# REDUCTION OF DIESEL ENGINE EXHAUST EMISSIONS USING NON-THERMAL PLASMA TECHNOLOGY

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Submitted in fulfilment of the requirements for the degree of

**Doctor of Philosophy (PhD)**

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Science and Engineering Faculty
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2015

# Keywords

Non-thermal plasma (NTP), Nitrogen oxides ($NO_X$) removal, Diesel engines, Catalyst, Emission treatment, Pollution, Diesel particulate matter (DPM), Particle mass reduction, Particle size distribution, Diesel exhaust emissions, Dielectric barrier discharge (DBD), Pulsed power, Push-pull converter, Particulate matter (PM) removal, Pulsed power supply, Diesel emission reduction, Ozone, Carbon monoxide (CO), Diesel engine emission regulations, Diesel engine emission standards, Particle number distribution, Accumulation mode, Nucleation mode, Condensation Particle Counter (CPC), Scanning Mobility Particle Sizer (SMPS), Median diameter particulate matter, DustTrak™ aerosol monitor, Diesel particulate filter (DPF), High Efficiency Particulate Air (HEPA) filter, Gaseous emissions, Hydrocarbon (HC), Multi Criteria Decision Analysis (MCDA), PROMETHEE-GAIA

# Abstract

In addition to the advantages of lower operating costs and higher thermal efficiency, diesel engines have produced one of the most complex environmental pollutant mixtures to have been thoroughly studied by researchers from a range of disciplines; Among the different components of diesel exhaust, only carbon monoxide (CO), hydrocarbon (HC), nitrogen oxides ($NO_X$) and diesel particulate matter (DPM) have been regulated by most of the emission standards. DPM is acknowledged as the major harmful pollutant emitted by diesel engines. Diesel particles are inhalable and they can be transferred to different parts of the body through the bloodstream. Recently diesel exhaust has been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC). Therefore, there is a clear need to strive for DPM reduction in all diesel engine applications.

DPM studies have been conducted in the literature based on particle mass and/or particle size. It has been observed that most of the PM mass is focused in the accumulation mode, where particle diameters are mostly in the fine particle range ($d_p$ > 100nm). On the other hand, number distributions are observed more in the nucleation mode ($d_p$ < 50nm), where DPM is composed of many nanoparticles with less mass. Particles deposit in the human respiratory system in a size-dependent manner, with smaller particles penetrating deeper into the human lungs and depositing more rapidly than the larger particles. Therefore, considering the size distribution in conjunction with mass distribution is very important in all DPM research.

Non-thermal plasma (NTP) is believed to be a promising candidate for controlling engine exhaust emissions. Plasma is known as the fourth state of matter, where both electrons and cathode-ions co-exist. NTP contains many kinds of chemically active species generated by numerous chemical reaction mechanisms such as electron attachment, dissociation, ionisation, excitation etc. For example, O, $O_3$, N, N*, $N_2^+$ and OH can be generated by the dissociation and ionisation of the ambient gases caused by the impact of energetic electrons. Both gaseous and particle emissions of diesel exhaust undergo chemical changes when they are exposed to

plasma. An extensive literature review on diesel exhaust treatment by plasma found an abundance of literature for $NO_X$ reduction by plasma, but a lack of literature for PM removal. This was particularly notable for particle size distribution effects. Therefore, the primary aim of this thesis is to investigate DPM mitigation from the actual diesel exhaust by using NTP technology. The effect of plasma, not only on PM mass but also on PM size distribution, physico-chemical structure of PM and PM removal mechanisms, has been investigated. Furthermore, the NTP influence on regulated emissions such as nitrogen oxides ($NO_X$), carbon monoxide (CO), and hydrocarbons (HCs) and unregulated emissions such as carbon dioxide ($CO_2$), ammonia ($NH_3$) and aldehydes (formaldehyde and acetaldehyde) during the DPM removal has been investigated and it was found that in some cases it connected with DPM trends.

A number of experimental campaigns have been conducted to attain the primary aims of this project. First, the capability of NTP technology for PM removal was evaluated to develop a primary study of pulsed power effects on PM mass reduction and PM size distribution. For initial experiments, a pulsed power supply based on the push-pull inverter is developed to generate voltages up to 19.44 kVpp across the dielectric barrier discharge load. The tests were conducted at voltage levels of 15, 17 and 19.44 kVpp at a fixed repetition rate of 10 kHz. PM mass reduction, PM removal efficiency and PM size distribution are investigated by evaluating the results obtained. A PM mass removal efficiency of about 43.9% has been achieved at a voltage level of 19.44 kVpp during the experiments. However, at this voltage level the number of ultrafine particles increased significantly. Therefore, it is important to consider PM size distribution in the NTP treatment of diesel exhaust emissions, as it is possible to achieve high PM removal efficiency with undesirable increase in the number of small particles. Regarding the PM mass and PM size distribution simultaneously, a 17 kVpp voltage level was introduced as an optimum point for the given configuration in this chapter.

The formation of nucleation mode particles at high voltage levels has been observed in primary experiments. To study the formation mechanism of those particles, a test has been designed by using a filter in reactor inlet. A high efficiency particulate air (HEPA) filter was added in the reactor inlet to remove all particles before entering the dielectric barrier discharge (DBD) reactor. Almost all particles

were removed from the exhaust before entering the DBD reactor. After introducing plasma, most of the un-trapped particles have been removed at the voltage levels of 15 kVpp and 17 kVpp. However, the effect of plasma at 20 kVpp on particle size distribution was found to be different. Without applying any pulse, the number of particles was very small, but by applying 20 kVpp and introducing plasma inside the reactor, the number of small particles was massively increased. This result indicated the formation of new particles from gaseous precursors and condensation of gaseous emissions to particle phase at this voltage level or, in other words, gas to particle partitioning.

Investigations were made into the influence of non-thermal plasma after treatment technology on DPM composition. The DBD reactor was employed for producing plasma inside the diesel exhaust. A range of discharge powers, by varying the applied voltage from 7.5 kV to 13.5 kV at a frequency of 50 Hz, have been evaluated during the experiments. Soot, soluble organic fraction (SOF) and sulfate components of diesel particulate matter were analysed separately and the consequence of NPT exposure on PM size distribution on both nucleation and accumulation mode was quantified. The formation of nucleation mode particles has been confirmed as well. A maximum soot removal of 73% at 13.5 kV was obtained. Despite some fluctuations in SOF data, the general trend of an increase in SOF concentration can be found. A major fall of about 37% in SOF concentration is observed at 10.5 kV; however, with the increase of voltage to 12 kV and 13.5 kV, the SOF increases slightly. This outcome is in agreement with the results of size distributions at these two voltage levels, which showed a considerable increase in number of nuclei mode particles at 12 kV and 13.5 kV. Furthermore, the sulfate fraction was very low at the reactor outlet measurements due to the low sulfur content of employed diesel fuel and remained almost unchanged under plasma treatment.

The NTP was characterised under a wide range of applied voltages and frequencies and also considered the role of ozone as the key parameter in PM oxidation. The minimum PM concentration was obtained at 19 $kV_{pp}$ and 10 kHz and the maximum ozone concentration of 547 ppm was found at 21 $kV_{pp}$ and 7.5 kHz. Furthermore, ozone, $CO_2$ and PM concentrations at different plasma states were analysed for time dependence. Based on this analysis, an inverse relationship

between ozone concentration and PM removal was found. This finding illustrates the key role of ozone in PM removal in plasma treatment of diesel exhaust.

The effect of NTP on regulated and unregulated diesel emission during the PM removal has been considered for 22 species including different hydrocarbons (C1-C7), carbon monoxide, carbon dioxide, nitrogen oxides (including NO, $NO_2$ and $N_2O$), sulfur dioxide, formaldehyde and others. It was found that the concentration of some emissions, such as aldehydes (summation of formaldehyde and acetaldehyde), increased in the presence of plasma. Furthermore, multivariable data analysis (MDA) was used to facilitate the interpretation of the data and investigate the interrelationships among a given data matrix. This analysis revealed that some emissions, such as CO, NO, $NO_2$, $N_2O$ and THC, have been affected more by changing the applied voltage, compared to other emissions in plasma state. Moreover, a reverse relationship between concentrations of $NO_x$ and NO with $NO_2$, and CO with NO and $NO_x$ was found from this analysis.

Overall, this thesis advances knowledge in the field of NTP application for diesel exhaust emission reduction, by delivering an extensive amount of new information about the NTP effect on DPM and the removal mechanisms involved in real engine operating conditions.

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# List of Abbreviations

| | |
|---|---|
| AC | Alternative current |
| BERF | Biofuel Engine Research Facility |
| CBP | Carbon black particles |
| CPC | Condensation Particle Counter |
| CRT | Continuous regeneration trap |
| CSF | Catalysed soot filter |
| DBD | Dielectric barrier discharge |
| DC | Direct current |
| DOC | Diesel oxidation catalysts |
| DPF | Diesel particulate filter |
| DPM | Diesel particulate matter |
| DSC | Digital signal controller |
| FBC | Fuel borne catalysts |
| FTIR | Fourier transform infrared |
| GHG | Greenhouse gas |
| HAPR | Hybrid adsorber plasma reactor |
| HC | Hydrocarbon |
| HEPA | High Efficiency Particulate Air |
| IARC | International agency for research on cancer |
| LD | Light-duty |
| LNT | Lean-burn $NO_x$ trap |
| MCDA | Multi criteria decision analysis |
| MDA | Multivariable data analysis |

| | |
|---|---|
| NSR | $NO_x$ storage reduction |
| NTP | Non-thermal plasma |
| PCA | Principal component analysis |
| PM | Particulate matter |
| PRAR | Plasma-adsorbent reactor |
| PRCR | Plasma-catalytic reactor |
| RF | Radio frequency |
| RTD | Residence time distribution |
| SCR | Selective catalyst reduction |
| SED | Specific energy density |
| SIE | Specific input energy |
| SMPS | Scanning mobility particle sizer |
| SNR | Selective $NO_x$ recirculation |
| SOF | Soluble organic fraction |
| THC | Total hydrocarbon |
| US FTP | United states federal test procedure |
| VOC | Volatile organic compounds |
| VOF | VOF Volatile organic fraction |

# List of Symbols

| Symbol | Quantity | Unit |
|---|---|---|
| V | Applied voltage | V |
| C | Capacitance | μF |
| Q | Charge | C |
| W | Energy per cycle | J/cycle |
| $\varepsilon$ | Energy cost | eV/molecule |
| $\dot{V}$ | Flow rate | L/min |
| f | Frequency/repetition rate | Hz |
| E | Input energy per cycle | J/pulse |
| $V_{PP}$ | Peak to peak voltage | $V_{PP}$ |
| P | Power | W |
| SED | Specific energy density | J/L |
| T | Temperature | °C |

# List of Publication

**Journal papers:**

Talebizadeh, P., M. Babaie, R. Brown, H. Rahimzadeh, Z. Ristovski and M. Arai. 2014. "The role of non-thermal plasma technique in NOx treatment: A review." Renewable and Sustainable Energy Reviews 40 (0): 886-901".

