et al. 1992). Serial or multi-staged treatment can improve

the energy efficiency in both systems although in the DBD reactor the discharge current required will increase with the increase in the number of stages. This was evidenced where only 7 tubes can process a 2SCFH flow of gases, at 35 kV input voltage. Increasing the number of tubes to 10 did not improve efficiency, unless the input current was also increased. Another way to improve the efficiency is to increase the frequency of the supplied voltage so that more discharges will occur per cycle (Cheng et al. 1992; Chen et al. 2002; Harling et al. 2008). However, the main reason for using 50 Hz power source in our case is simplicity and low cost if commercialisation is to be considered.

CONCLUSION

Based on the experiments, it was shown that nitric oxide can be removed by energized electrons. The electrons can be in the form of simple random discharge as occurred in the DBD tube or as accelerated particles in an electron beam machine.

The EB system requires high current to remove more than 90% nitric oxide. The optimum EB parameter can be considered at 1 MeV and 10 mA for this particular set up. The accelerator voltage could be lowered but it could cause instability to this particular machine. Higher beam current would mean higher operating cost. Since the experiments were done using actual emission, it can be concluded that the system can be implemented to treat nitric oxides from diesel combustion. However, studies on the post irradiation treatment are required to ensure that the final output is safe for release to the environment. Other areas that need further fine tunings are the irradiation vessel design and the processing flow rate, to make it more cost and power efficient.

In the DBD process, with the right flow and configuration, total removal of NO can be achieved. Since the intended application is for small setups with low emission volume such as for motor vehicle and small incinerator, additional processing is undesirable. The modular design made it adaptable to the specific size of the application. It also requires low energy consumption and has manageable size compared to the EB system. However, further works are needed especially to test the reactor to treat real emission before a final configuration can be recommended.

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