Babaie, M., P. Davari, F. Zare, M. M. Rahman, H. Rahimzadeh, Z. Ristovski and RJ Brown. 2013. "Effect of Pulsed Power on Particle Matter in Diesel Engine Exhaust Using a DBD Plasma Reactor." IEEE Transactions on Plasma Science 41 (8): 2349-2358".

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**Conference papers:**

Babaie, M., P. Talebizadeh, S. Saha, H. Rahimzadeh, F. Zare and R.J. Brown. 2012. "Residence Time Investigation in a Co-axial Dielectric Barrier Discharge

Reactor." Paper presented at the 4th International Conference on Computational Methods (ICCM 2012), Gold Coast, Australia".

Babaie, M, P Davari, P Talebizadeh, Z Ristovski, H Rahimzadeh and RJ Brown. 2013. "Study of particulate matter removal mechanism by using non-thermal plasma technology." Paper presented at the XIII International Conference on Electrostatic Precipitation (ICESP 2013), Bangalore, India".

Babaie, M., P. Davari, P. Talebizadeh, H. Rahimzadeh, R. Brown, K. H Sia, A. J. Yi. 2014. " Diesel particle emission reduction of diesel engines by using Non-thermal plasma technology." Paper presented at the 8th International Conference on Internal Combustion Engines and Oil (ICICE&O-8), Research Institute of Petroleum Industry, Tehran, Iran".

# Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.



Signature:

Date: 28.01.2015

# Acknowledgements

When I first entered Shahrood University of Technology to start my Bachelor degree after passing a highly competitive entrance exam, I never thought that one day I would complete a PhD in such a high quality international university, but it happened. This was due to the excellent education and support I received in all levels of my studies, support which was provided by my family, friends, teachers and supervisors.

First, I would like to acknowledge all my teachers, who provided me with high quality education during my elementary and high school studies, especially Mr Yarmohammad Rahimi, who awakened a sense of wonder and curiosity about mathematics and engineering within me.

I also would like to express appreciation for the support of all academics and staff during my Bachelor and Master studies at Shahrood University of Technology and K.N.Toosi University of Technology.

I would like to especially thank Professor Hassan Kayhani, a prominent scientist in Shahrood University of Technology, who had a key role in starting my academic journey.

I wish to extend thanks to my Master supervisors, Dr Hosein Sayyaadi and Dr Alireza Novinzadeh, for their kind support during my Master studies, specifically Dr Hosein Sayyaadi, who introduced me the area of research for the first time.

My PhD supervisor, at Queensland University of Technology, Associate Professor Richard Brown, is the most important contributor to this work. I found him not only a great supervisor and scientist, but also a caring and supportive man. Since 2011, when I started my PhD, we have both learnt a great deal from each other and have enjoyed research and teaching together. He has always kept me on the right track, whilst allowing me the freedom to really explore ideas. Even during the times in which this research was slow and challenging, Associate Professor Richard Brown always encouraged me to push through and helped me to find new solutions. It was a great pleasure for me to work with Associate Professor Richard Brown; I would like to keep in touch with him, as it is hard to think about finishing my PhD and that

being the end of all our valuable and enjoyable time together. It is not easy to find the right words to thank him; I would just like to express my sincere gratitude to Associate Professor Richard Brown for giving me this opportunity, and for all his support during my PhD.

I wish also to extend my sincere thanks to my associate supervisor, Professor Zoran Ristovski. He has supported me in many ways that this brief acknowledgement could never possibly do justice to. He opened a new window to me in the area of aerosol science, which until that point had been completely unknown to me. Extensive scientific consultation at all stages of my candidature has been provided by him. Without his continued guidance and advice, this thesis would not have materialised.

I wish to extend thanks to Professor Hassan Rahimzadeh and Associate Professor Firuz Zare. When I came to Australia in 2011, I met Professor Hassan Rahimzadeh for the first time when he was a visitor at QUT. He had a very important role in defining this project and he shifted my thesis towards the Emission Reduction Application. He helped me a great deal to develop this project in the beginning and also during my PhD. He supported many aspects of this project and also provided me personal counsel during my PhD journey. Associate Professor Firuz Zare had a key role in developing the experimental set-up. I would like to acknowledge appreciation for his continued patience and support at the beginning of my PhD and also his contribution in providing financial support for my study. Unfortunately, Associate Professor Firuz Zare left QUT and his part in my PhD journey was shortened but without his support this project could not have started or continued.

Some parts of my research have been conducted in collaboration with Gunma University in Japan. I would like to acknowledge my gratitude to Professor Masataka Arai, Professor Tomohiko Furuhata, Dr Yoshio Zama and Mr Takahiro Kishi, for their assistance during the experiments. Furthermore, the support of other members of the Department of Mechanical Systems Engineering, Gunma University, was greatly appreciated.

I wish to commend the efforts of all undergraduate and postgraduate students involved in this project for their assistance, especially, Dr Pooya Davari for his

support with regard to the electrical side and Mr Md Mostafizur Rahman for his contribution during experimental campaigns. Also, special thanks go to Mr Noel Hartnett and Mr Scott Abbett and other technical staff of QUT who also contributed to this work.

The financial support provided by Queensland University of Technology, through the Higher Degree Research Tuition Award, Faculty of Built Environment and Engineering Postgraduate Scholarship, Queensland Program for Japanese Education Postgraduate Research Grant and Supervisor Top-up Scholarship Award (from Associate Professor Firuz Zare and Richard Brown) is greatly appreciated as well.

Last but not least, thanks to my family. This thesis would not have been completed without the emotional, moral and spiritual support of my lovely wife Mahsa. She helped me in all stages of my research and without her assistance it would not have been possible to finish this thesis. I would especially like to note and appreciate her support during the writing phase of my thesis.

I also wish to thank my mother Effat and my father Ahmad for all their help during my life as well as my PhD studies. I would like to say thanks to my mother for all her concern and her daily calls to talk to me during my PhD.

I wish to thank my calming brother, Hosein, and my full-of-fun sister, Atefeh, for being so thoughtful and helpful and lastly, thanks to my aunt Fatemeh for her support, especially during my Master studies.

# Chapter 1: Introduction

## 1.1 BACKGROUND AND MOTIVATION

A human being typically inhales up to about 10.8 $m^3$ of air per day, thus achieving good air quality is of global concern from a health point of view (Ristovski et al., 2012). Passenger cars and light trucks contribute a considerable share of emissions and collectively produce almost one-eighth of the total global warming pollution. Furthermore, there is a continuous increase in the number of diesel engines in both stationary and mobile applications, due to the lower operating cost, higher thermal efficiency and longer durability than that of gasoline/ethanol engines. However, diesel engines emit more particulate matter (PM) and nitrogen oxides ($NO_X$) compared to gasoline engines. On the other hand, emission standards are getting more stringent day by day and there is a considerable concern about the deleterious effect of diesel emissions on human health. Therefore, there is a need to reduce harmful components of diesel exhaust emissions, especially for particulate matter (PM) and NOx emissions.

Different technologies have been developed for $NO_X$ and particulate treatment of diesel exhaust to date. The selective catalyst reduction (SCR) method has been considered for $NO_X$ reduction of automobile and stationary engines. In this method, ammonia or urea is used as a reactant. However, there are some problems in using SCR catalysts such as the possibility of ammonia leakage, catalyst poisoning, catalyst discharge under the high temperature condition or under influence of sulfur, and the need for construction of urea solution stations. Diesel particulate filters (DPF) have been used widely for PM removal in diesel engines (Kuki et al., 2004, Ohno et al., 2002 -a). There are also some drawbacks in using DPF as an after treatment system, such as extra pressure drop, filter choking and extra fuel consumption for filter regeneration.

Therefore in this research, a new technique called non-thermal plasma (NTP) will be considered for emission reduction of diesel engines. Plasma is the fourth state of matter. It is made up of ionised gas, a gas into which sufficient energy is provided to free electrons from atoms or molecules and to allow species, ions and electrons, to coexist. Plasma is divided into thermal or hot plasma and non-thermal or cold plasma. In the thermal variety, the kinetic energy (temperature) of charged particles and the kinetic energy (temperature) of the

background gas are similar. In non-thermal plasma, electrons have a kinetic energy higher than the energy corresponding to the random motion of the background gas molecules. The purpose of using non-thermal plasma is to selectively transfer the input electrical energy to the electrons, which would generate free radicals through collisions and promote the desired chemical changes in the exhaust gas. These reactions can be accomplished at a fraction of the energy that is required in the thermal plasma system. An example of non-thermal plasma is the gas filling of a fluorescent tube. It has a temperature of only about 40℃ but the temperature of free electrons in the system exceeds 10000 ℃. (Majewski, 2004)

When plasma is introduced in the exhaust gas, oxidation processes will be initiated. Since free radicals and ions in the plasma state are highly reactive, they can recombine with other atoms and/or molecules to produce new components (EPA, 2005). For example, nitric oxide (NO) is one of the exhaust gas components, and is a molecule containing one oxygen and one nitrogen atom in the normal state. In the plasma state, it can be reduced to $N_2$ by N radicals or oxidised into $NO_2$ by other free radicals and ions such as O, OH and $O_3$ (Basfar et al., 2008). NTP is believed to show potential to improve catalyst selectivity and removal efficiency as well (Rajanikanth et al., 2009, Rajanikanth et al., 2003). Moreover, when plasma is introduced in the exhaust gas, unburned hydrocarbons (HC), carbon monoxide (CO) and PM will be oxidised (Yao et al., 2006b, Okubo et al., 2003a, Babaie et al., 2013b). Therefore, NTP has a good potential for pollution reduction applications (Narula et al., 2005, Meloni and Naso, 2013, Jeong et al., 2011).

Most of the studies in this area have been conducted on simulated exhaust gas instead of the actual diesel exhaust. Furthermore, to date the researchers have mostly emphasised NOx removal with a focus on the electrical aspect of plasma treatment. Very little research has been conducted to study the effect of plasma on PM. The capability of plasma for the simultaneous removal of $NO_X$ and PM in the real exhaust of diesel engines needs to be studied in order to evaluate and improve this technique for commercialisation. The effect of NTP not only on PM mass, but also on PM size distribution and PM structure, should be considered in detail. Furthermore, the PM removal mechanism by using NTP technology has not been trialled effectively yet. A comprehensive study of different mechanical, chemical and electrical parameters which play important roles in plasma treatment and plasma reactor design should be developed in an actual diesel operating conditions.

## 1.2 SIGNIFICANCE

This research has significant benefits in the areas of environment, health and emissions research.

**Environment:** DPM contributes significantly to air pollution, water and soil contamination, solar radiation and visibility reduction by both primary and secondary particle formation (Prasad and Rao Bella, 2011). Therefore, there will be a direct improvement in economic and environmental performance indicators through the reduction DPM from diesel exhaust emissions. The work is significant because it evaluates the DPM reduction from diesel exhaust, using a new and effective after treatment system. This is clearly relevant to current societal, government and global objectives.

**Health:** The health effects of diesel emissions have been emphasised in the literature (Ristovski et al., 2012, Sydbom et al., 2001b) and in recent years, diesel exhaust has been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC, 2012). However, the health effects are not limited to regulated emissions only. Different diesel emitted hydrocarbons and other chemical components such as aldehydes, 1,3-butadiene and polycyclic organic materials are reported to be carcinogens with various levels of toxicity (Loh et al., 2007). Carcinogenic and mutagenic features of unsaturated hydrocarbons have been testified by many studies (Melnick et al., 1994, Huff et al., 1985). Thus, it is crucial to address these concerns by using new, after treatment systems (Maiboom and Tauzia, 2011, He et al., 2010, Biswas et al., 2009). The significance of this project lies in its potential to improve air quality and reduce the occurrence and severity of those health effects related to human exposure to airborne pollution, caused by the diesel engine fleet.

**Research:** The NTP after treatment system from this research will be of great benefit, to both researchers and the transport industry. Currently, NTP is used in NOx removal, mostly through the discharge of a high amount of energy to change gas into plasma. The detailed study of the NTP effects on particles and other regulated and unregulated emissions has been considered in this research. Hence, the research significance of this project rests in the knowledge it provides in the ongoing quest to reduce pollutant emissions coming from diesel engines by using NTP technology.

## 1.3 STUDY AIMS AND OBJECTIVES

Plasma application for exhaust treatment is an interdisciplinary research topic centred at the interface between mechanical, electrical and environmental engineering, chemistry, nanoscience, numerical simulation and physics. The primary aim of this project is to employ a new and promising technique called non-thermal plasma (NTP) for PM removal from diesel exhaust, to enable the reduction of relevant environmental and health risks. This project will meet this need through the following objectives:

1. Design and develop a dielectric barrier discharge (DBD) reactor to introduce plasma inside the actual diesel exhaust
2. Investigate the possibility and effectiveness of introducing plasma into the actual diesel exhaust by using pulsed power technology for PM removal
3. Evaluate the basic capability of NTP technique for PM reduction of diesel engines with respect to particle mass and particle size distribution simultaneously
4. Study the mechanism of PM removal and possible particle formation by plasma
5. Study the effect of NTP on PM structure and different PM components such as soot, SOF and sulfate
6. Find the most important parameters and components in PM removal
7. Characterise the NTP formation by varying the applied voltage and frequency to study the effect of different operating conditions on PM mass, PM size distribution, NOx and other gaseous emissions
8. Introduce the appropriate method for calculating discharge power at each operating condition and find the possible optimum operating condition with respect to PM removal efficiency and discharge power
9. Evaluate the formation or increase of other harmful emissions by considering NTP technology for PM removal
10. Study the effect of using NTP technology on PM, $NO_X$, CO, HC and also unregulated emissions

## 1.4 RESEARCH DESIGN AND METHODOLOGY

Plasma treatment of exhaust has shown a notable potential for application as an after treatment technology. To achieve the objectives of this project and investigate the effect of NTP technology on PM removal, different experimental campaigns were carried out. The methodological aspects of this project can be divided into six main steps, which include different experimental perspectives in actual diesel operating condition:

1. NTP set-up design and preliminary evaluation of NTP capabilities for PM removal (Chapter 4)
2. PM removal mechanism exploration (Chapter 5)
3. Detailed study of NTP effect on PM structure and composition (Chapter 6)
4. NTP effectiveness for PM removal at different modes of operation (Chapter 7)
5. Evaluating the role of ozone as the key parameter in PM removal (Chapter 7)
6. Exploring the NTP technology effects on a wide range of regulated and unregulated diesel emissions (Chapter 8)

**Step I. NTP set-up design and preliminary evaluation of NTP capabilities for PM removal**

The DBD reactor has been chosen as the most suitable configuration due to the simplicity and effectiveness for exhaust treatment. A DBD reactor with a 1 mm gap has been designed for the primary study of NTP effects on PM. The DBD was connected to the pulsed power supply using internal and external electrodes. Pulsed power technology was employed for producing plasma inside the exhaust due to its high efficiency. Diesel exhaust after dilution with air was passed through the DBD reactor. The dilution ratio was calculated by measuring the $CO_2$ concentrations by a CAI 600 series gas analyser before and after dilution. Experiments were conducted on a modern turbo-charged 6-cylinder Cummins diesel engine in the QUT Biofuel Engine Research Facility (BERF). PM size distribution was measured with a scanning mobility particle sizer (SMPS) in a range of 10-500 nm and PM mass was measured by a TSI 8530 Dust-Trak II. For the preliminary tests, applied frequency was fixed at 10 kHz and three different voltages were examined. To study the effect of NTP on diesel exhaust, PM mass concentration and PM size distribution were measured and compared before and after applying the pulse. In addition, the median particle diameter, which is another useful parameter to study the effect of plasma technique, is also measured. It is to be

noted that all results in each experiment have been obtained as an average over three consecutive measurements. PM mass removal efficiencies of 43.9%, 38.6% and 27.1% were obtained at 19.44 kVpp, 17 kVpp and 15 kVpp, respectively. Despite the effective performance of NTP technology for PM mass reduction, a significant increase in the number of ultrafine particles was observed at 19.44 $kV_{PP}$. This formation of new particles at high voltage levels leads to the proposal of new experiments to study the PM removal mechanism and PM structural effects under NTP treatment, which has been developed in step II and step III.

**Step II. PM removal mechanism exploration**

From the first study, it is found that the increase of applied voltage does not necessarily have a positive effect on PM removal from the diesel engine exhaust. A considerable increase in the number of ultrafine particles has been observed at a high voltage level of about 20 kVpp. To evaluate the mechanism of PM removal by plasma and the possibility of gaseous emission condensation to particle phase at high voltage levels, a HEPA filter was placed at the reactor inlet and diluted exhaust passed through this filter before entering the DBD reactor. The HEPA filter is also known as the High Efficiency Particulate Air filter, which possesses high efficiency for filtrating the smallest as well as the largest particles. The experimental set-up and other operating conditions for this study were kept the same as for the primary experiments. The HEPA filter removed almost all the particles prior to introducing plasma into the exhaust. A significant increase in the number of ultrafine particles was observed when applied voltage approached 20 $kV_{PP}$ while SMPS recorded a small number of particles before plasma formation. Therefore, it was concluded that the condensation of gaseous emissions to particles (gas to particle change) is possible by introducing plasma into the exhaust at high voltage levels.

**Step III. Detailed study of NTP effect on PM structure and composition**

This part of the research has been conducted in collaboration with Gunma University in Japan. NTP was found to be effective for PM removal from step I, while the formation of ultrafine particles at high voltage levels was discussed in step II. Diesel particulate matter is essentially composed of a solid fraction (soot), soluble organic fraction (SOF) and sulfate particulates. To expand the knowledge obtained from step II and step III for PM removal, the effect of NTP on each component of diesel particulate matter (soot, SOF and sulfate) was considered separately. A 0.4-litre, two-cylinder, four-stroke, indirect injection diesel engine with a swirl combustion (Kubota, Z-402E) was the source of diesel exhaust for the

experiments. Diesel emission characterisation was conducted before the evaluation of NTP technology. A dielectric barrier discharge (DBD) reactor was used to create plasma inside the exhaust. NTP was introduced inside the diesel exhaust at more operating points, compared to previous experiments (Step I and Step II). A range of applied voltages, ranging from 7.5 kV to 13.5 kV at a frequency of 50 Hz, were evaluated during the experiments and discharge power at each operating point was calculated by using Lissajous method and image processing. Experiments were conducted at low discharge power levels to test the system in an applicable range. PM size distributions at five different voltage levels were measured and compared with PM size distribution in the reactor inlet and the reactor outlet without any plasma. Furthermore, the effect of NTP on PM structure was studied in more detail. PM samples were collected on QR-100 Silica filters (Gas Collection Efficiency of 99.99% for 0.3 µm DOP) at the reactor outlet and then analysed by a Horiba MEXA 1370PM. The effect of NTP at different operating conditions on PM components including soot, SOF and sulphate, was considered separately. Among three different components of diesel particulate matter, NTP was found to be very effective for soot removal and complete removal efficiency for accumulation mode particles was achieved. However, at high levels of applied voltage, the total number of nucleation mode particles increased by a factor of more than 50 times higher than the total particle numbers at the reactor inlet. This trend is in agreement with the result in step I experiments for nucleation mode particles.

Due to the high concentration of emitted $NO_X$ by diesel engines and the effect of $NO_X$ on PM oxidation, $NO_X$ concentration was monitored during the experiments simultaneously. Concentrations of NO, $NO_2$, $N_2O$ and total $NO_x$ ($NO+NO_2$) were measured under each plasma condition using a Fourier transform infrared spectroscopy exhaust gas analyser (Horiba Co., Ltd, MEXA-4000FT). By increasing the energy density, a continuous increase on $NO_x$ removal efficiency has been observed. For the given configuration, the maximum $NO_x$ removal efficiency of about 18% has been achieved when energy density was about 27 J/L.

The effect of plasma on PM and $NO_X$ emissions for a number of operating conditions was discussed in steps I to III. The range of operating conditions has been extended in step IV and step V and NTP characterisation for a wide spectrum of discharge powers has been considered. The following two steps broadened the boundary of previous studies in terms of NTP evaluation for PM removal to find out the possible optimum operating points and to

analyse the discharge power variation, not only by changing the applied voltage, but also by taking the frequency into account.

**Step IV. NTP effectiveness for PM removal at different modes of operation**

Discharge power has been emphasised as the main challenge of NTP application in literature and in previous steps, the dependency of NTP performance for PM removal on amount of discharge power into the exhaust was found. Discharge power can be controlled by varying the applied voltage and frequency. Therefore, to characterise the effectiveness of NTP technique for PM removal under varied conditions and find the possible optimum operating points, a range of applied voltages from 11 $kV_{PP}$ to 21 $kV_{PP}$ at repetition rates of 2.5, 5, 7.5 and 10 kHz, were experimentally investigated. Experiments were conducted on a Cummins diesel engine in the QUT Bio Engine Research Facility (BERF). DBD reactor was employed with pulsed power technology to produce plasma inside the diesel exhaust. Due to the oxidation of PM to $CO_2$, and the key role of ozone in this process, PM, $CO_2$ and ozone concentrations were measured in all experiments. Different contour plots have been presented to evaluate the effect of NTP on discharge power, ozone production, and $CO_2$ and PM concentrations. All these parameters have been plotted against voltage and frequency using a minimum to maximum mesh grid, with interpolation for every single unit of frequency and voltage. Mathwork, the MATLAB version 2013a, was used for the data interpolation process. The "griddata" function in MATLAB with the 'Cubic interpolation' method of voltage (x axis), and frequency (y axis) grid has been employed. The cubic method ensures 'the interpolating surface is $C_2$ continuous' (second order derivatives). The results showed that by increasing the applied voltage and frequency, higher discharge power and $CO_2$ dissociation can be achieved. However, discharge power was influenced by the applied voltage more than the repetition rate especially by approaching the higher voltage levels. The minimum PM concentration was obtained at 19 $kV_{PP}$ and 10 kHz and the maximum ozone concentration of about 547 ppm was found at 21 $kV_{PP}$ and 7.5 kHz.

**Step V. Evaluating the role of ozone as the key parameter in PM removal**

Due to the high concentration of ozone in the previous experiment, ozone was considered to be an important parameter in PM removal when using NTP technology. Therefore, in experiments described in Step IV, PM, ozone and $CO_2$ concentrations were monitored over the time to find out the correlation between them. First, the concentration of PM, ozone and $CO_2$ were measured at the reactor outlet without applying any pulse. Then,

plasma was tested at 2.5, 5, 7.5 and 10 kHz for the voltages of 11, 13, 15, 17, 19 and 21 $kV_{PP}$ at each point. Diesel exhaust was passed through the plasma reactor and plasma treatment was considered for a period of 180 s at each operating condition. A TSI 8530 Dust-Trak II, CAI 600 series gas analyser and Model 202 Ozone Monitor™ were used to measure the PM, $CO_2$ and ozone concentrations respectively. The correlation study of emissions showed the key role of ozone in PM and $CO_2$ concentrations. $CO_2$ concentration decreased continuously by increasing the voltage level at all repetition rates over the time period of study, except at the end of the test with 21 kVpp/10 kHz, which is due to the reduction in ozone concentration. Furthermore, an opposite trend has been observed in concentration of ozone and PM. For all operating conditions at the beginning of experiments when ozone is increasing, PM concentration decreases continuously. However, at three combinations of 19 kVpp/10 kHz, 21 kVpp/10 kHz and 21 kVpp/7.5 kHz reduction of ozone production by plasma over the time resulted in PM concentration increase due to the PM oxidation reduction.

**Step VI. Exploring the NTP technology effects on a wide range of regulated and unregulated diesel emissions**

A detailed study of NTP effects for PM removal from actual diesel exhaust has been developed through the previous steps. However, the ultimate goal of all NTP research for exhaust treatment is to contribute in designing an effective after treatment system for real applications in the future. A soot component of diesel particulate matter can be formed due to the incomplete combustion of hydrocarbons, while the organic fraction will be formed due to the absorption of different hydrocarbons on the surface of soot particles. Besides the particulate matter, diesel exhaust is a complex mixture of gaseous emissions, which should be considered during NTP treatment. Furthermore, the formation of extra harmful gaseous emissions is possible during PM removal by using NTP technology. Therefore, it is important to examine the effect of NTP technology on hydrocarbons and other unregulated diesel emissions. This part of the research has been conducted in collaboration with Gunma University in Japan. The concentrations of 22 different species, including different hydrocarbons, carbon monoxide, carbon dioxide, nitrogen oxides, sulfur dioxide, formaldehyde etc., were measured in several experiments. A Kubota, Z-402E diesel engine was employed for these experiments. To achieve the steady state condition, engine load was kept constant at 2 kW during the experiments and a warm-up period of 30 minutes has been considered at the beginning of the experiments. A sample of diesel exhaust was cooled down

to the ambient temperature and passed through a DBD reactor to introduce plasma inside the exhaust for all experiments. Plasma was introduced into the exhaust at fixed frequency of 50 Hz and variable applied voltages of 7.5, 9, 10.5, 12 and 13.5 kV during the experiments. A Tedlar bag was used for collecting exhaust gas samples after passing through the DBD reactor. The concentration of different components of diesel exhaust gas was measured by an FTIR exhaust gas analyser (Horiba Co., Ltd., MEXA-4000FT). Furthermore, PROMETHEE-GAIA ranking analysis has been considered for all emissions by making a matrix with 20 criteria (different diesel engine emissions) and six variables (applied voltages) to find the interrelationships among the data and provide a summary of the necessary information for ranking and interpretation patterns in the entire data set. From this analysis $CO_2$, $C_7H_8$, $C_3H_6$, $CH_4$, $NH_3$, 1, 3-$C_3H_6$, $CH_3OH$, $H_2O$, etc. with very short criteria are found not to be affected so much by varying the applied voltages. In contrast, NTP affected $NO_X$, $C_2H_4$, CO and to some extent aldehydes with longer criteria vectors. The reverse relationship between $NO_x$ and NO with $NO_2$ concentration under plasma condition is confirmed from this analysis as well. Besides this, an anti-correlation between CO with NO and $NO_x$ has been observed. This is relevant to the existence of hydrocarbons in diesel exhaust and promotion of NO to $NO_2$ conversion by producing a considerable amount of CO. All previous six steps are conceptually presented in Figure 1.1.

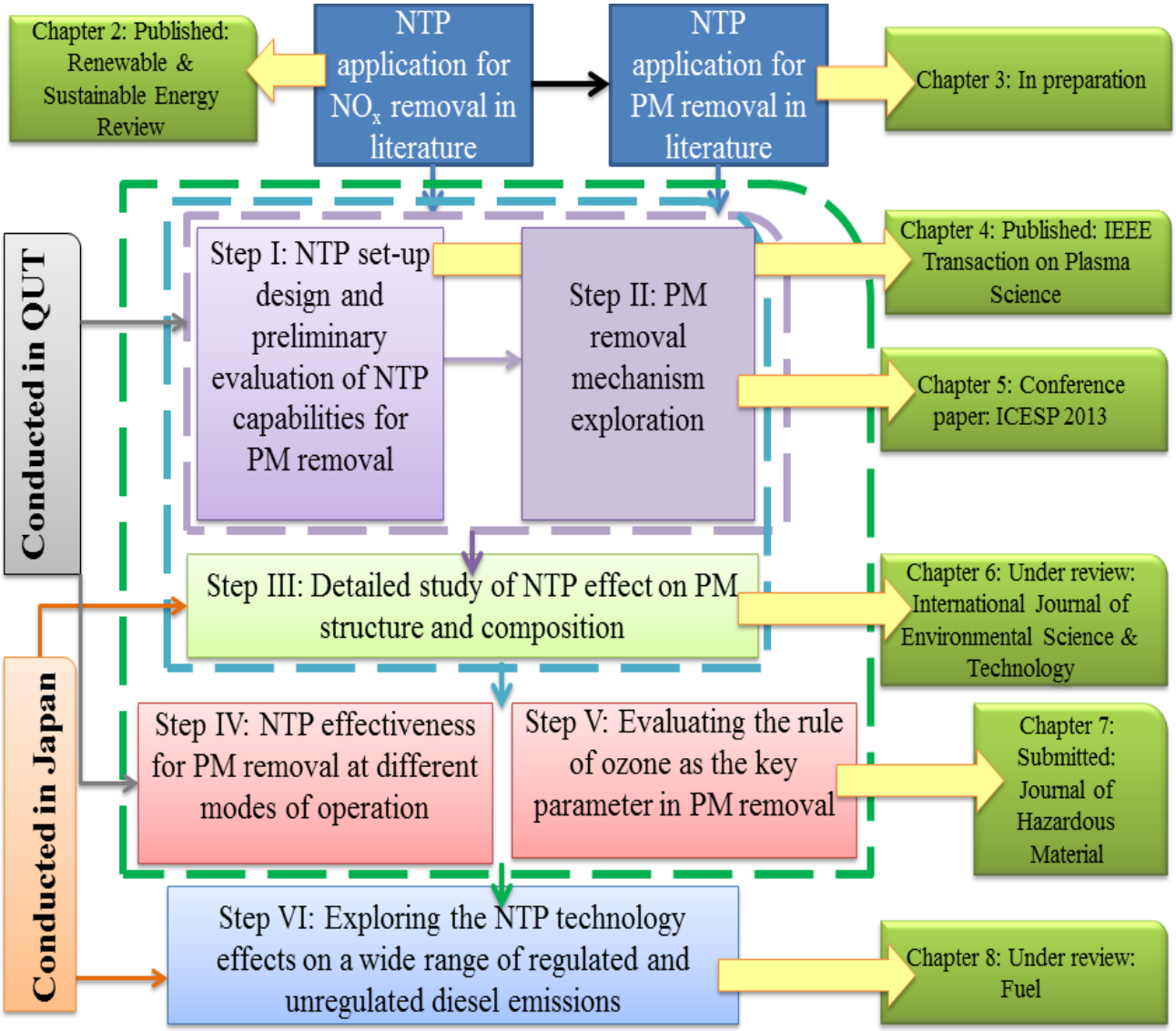


Figure 1.1: Outlining the structure of this PhD thesis

# Chapter 2: The role of non-thermal plasma technique in $NO_x$ treatment: A review

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Publication: Renewable and Sustainable Energy Reviews 40, 886-901

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| P. Talebizadeh | Analysed the literature and drafted the manuscript |
| R. Brown | Supervised the project, aided with the development of the paper and extensively revised the manuscript |
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**Abstract**

Non-thermal plasma (NTP) has been introduced over the past several years as a promising method for nitrogen oxide ($NO_x$) removal. The intent, when using NTP, is to selectively transfer input electrical energy to the electrons, and to not expend this in heating the entire gas stream, which generates free radicals through collisions, and promotes the desired chemical changes in the exhaust emissions. The generated active species react with the pollutant molecules and decompose them. This paper reviews and summarises relevant literature regarding various aspects of the application of NTP technology on $NO_x$ removal from exhaust emissions. A comprehensive description of available scientific literature on $NO_x$ removal using NTP technology is presented, including various types of NTP, e.g. dielectric barrier discharge, corona discharge and electron beam. Furthermore, the combination of NTP with catalyst and adsorbent for better $NO_x$ removal efficiency is presented in detail. The removal of $NO_x$ from both simulated gases and real diesel engines is also considered in this chapter paper. As NTP is a new technique and is not yet commercialized, there is a need for more studies to be performed in this field.



**Keywords:** Non-thermal plasma (NTP); Nitrogen oxides removal; Diesel engines; Catalyst; Emission treatment; Pollution.

## 2.1 INTRODUCTION

There has been a continuous increase in the number of diesel engines operating in both stationary and mobile applications, due to their lower operating cost, higher thermal efficiency, longer durability, and their lower hydrocarbon (HC) and carbon monoxide (CO) emissions (Guibet and Faure-Birchem, 1999). However, these engines emit higher amount of $NO_x$ and particulate matters (PM) than gasoline engines. Moreover, conventional energy sources are close to extinction, and environmental concerns necessitate cleaner fuels being used. Indeed, exhaust emission regulations have become much more stringent in recent times. Alongside these increasingly stringent emission standards, there is still considerable concern that unregulated pollutants are having a deleterious effect on human health and the environment generally (Holzer et al., 2002, Roland et al., 2005a, Roland et al., 2005b, Subrahmanyam et al., 2006a, Subrahmanyam et al., 2006b, Gu et al., 2013). Given the likely health effects associated with gaseous pollutants and ultrafine particles, there is a clear need to monitor the emissions of diesel engines.

### 2.1.1 Diesel engine emissions

Diesel engines are used as the power source in a wide variety of industries and their applications are growing rapidly all over the world. Diesel engines have been employed in transportation as the power source for buses, trucks, trains and ships. Moreover, they are used in power plants for power generation, and also in farming, construction and industrial settings. In spite of the large number of diesel engine applications, they continue to produce significant amounts of pollution, particularly $NO_x$. Therefore, their increasing numbers in transportation vehicles will cause an increase in global emissions, with nitrogen oxides being the main pollutant from diesel exhaust.

Complete combustion of a hydrocarbon fuel, which has been basically composed of carbon and hydrogen, would only generate $CO_2$ and $H_2O$ without formation of any other harmful products. However, due to the existence of several parameters such as short time of the chemical oxidation inside the combustion chamber, the non-homogeneity of the air fuel mixture inside the cylinders, and the heterogeneity and quick change of the temperature the ideal thermodynamic equilibrium cannot be achieved (Schuetzle and Hammerle, 1986). Instead, an incomplete combustion will occur and a wide range of organic and inorganic components will be generated as the particle and gaseous emissions (Stratakis, 2004a) which

has been summarized Table 2-1 (Jelles, 1999). It should be noted that the mg/mile is mile travelled by the vehicle.

Table 2-1: Typical diesel exhaust composition (Jelles, 1999)

| | Component | Concentration |
|---|---|---|
| Components naturally occurring in air | $N_2$ | 70-75 vol% |
| | $O_2$ | 5-15 vol% |
| | $CO_2$ | 2-12 vol% |
| | $H_2O$ | 2-10 vol% |
| Regulated harmful components | CO | 100-10000 ppm |
| | HC | 50-500 ppm, C1 |
| | $NO_x$ | 30-600 ppm |
| | $SO_x$ | Proportional to fuel S content |
| | PM | 20-200 mg/m3 |
| Unregulated harmful components | Ammonia | 2.0 mg/mile |
| | Cyanides | 1.0 mg/mile |
| | Benzene | 6.0 mg/mile |
| | Toluene | 2.0 mg/mile |
| | PAH | 0.3 mg/mile |
| | Aldehydes | 0.0 mg/mile |

Diesel exhaust is different from gasoline exhaust in two major ways. Diesel exhaust contains a far higher amount of $NO_x$. Furthermore, the exhaust is far leaner, it means the amount of unburned hydrocarbon and carbon monoxide in diesel exhaust is much lower than the gasoline exhaust. Thus, nowadays, the focus of the research on reduction of harmful emissions in diesel engines is mainly on $NO_x$ (Prasad and Rao Bella, 2010).

### 2.1.2 Health and environmental impacts of NOx and emission legislations

Several types of nitrogen oxides exist in the environment: $N_2O$, NO, $NO_2$, $N_2O_3$, $N_2O_4$, $NO_3$, and $N_2O_5$. The abbreviation $NO_x$ usually relates to nitric oxide (nitrogen monoxide) NO and nitrogen dioxide $NO_2$, which can be called ‘fresh’ nitrogen oxides from a photochemical point of view, since they reach atmosphere in these forms. Another important nitrogen oxide is $N_2O$ (Nitrous oxide), and it may also be called ‘fresh’ for the same reasons (Skalska et al., 2010). Nitrogen oxides form when fuel is burned at high temperatures, as in a combustion process. The primary sources of $NO_x$ are motor vehicles (49%), electric utilities (27%),

industrial, commercial, and residential sources (19%) and all other sources (5%) that burn fuels (Riess, 1998).

Among the various types of $NO_x$, nitric oxide and nitrogen dioxide are considered toxic. Around 95% of $NO_x$ emitted from incineration processes is NO and 5% $NO_2$ (Gómez-García et al., 2005). Nitric oxide is less toxic than nitrogen dioxide. However, as with most radicals, NO is unstable and reacts readily with oxygen through photochemical oxidation to form $NO_2$ (Skalska et al., 2010).

Studies focused on risk assessment have showed that high outdoor $NO_2$ concentrations observed in residential areas contribute to increased respiratory and cardiovascular diseases and mortality (Chaloulakou et al., 2008b). Some of the other negative effects of $NO_x$ are acid rain, ground-level ozone (smog), photochemical smog, global warming, nose and eye irritation, visibility impairment, the formation of toxic products and water quality deterioration (Sher, 1998).

$NO_x$ is responsible for tropospheric ozone/particulate (urban smog) through photochemical reactions with hydrocarbon (Devahasdin et al., 2003). The mixture of $NO_x$ and volatile organic compounds (VOC) in the atmosphere when exposed to sunlight can result in the formation of photochemical smog, which can cause infection and encourage the spread of cancer. The yellowish colour of $NO_2$ decreases the visibility, contributes to heart and lung problems and can suppress plant growth. $NO_2$ can also react with radicals produced from VOCs in a series of reactions to form toxic products, such as peroxyacetyl nitrates (PAN) (Tunnicliffe et al., 1994, Koenig, 2000, Devahasdin et al., 2003).

NO and $NO_2$ together with sulfur dioxide ($SO_2$) are the major contributors to acid rains (Devahasdin et al., 2003). When $NO_x$ and $SO_2$ are exposed to the atmosphere, they react with water to form sulfuric acid and nitric acid, which are the main components of acid deposition. Indeed, $NO_2$ reacts with OH in the atmosphere to form nitric acid ($HNO_3$). Nitric acid can also form when nitrogen dioxide ($NO_2$) reacts with the nitrate radical ($NO_3$) in the presence of atmospheric water or aldehydes. Nitrogen oxides account for approximately 30% of all acid deposition (Likens et al., 1972). Nitrous oxide ($N_2O$) has some negative effects as well. $N_2O$ is a greenhouse gas that has a global warming potential more than 300 times higher than that of carbon dioxide (Pauleta et al., 2013). $N_2O$ can destroy the stratosphere ozone which increases UV-B radiation at the earth's surface (Smith, 1997). Furthermore, animal and human studies indicate that the toxic effects of $N_2O$ depend on concentration and time. For a

time-weighted average of 100 ppm for an eight-hour workday and/or a time weighted average of 400 ppm per anaesthetic administration, it would provide adequate protection of dental personnel and be acceptable to existing pollution control methods (Yagiela, 1991). However, in patients who have been administered $N_2O$ for extended periods of time, and the neurological abnormalities found in health care workers who inhaled $N_2O$ recreationally, some effects like anaesthetic action and bone marrow depression (Yagiela, 1991) have been disproved.

The health effects of breathing in diesel exhaust has been shown to be toxic, mutagenic or carcinogenic in animal exposure tests (McClellan, 1989). Also, the exposure of animals to diesel exhaust has produced morphological and biochemical changes in the lungs, with an increase in susceptibility to bacterial infection, and the possibility of producing systemic toxic effects. Some human diseases that can be caused from $NO_x$ are pulmonary edema (swelling), bronchitis, and even pneumonia (Hariri, 1994). Due to the negative effects of $NO_x$ on health, regulation of exhaust emissions has recently become increasingly stringent. Government legislation for permissible exhaust emission standards was first introduced for light-duty vehicles only, in both Europe and the United States in 1982, and then for heavy-duty engines in 1990 (Van Setten et al., 2001a). In Table 2-2, emission regulations concerning $NO_x$ are indicated as shown, with more and more stringent standards being employed day by day (NV et al., 2008, Prasad and Venkateswara, 2010).

Table 2-2: NOx emission standards for diesel vehicles (NV et al., 2008, Prasad and Venkateswara, 2010)

| Year | Reference | Light duty diesel (g/km) | Heavy duty diesel (g/km) |
|---|---|---|---|
| 2000 | Euro I | - | 0.36 |
| 2005 | Euro II | - | 0.15 |
| 2008 | Euro III | 0.5 | 0.10 |
| 2010 | Euro IV | 0.25 | 0.02 |
| 2011 | Euro V | 0.18 | 0.005 |

Furthermore, Euro VI regulations ,which has been introduced in 2013, enables the harmonisation of the European standards with those of the US and Japan (Johnson, 2006, Johnson, 2009).

### 2.1.3 $NO_x$ removal after treatment systems

Up until now, several technologies have been applied for $NO_x$ removal from exhaust gases. Selective catalyst reduction (SCR), active lean $NO_x$ catalysts, lean $NO_x$ trap catalysts and multiple injection combustion have been considered for $NO_x$ removal in automobile and stationary engines (Narula et al., 2005, Meloni and Naso, 2013, Jeong et al., 2011). SCR is used to convert $NO_x$ into diatomic nitrogen ($N_2$), and water ($H_2O$), with the aid of a catalyst i.e. a gaseous reductant such as anhydrous ammonia, aqueous ammonia or urea (Gieshoff et al., 2001, Radojevic, 1998). Zeolite catalysts will also be the mainstay for Japan, US, and Euro VI applications (Johnson, 2009).The advantage of using SCR is that the major by-products of SCR are harmless nitrogen and water vapours. However, SCR catalysts need high temperatures (around 300°C) for activation. There are some problems in using SCR catalysts, such as the possibility of ammonia leakage, catalyst poisoning, catalyst discharge under high temperature conditions or through the influence of sulfur, and the need for the construction of urea solution stations (Tayyeb Javed et al., 2007, Skalska et al., 2010). In addition, diesel exhaust is a highly oxidising environment, and the SCR catalysts used on gasoline engines are not suitable for $NO_x$ removal in diesel applications (Yamamoto et al., 2003b).

Active lean $NO_x$ or $DeNO_x$ catalysts are another important $NO_x$ reduction, after treatment system, while the reductant is different from the SCR catalysts. Hydrocarbons were employed as the $NO_x$ reductant (M Palash et al., 2013) while in the reduction process, $NO_x$ reacted with hydrocarbons and produces $N_2$, $CO_2$, $H_2O$ and $N_2O$. Both $CO_2$ and $N_2O$ are greenhouse gases with great global warming ability (Huttunen et al., 2003, Iglesias-Juez et al., 2003). Moreover, in the active system applications, it is necessary to occasionally add supplementary HC to the exhaust gas to maintain the reactions.

Lean-burn $NO_x$ trap (LNT) catalysts include three main components. The first is a noble metal such as Pt, which enables NO oxidation in the lean-burn phase and $NO_x$ reduction in the rich-burn phase. The second component contains a storing element such as Ba, which captures $NO_x$ as nitrates or nitrites. The third component has a large surface area to increase noble metals and the storage medium, which consists of the supports such as $Al_2O_3$ (He et al., 2010). Some of the disadvantages of the system are the high cost of the catalyst and noble metal, as well as a periodic regeneration requirement (West et al., 2004).

Multiple injection and high pressure fuel injection is applied in order to simultaneously reduce both soot and $NO_x$ emissions from combustion (Han et al., 1996), however, it is not an after treatment system. The technique can optimise emission from the combustion chamber

and has advantages such as reduction of pollutants and noise, higher thermal efficiency and power and lower specific fuel consumption (Bhatt et al., 2008). Although this technique can reduce toxic combustion by-products from the exhaust gas, an after treatment system is still required to meet the current increasing emission standards.

The NTP technique will be considered for emission reduction in diesel engines fuelled by diesel or biodiesel. NTP treatment of exhaust emissions is a promising technology for $NO_x$ removal, which is effective through the introduction of plasma inside the exhaust. Plasma is the fourth state of matter, consisting of positive and negative charges, which have a tendency to remain electrically neutral overall, and over large length scales. It is composed of free electrons, ions, radicals, atoms, and molecules in various states of excitation (Gomez et al., 2009). Vehicle exhaust emissions, both diesel and gasoline, undergo chemical changes when exposed to plasma. Logically, oxidation processes dominate in the presence of oxygen. These reactions include oxidation of hydrocarbons, carbon monoxide, and nitrogen oxides (Majewski, 2004).

This chapter provides an overview of the literature concerning $NO_x$ removal from exhaust, as conducted by various groups of researchers. The first part of this chapter is about diesel engine emissions. The second section contains an overview of pulse power technology and its application on plasma treatment of exhaust gases. The final section provides a summary of findings as to how plasma can be effective for $NO_x$ removal from simulated gases and diesel engines, whilst highlighting the significance of exploring various views concerning plasma emission treatment, as held by a number of researchers. The main argument presented in this section suggests that there is a strong correlation between mechanical, chemical and electrical parameters involved in plasma production and exhaust gas treatment, which will ultimately result in the improvement of diesel engine emission treatment. This chpter seeks to bring together in a systematic way the disparate material on $NO_x$ removal from exhaust gases.

## 2.2 PLASMA AND VARIOUS POWER GENERATORS

The term plasma was first introduced by Irving Langmuir (1881-1975) and his colleague Lewi Tonks (1897-1971) in 1929, to describe the inner region of a glowing ionised gas phase produced by means of an electric discharge in a tube (Tonks and Langmuir, 1929). Plasma is the fourth state of matter, that is, an ionised gas into which sufficient energy is provided to free electrons from atoms or molecules and to allow species, ions and electrons to

coexist. Generally, plasma is electrically neutral. The plasma ionisation degree is the proportion of atoms that have lost (or gained) electrons (Gomez et al., 2009).

As discussed before, in order to introduce plasma into a gas, the electronic structure of the species (atoms, molecules) should be changed, and then excited species and ions will be produced. The required energy for this process can be provided by thermal force, or carried by either an electric current or electromagnetic radiations (Tendero et al., 2006). Therefore, plasma is divided into thermal or hot plasma and non-thermal or cold plasma. In the thermal variety, molecules dissociate into the atoms at high temperatures around 2000 ◦C. Gas molecules will be ionised by losing electrons if the temperature goes up to more than 3000 ◦C. In this state, gas has a liquid-like viscosity at atmospheric pressure and the free electric charges confer relatively high electrical conductivities that can approach those of metals (Auciello and Flamm, 1989). In thermal plasma, the kinetic energy (temperature) of charged particles and the kinetic energy (temperature) of the background gas are similar. Since all particles are in thermal equilibrium, thermal plasma is also known as equilibrium plasma (Fridman, 2008). In non-thermal plasma (NTP), the electric field transmits energy to the gas electrons and then energy will be transferred to the neutral species by collisions (Tendero et al., 2006). In NTP, electrons have a kinetic energy higher than the energy corresponding to the random motion of the background gas molecules, generally in the range of between 10,000K and 100000K (2-3 order of magnitude greater than the background gas) (Kogelschatz et al., 1999). An example of non-thermal plasma is the gas filling a fluorescent tube. Its temperature is only around 40°C, but the temperature of free electrons in the system exceeds10000°C (Majewski, 2004). The intent when using non-thermal plasma is to selectively transfer the input electrical energy to the electrons, which then generate free radicals through collisions, and promote the desired chemical changes in the exhaust gas. These reactions can be accomplished with just a fraction of the energy that is required in the thermal plasma system (Kogelschatz et al., 1999, Yao et al., 2007, Jaffré et al., 2009).

Generally, three kinds of power generators (namely AC, DC and Pulse) can be used in order to generate plasma. AC and Pulse energisations show a superior $NO_x$ removal efficiency, when compared with DC energisation. However, Pulse energisation is found to be more energy efficient (Srinivasan et al., 2009).

Pulsed power is generated by instantaneously but gradually delivering the energy accumulated and stored in an energy component to a load. By releasing stored energy over a very short time interval, a huge amount of peak power can be delivered (Winands, 2007). In

other words, the energy, which can be generated with extra low voltage, is released in a shorter period of time, which causes higher amplitude (Ahlfont and Sandborgh, 1999). This strategy is called pulsed power. Recently, many studies of industrial applications of pulsed power technology, such as food processing, medical treatment, water treatment, ozone generation, engine ignition, ion implantation, exhaust gas treatment and others, have resulted from the development of pulsed power generators (Akiyama et al., 2007, Ahlfont and Sandborgh, 1999).

Recently, repetitively operated pulsed power generators with a moderate peak power have been developed. These generators are compact, reliable, low maintenance, and have high reproducibility. Using pulsed power technology, non-thermal plasmas have been generated by a pulsed electron beam (Xu and et al., 2003) or a pulsed streamer discharge (Yao, 2009a), and can be used to treat nitric oxides ($NO_x$), sulfur dioxide ($SO_2$), carbon dioxide ($CO_2$), particulate matter and volatile organic compounds (VOCs), and also to generate ozone. Non-thermal plasmas have many kinds of chemically activated radicals, such as O (Oxygen radical), $O_3$ (Ozone), N (Nitrogen radical), $N^*$ (excited Nitrogen radical), $N_2^+$ (positive ions of nitrogen) and OH, which are generated by the dissociation and ionisation of the ambient gases caused by the impact of energetic electrons (Akiyama et al., 2007, Takaki and Katsuki, 2009, Mueller et al., 2011).

When plasma is introduced inside the exhaust gases, oxidation processes will be started. $NO_x$, unburned hydrocarbons, carbon monoxide (CO) and particulate matter (PM) will be oxidised (Babaie et al., 2013b). In spite of $NO_x$ reduction to $N_2$ and $O_2$, plasma treatment of exhaust gases is more related to NO oxidation to $NO_2$ (Penetrante, 1994, Penetrante et al., 1999). The plasma is believed to show potential to improve catalyst selectivity and removal efficiency.

## 2.3 PLASMA REACTORS

NTP can be generated in several ways, such as through electrical corona discharges, radio frequency discharges, microwave discharges (Radoiu, 2004, Chang et al., 1991a), dielectric barrier discharges and electron beams. The following NTP technologies are considered for pollution reduction in engine exhaust gases, with each having its advantages for different applications. The plasma reactors can be divided into different categories with respect to the type of power supply (DC, pulse, DC and pulse, AC, AC and DC, RF), the presence of a dielectric barrier or catalyst, geometry, mode of discharge, polarity, and voltage

level and gas composition. Therefore, the comparison of NTP reactors is complicated due to the dependency on different aforementioned conditions (Kim, 2004b, Vandenbroucke et al., 2011b) and there are no well-established common criteria for comparing different plasma reactors. Based on this finding, we propose the criteria such as energy density, removal efficiency, energy efficiency, residence time, pressure drop, scalability and cost, for future plasma reactor research.

### 2.3.1 Electron beam

An electron beam is formed in a separate generator, such as a cathode tube, and then the electrons will be injected into the exhaust gas. The energy of the electrons is absorbed by the components of the gaseous mixture proportionally to their mass fraction (Chmielewski et al., 2001). The energy of electrons can be much higher in the e-beam reactor than in other reactors. Disadvantages of the e-beam reactor include the need for a special reactor for generating the electrons, and poor efficiency in transferring the electrons into the exhaust gas (Bhasavanich et al., 1993, Penetrante et al., 1995a, Majewski, 2004).

### 2.3.2 Corona discharges

The term corona comes from the crown-like appearance of the plasma discharge when the voltage exceeds a certain value (Chang and Urashima, 2000). In a corona discharge reactor, a non-uniform electric field is formed between two concentric electrodes by the sharp edges or points of its electrodes where the radius of the curvature is small. In other words, the mode of discharge in corona discharge is usually the streamer mode and the ionisation zone is spread over the entire gap. Therefore, the discharge gap can be set as large as 10 cm or more, which is highly appropriate for large scale application (Kim, 2004b). A characteristic of corona discharges is that there is no need to use a dielectric to generate plasma (Whealton et al., 1997, McAdams, 2001). In corona discharge, the strong electric field, ionisation and luminosity are actually located close to one of the electrodes and the electric current is transferred to the outside electrode by the drift of charged particles in the relatively low electric field (Fridman et al., 2005). Therefore, a low current and, as a result, very low discharge power, is achieved, and increasing the applied voltage can form a spark. This problem can be solved by using pulse voltage circuits. The produced pulsed electric field can prevent plasma from going into the thermal mode and forming an arc (Majewski, 2004).

In some environmental applications such as decomposition of $CCl_4$ (Penetrante et al., 1995a), pulsed corona processing is found to be considerably less energy efficient than the

electron beam processing. However, the requirement of using a separate reactor and difficulty of electron generation is an important limiting factor for the application of electron beam processing.

### 2.3.3 Dielectric barrier discharge

The basic design of a dielectric barrier discharge (DBD) reactor consists of a set of electrodes with at least one dielectric barrier between them. As a result of the presence of the dielectric barrier, the discharges require higher voltage for their operation. In other words, the electric field must be high enough to cause breakdown in the gas (Kogelschatz, 2003). The gas is passed through the dielectric surfaces, while the electrodes produce the sufficient electrical field between them to form the plasma. The material used for dielectric barriers is usually quartz glass, silica glass or alumina; however, they can also be made from ceramic materials, and thin enamel or polymer layers in special cases (Kogelschatz, 2003, Majewski, 2004).

A common feature of both DBD and corona discharge is that small scale electron streamers are formed (Whealton et al., 1997). However, a DBD produces a homogenous discharge with low energy consumption and this discharge process is also the mechanism through which charges are transported (Wang et al., 2011). Furthermore, DBD can avoid spark formation inside the streamer channels, which are therefore called silent discharges, and the absence of sparks causes the absence of overheating, local shock waves and noises (Fridman et al., 2005). High discharge power can also be achieved without employing pulse power generators (Fridman et al., 2005). Whealton et al. (Whealton et al., 1997) explained that after applying the electric field perpendicular to the dielectric, electron streamers are formed. Space charge then builds up on the dielectric surface, locally terminating the external applied electric field, and then finally extinguishing the discharge. Eventually, in a DBD reactor, the large volume excitation of the glow discharge with the high pressure of the corona discharge can be formed (Tudor et al., 2005). Therefore, in general, employing the dielectric has two benefits: firstly, limiting the charge transferred by an individual micro-discharge and so preventing the formation of arc discharge, and secondly, spreading the micro-discharge over the electrode surface, which increases the probability of collision between the electron and ions and gas molecules (Eliasson et al., 1987).

In addition to the easy formation of stable plasmas and homogeneous discharge in DBD, there are some more advantages such as scalability, effectiveness and low operational

cost which influence researchers to use DBD more than other types of reactors (Fang et al., 2007, Kogelschatz, 2003). Furthermore, the discharge characteristics depend on the gas composition, type of dielectric material, and operating conditions of voltage and frequency (Kim, 2004b). According to the above advantages of DBD, it has more potential for exhaust cleaning from CO, $NO_x$ and VOCs (Penetrante et al., 1999), furthermore, it has been used for a long time for ozone generation (Mizuno, 2007).

### 2.3.4 Dielectric packed bed reactor

The dielectric packed bed reactor is similar to the DBD, but with a different configuration of dielectrics. Pellets of dielectric material are placed in the gap between the barrier and the electrode. One advantage of this system is that relatively low applied voltages can be used to form a plasma over a relatively large separation of the electrodes (McAdams, 2001). In other words, when the pellets are exposed to an external electric field, a spontaneous polarisation occurs in the direction of the electric field, resulting in a high electric field at the contact points of the pellets (Kim, 2004b). Another advantage of this system is that it is possible to use catalyst pellets, which makes this type of reactor a possible choice for plasma-catalyst systems. In the plasma-catalyst systems, the plasma discharge is introduced right on the catalyst surface, which enhances the properties of the catalyst and its corresponding performance (Chen et al., 2008). Furthermore, residence time is proposed as one of the common criteria to be used to compare different plasma reactors (Futamura et al., 2001). Residence time can be improved by using pellets in Dielectric packed bed reactors. However, the high pressure drop and attrition of the pellets are disadvantages of this system (Majewski, 2004).

### 2.3.5 Surface plasma discharge

In this system, one of the electrodes covers one side of the dielectric barrier completely; however, the other electrode only partially covers it, making it distinct from the corona discharges and DBD. The plasma is generated next to this dielectric surface, which is in contact with the gas. When the electric field is applied, the surface plasma covers the entire dielectric surface (Whealton et al., 1997). A feature of this discharge is that after a few nanoseconds, charge begins to build up at the dielectric surface, which has the effect of reducing the electric fields outside the dielectric, eventually extinguishing the discharge (Majewski, 2004).

### 2.3.6 NTP reactor comparison

Energy consumption in an NTP application for emission reduction is a major challenge. Specific energy density (SED), which is defined as the ratio of discharge power to the gas flow rate, and energy efficiency, which is the ratio of the substance removal measure to the plasma energy, are the common criteria in NTP energy evaluation. Some studies about the effect of NTP processing in the conversion of NO to $N_2$ and $O_2$ show that the specific energy consumption of corona discharge, DBD and Dielectric packed bed reactors are all similar (Penetrante et al., 1995d, Penetrante et al., 1996). In the decomposition of bromomethane, ($CH_3Br$), and tetrafluoromethane ($CF_4$), it was shown that DBD and Dielectric packed bed reactors have better energy performance, thus showing higher performance than corona discharge reactors (Futamura et al., 2001).

On the other hand, the energy efficiency of NO removal from the air was found to be higher for surface plasma than the corona and DBD reactors as reported by Malik et al. (Malik et al., 2011a). However, they outlined the dependency of NO removal on gas composition especially on oxygen concentration. Besides that, the energy efficiency of DBD and corona discharge reactors was found to be reduced with an increase of the discharged energy, while for surface plasma it remained constant. This indicates a greater potential for using surface plasma reactors at high energy densities and in more compact reactors than conventional DBD or corona reactors (Malik et al., 2011a).

Therefore, for the proper applications of NTP reactors, it is necessary to consider not only the physical properties (such as voltage, frequency, ionisation, geometry, type of power supply, volume, etc.) but also the variations in energy efficiency. It is still controversial to compare NTP reactors with the same physical properties, regardless of the mode of the application and gas composition (Penetrante et al., 1995d, Penetrante et al., 1995a, Penetrante et al., 1996, Futamura et al., 2001, Kim, 2004b). It has also been shown that the design of a reactor and the materials of the electrodes can greatly affect removal and energy efficiency (Kim et al., 2005b).

## 2.4 PLASMA $NO_X$ REMOVAL

After introducing different plasma reactors in the previous section, different publications are now analysed, concerning the application of NTP on $NO_x$ removal. Firstly, the relevant chemical reactions have been presented. Then, the relevant publications for the

engine exhaust and simulated exhaust have been reviewed in two main categories. In each category, a variety of publications for different types of reactor have been considered.

$NO_x$ storage reduction (NSR), selective $NO_x$ recirculation (SNR) and non-thermal plasma have been considered increasingly in recent years, with a view to developing techniques to reduce $NO_x$ emissions in diesel engines (Roy and Baiker, 2009, Roy et al., 2009, Epling et al., 2004, Penetrante, 1994). Non-thermal plasma (NTP) technology has been introduced as a promising method for NOx removal from simulated gases as well as real diesel engine exhaust. In an NTP reactor, NOx concentration is reduced by a set of reactions between free electrons, ions, radicals, atoms, and molecules, which are formed in plasma. The $NO_x$ reduction reactions generally can be divided into two groups:

- $NO_x$ removal reactions, and
- NO – $NO_2$ conversion reactions.

In the first group, some of the primary and main $NO_x$ removal reactions could be summarised as the following (Atkinson et al., 1989, Kossyi et al., 1992b, Penetrante, 1994, Atkinson et al., 1997, Sathiamoorthy et al., 1999, Zhao et al., 2004):

$$N_2 + e \rightarrow N + N + e \qquad 2.1$$

$$NO + N \rightarrow N_2 + O \qquad 2.2$$

$$O_2 + O \rightarrow O_3 \qquad 2.3$$

$$N_2 + e \rightarrow e + N_2(A) \qquad 2.4$$

$$N_2(A) + NO \rightarrow N_2 + N + O \qquad 2.5$$

$$N_2(A) + N_2O \rightarrow 2N_2 + O \qquad 2.6$$

$$NO_2 + N \rightarrow N_2 + O_2 \qquad 2.7$$

where $N_2(A)$ represents $N_2$ metastable state.

The second group of reactions (which involves the reactions of oxidising NO to $NO_2$) could be summarised as the following (Penetrante, 1994, Zhao et al., 2004, Sathiamoorthy et al., 1999, Rajanikanth et al., 2004):

$$O_2 + e \rightarrow O + O + e \quad 2.8$$

$$NO + O \rightarrow NO_2 \quad 2.9$$

$$O_2 + O \rightarrow O_3 \quad 2.10$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad 2.11$$

Hydrocarbons are attributed an important role in $NO_x$ removal by using plasma discharge. The reaction paths for $NO_x$ removal change significantly from that without hydrocarbon additives. In the presence of hydrocarbons, the efficiency of $NO_x$ reduction and NO – $NO_2$ conversion is greatly increased, due to the reactions between the hydrocarbons and $NO_x$ such as (Majewski, 2004):

$$C_3H_6 + OH \rightarrow C_3H_6OH \quad 2.12$$

$$C_3H_6OH + O_2 \rightarrow C_3H_6OHOO \quad 2.13$$

$$C_3H_6OHOO + NO \rightarrow C_3H_6OHO + NO_2 \quad 2.14$$

Furthermore, the NO-$NO_2$ conversion due to the oxidation by O/OH radicals or by hydrocarbons is less probable since the O/OH radicals decrease in the presence of soot inside the diesel engine exhaust. Moreover, some $NO_2$ can react with soot by the following reaction (Rajanikanth and Sinha, 2008):

$$NO_2 + soot \rightarrow CO + CO_2 + N_2 + H_2O + NO \quad 2.15$$

In addition, in the presence of water, some other reactions are also involved, which are as follows (Jolibois et al., 2012a):

$$H_2O + e \rightarrow OH + H + e \quad 2.16$$

$$NO + OH \rightarrow HNO_2 \quad 2.17$$

$$NO_2 + OH \rightarrow HNO_3 \quad 2.18$$

and

$$NO + H_2O \rightarrow NO_2 + OH \quad 2.19$$

Therefore, the reactions taking place during the treatment of actual diesel exhaust vary largely from that of the simulated gas mixtures, due to the presence of various hydrocarbons, aldehydes and water in the diesel exhaust.

On the other hand, many studies suggest that the conversion of NO to $NO_2$ is an important intermediate step in the reduction of NO to $N_2$ (Hoard and Balmer, 1998), and that the most efficient way to do this is to use a plasma reactor along with an additional catalyst reactor. In the first step, the plasma oxidises NO to $NO_2$ in the presence of HC (Puchkarev et al., 1999):

$$Plasma \quad + NO + HC + O_2 \rightarrow NO_2 + HC - products \quad 2.20$$

In the second stage, the catalyst reduces $NO_2$ to $N_2$ by selective reduction using hydrocarbons (Puchkarev et al., 1999):

$$Catalyst \quad + NO_2 + HC \rightarrow N_2 + CO_2 + H_2O \quad 2.21$$

In general, some researchers have employed NTP using different combinations of gases to simulate real exhaust from engines, in order to examine the ways that different parameters have affected the system (Mizuno et al., 1998, Yamamoto et al., 1999b, Namihira et al., 2000, Namihira et al., 2001a, Rajanikanth and Rout, 2001, Ravi et al., 2003b, Arai et al., 2004, Mok et al., 2004, Saito et al., 2006, Koga et al., 2006, Matsumoto et al., 2009, Matsumoto et al., 2010b, Jolibois et al., 2011, Jolibois et al., 2012a, Wang et al., 2012, Vinh et al., 2012c, Vinh et al., 2012b, Ravi et al., 2003a), while others have studied real engines to enhance the efficiency of the NTP (Puchkarev et al., 1998, Slone et al., 1998, Puchkarev et al., 1999, Rajanikanth and Ravi, 2002, Yamamoto et al., 2003b, Rajanikanth et al., 2003, Rajanikanth et al., 2004, Rajanikanth and Ravi, 2004, Rajanikanth et al., 2005, Rajanikanth and Sushma, 2006, Koga et al., 2006, Rajanikanth and Srinivasan, 2007, Srinivasan and Rajanikanth, 2007b, Srinivasan and Rajanikanth, 2007a, Vinogradov et al., 2007, Vinogradov et al., 2008,

Rajanikanth and Sinha, 2008, Rajanikanth et al., 2008, Rajanikanth et al., 2009, Srinivasan et al., 2009, Mohapatro and Rajanikanth, 2011a).

Various kinds of NTP reactors were studied by these researchers. The earlier kind of NTP reactors were electron beam reactors, which were mostly employed from 1980 to 2000 (Penetrante, 1997, Behbahani et al., 1982, Penetrante, 2000, Masuda et al., 1981). The majority of researchers applied dielectric barrier discharge (DBD) reactors (Mizuno et al., 1998, Rajanikanth and Ravi, 2002, Yamamoto et al., 2003b, Rajanikanth et al., 2003, Rajanikanth et al., 2004, Rajanikanth and Ravi, 2004, Rajanikanth et al., 2005, Rajanikanth and Sushma, 2006, Rajanikanth and Srinivasan, 2007, Srinivasan and Rajanikanth, 2007b, Srinivasan and Rajanikanth, 2007a, Rajanikanth and Sinha, 2008, Rajanikanth et al., 2008, Rajanikanth et al., 2009, Mohapatro and Rajanikanth, 2011a, Vinh et al., 2012c, Vinh et al., 2012b, Ravi et al., 2003a). Some used packed bed DBD reactors (Yamamoto et al., 1999b, Rajanikanth and Rout, 2001, Ravi et al., 2003c, Rajanikanth and Ravi, 2002, Yamamoto et al., 2003b, Rajanikanth and Sushma, 2006, Srinivasan and Rajanikanth, 2007a, Srinivasan et al., 2009) and others used DBD assisted reactors along with another catalyst or adsorbent reactor (Yamamoto et al., 1999b, Ravi et al., 2003b, Rajanikanth et al., 2003, Rajanikanth et al., 2004, Rajanikanth and Ravi, 2004, Rajanikanth and Srinivasan, 2007, Srinivasan and Rajanikanth, 2007b, Srinivasan and Rajanikanth, 2007a, Rajanikanth et al., 2008, Rajanikanth et al., 2009, Mok et al., 2004). However, some researchers studied corona reactors (Slone et al., 1998, Puchkarev et al., 1998, Puchkarev et al., 1999, Namihira et al., 2000, Namihira et al., 2001a, Arai et al., 2004, Saito et al., 2006, Koga et al., 2006, Vinogradov et al., 2007, Vinogradov et al., 2008) and others examined surface plasma discharge reactors (Jolibois et al., 2012a, Jolibois et al., 2011, Malik et al., 2011b). Note that in some studies, the packed bed DBD reactor is called a single stage plasma-catalytic system, with the catalyst or adsorber placed in the discharge zone. The DBD assisted reactor (used with another catalyst or adsorbent reactor) is also called a two-stage system, with the catalyst or adsorbent placed downstream of the plasma. The advantage of single-stage reactors is that the active species reacts on the catalyst surface in the discharge zone. However, in the two-stage systems, the oxidation of NO to $NO_2$ in the plasma increases the catalyst performance, since the $NO_2$ removal is better than the NO removal near the catalyst (Magureanu and Pârvulescu, 2007).

### 2.4.1 NOx removal from simulated gases

***Corona reactor***

In 2000 and 2001, Namihira et al. (Namihira et al., 2000, Namihira et al., 2001a) studied the effects of pulse-width in improving $NO_x$ removal efficiency. They designed a new DC voltage generator in the order of 10 nanoseconds pulse-width. A corona discharge reactor and gas cylinders of $N_2$, NO and $H_2O$ were used, and the concentration of NO and $NO_2$ was measured at ambient temperature. They studied low pulse frequencies ranging from 1-13 pps (pulses per second) and various pulse widths from 40-120 ns. It was shown that the removal ratio of NO decreased with an increasing pulse repetition rate and an increasing pulse-width. However, the removal energy efficiency increased with a decreasing pulse-width. In other words, the removal energy efficiency was higher for shorter pulse-widths at a fixed NO removal ratio. The authors claim that their results are clearly in alignment with another study which used electron beam irradiation without any additive (Penetrante et al., 1995b, Penetrante et al., 1995c). The removal energy efficiency for the comparison was calculated as follows:

$$NO_E = \frac{\frac{\dot{V}}{22.4[l/min]} \times (NO_i - NO_e) \times 60[min/h] \times 10^{-3}}{f \times E}[mol/kWh] \qquad 2.22$$

where $f$ is the pulse repetition rate [pulses/s], $E$ is the input energy to the reactor per pulse [J/pulse] and G is the gas flow rate [lit/min].

In 2004, $NO_x$ removal mechanism by a DC corona discharge has been considered by Arai et al. (Arai et al., 2004). A mixture of $N_2$, $O_2$, and NO was used as the test gas. In their experiments, oxygen concentration was changed between 0 and 20%. The initial concentration of NO was kept at 100ppm and the residence time inside the reactor was 17sec. It was shown that the $NO_x$ removal mechanism depends on oxygen content. In the case of NO+$N_2$ mixture, the NO reduction process has been controlled by exited $N_2$ radicals. However, in the case of NO/$N_2$/$O_2$ mixture, NO was mainly converted to $NO_2$ and $N_2O_5$ by ozone generated from corona discharge.

In 2006, Saito et al. (Saito et al., 2006) studied the effect of $H_2O$, $CO_2$, $CH_4$ and $C_2H_4$ on NO removal by using a DC corona discharge. The base gas in their experiments was a mixture of $N_2$/$O_2$ (20%)/NO (100ppm) and the coexisting gases were added to the base gas. They considered both positive and negative discharge in their tests. When moisture was added to the base gas, $NO_x$ removal was 30% at energy density of 50J/L in the case of

positive corona discharge and 90% at 250J/L for negative discharge. It was found that the existence of $CO_2$ in the base gas was not desirable. When $CO_2$ was added to the base gas, the $NO_x$ concentration increased up to twice at 920 J/L compared to the case of $CO_2$ free for positive discharge. In the case of negative discharge, about 200 J/L more energy was needed to get 90% $NO_x$ reduction compared to the base case. In the case of $C_2H_4$ addition, NO was oxidised to $NO_2$ for positive discharge and hardly any $NO_x$ was removed. However, $NO_x$ was decreased with a lower energy density in the case of negative discharge. In the case of simulated gas ($N_2/O_2/NO/H_2O/CO_2/C_2H_4$ mixture), the $NO_x$ removal efficiency was more than 90% and the energy density was lower compared with the base gas. However, some by-products such as CO, $O_3$, $NO_3$, and $NO_2$ have been increased in the case of simulated gas.

***DBD reactor***

Mizuno et al. (Mizuno et al., 1998) in 1998 investigated NTP at very low temperatures of below 100ºC. Different simulated gases ($NO+O_2$, $N_2O$, $O_2$, $N_2$, $CO_2$ and $H_2O$ gas cylinders) were examined to simulate the exhaust of a thermal power plant. A straight wire DBD reactor was used for all simulations. The concentration of NO and $NO_2$ was measured at three different temperatures: room temperature, liquid nitrogen temperature and solid ethanol temperature. The voltage source for this study was pulse DC voltage, and the maximum supplied voltage and pulse frequency was 30 kV and 60 Hz respectively. At low temperature, it was claimed that the plasma process is effective in removing gaseous pollutants, as well as in promoting plasma chemical reactions. To cite one particular case, the removal efficiency of nitrogen (DeNO) at room temperature was 20%, at liquid nitrogen temperature (-196ºC) it was 60% and at solid ethanol temperature (-114ºC) it was 98%. Note that the removal efficiency or removal ratio was defined as follows:

$$NO_R = \frac{(NO_i - NO_e) \times 100}{NO_i} \qquad 2.23$$

The influence of gas flow rate on the removal efficiency of NO was also studied, and showed that the DeNO decreased when increasing the gas flow rate from 1 to 8 L/min, because the gas exposure to the electrical field decreases. It was also shown that by decreasing the temperature, the discharge power decreased at a fixed input power. In this paper, although it was reported that the plasma-treated gas was more effective at low temperature, no clear reasons were outlined. A real engine was not studied, and an extremely low temperature was considered, which is not applicable in everyday situations.

Wang et al. (Wang et al., 2012) conducted a complete investigation on the effects of electrode connection, diameter, material, shape of the inner electrode, and dielectric material on NO removal in order to improve the performance of dielectric barrier discharge reactors. The simulated gas examined in this paper is the combination of NO and $N_2$. An AC power supply with a peak voltage of 30 kV and peak frequency of 10 kHz was employed. The specific energy density (SED) parameter is considered, to compare different case studies. For the same removal efficiency, it is better to have a lower specific energy density, regarding energy consumption. The SED level of about 10 J/L can be considered as the practical level for plasma application. This value corresponds to about 3% of the output power for a 3-L-class diesel engine over the United State Federal Test Procedure (US FTP) test cycle, it will reach a practical level (Hoard et al., 2000a, Okubo et al., 2004).

It was shown that when a high voltage was applied to the outer electrode and when a smaller discharge gap was selected in the coaxial reactor, a smaller breakdown voltage was required, and therefore better NO removal could be achieved with the same high voltage. Furthermore, increasing the inner electrode diameter increased the NO removal efficiency due to the decrease in the discharge gap. Three different materials were tested for the inner electrode, and showed that tungsten had a higher NO removal efficiency than copper or stainless steel, due to a larger secondary electron emission. Copper proved more effective than stainless steel (Konuma, 1992). The use of a screw electrode as an inner electrode was also tested in comparison with a rod electrode, and this showed that the NO removal efficiency was higher with the screw electrode than the rod electrode, as the equivalent gap capacitance of the reactor with the screw electrode was lower. The screw electrode generates a large number of micro discharges with a small energy deposition per micro discharge (Takaki et al., 2008), and the discharge is more intense in the screw electrode reactor, due to the higher input power when compared with the rod electrode reactor under the same applied voltage. In addition, the accidental surface of the screw electrode makes the moving gases become turbulent, increasing the probability of particle collisions and intensifying the plasma reaction. Finally, the researchers examined various dielectric materials and showed that the NO removal efficiency was higher when using corundum when compared with ceramic and quartz materials, since the relative permittivity of corundum is higher than ceramic materials. Quartz was the least effective material to be used.

In 2012, Vinh et al. (Vinh et al., 2012c, Vinh et al., 2012b) investigated the effects of different PM compositions and oxygen fraction on $NO_x$ removal efficiency in simulated

exhaust gas by a dielectric barrier discharge needle-to-cylinder reactor at room temperature. They also studied the combination between a dielectric barrier discharge reactor and a wall-flow type diesel particulate filter (DPF) (Arai et al., 2007). A diffusion flame formation system was used to produce PM (Kobayashi et al., 2008). The simulated gas was the combination of NO, $N_2$, $O_2$ and PM. A 50 Hz alternative high voltage supply in the range of 5 kV to 15 kV was used. It was shown that PM could increase the $NO_x$ removal efficiency intensely; however, PM was more effective when fresh PM was introduced into the reactor. For example, by using 100 mg fresh PM in a special case, the $NO_x$ removal efficiency was 28%; however, it was around 12% without using PM. It was claimed that the existence of PM inside the reactor incurs O radicals that react with HC or soot, besides other reactions. Therefore, the $NO_2$ formation process is slower and consequently, the $NO_x$ removal efficiency is higher. Accordingly, PM has worked as a reactive agent in the reactor (Vinh et al., 2012c). Furthermore, the NO removal efficiency is much higher in the presence of oxygen than in the case without oxygen; however, the $NO_x$ removal efficiency is not different.

***Packed bed DBD reactor***

In 1999, Yamamoto et al. (Yamamoto et al., 1999b) compared two types of plasma reactors, studying reaction by-products and $NO_x$ removal efficiency. One was an ordinary packed-bed reactor without any barrier, and the other was a barrier type packed-bed plasma reactor. In addition, the effect of using $Na_2O_3$ after the plasma reactor to reduce the amount of produced $NO_2$ was studied. The $NO_2$ will react with sodium sulfite ($Na_2SO_3$) to form a non-toxic water-soluble $Na_2SO_4$ as a final product. Mok and Lee (Mok and Lee, 2006) in 2006 also used $Na_2SO_3$ as a reducing agent to remove sulfur dioxide and nitrogen oxides simultaneously. Ferroelectric $BaTiO_3$ pellets were used inside the reactors, with a 15 kV and 60 Hz AC power supply. A mixture of NO balanced with $N_2$ in a gas cylinder, and dry air supplied by a compressor was employed to simulate the exhaust gas. The concentrations of NO, $NO_2$, $NO_x$, CO, $CO_2$, $N_2O$, $HNO_2$ and $HNO_3$ (aqueous solution) were measured. It was shown that the hybrid system using the barrier type packed-bed plasma reactor, followed by the chemical reactor with $Na_2SO_3$, provided nearly 100% $NO_x$ removal efficiency with negligible reaction by-products of $N_2O$, CO, $HNO_2$ and $HNO_3$. It was claimed that the cost of this system was approximately 15 times more economical than the conventional, selective catalyst reduction (SCR) process. The effect of reactor diameter and the optimum diameter of pellets for hybrid systems was also investigated. It was found that the $NO_2$ conversion was

higher and $NO_x$ reduction was smaller for 1.5 mm diameter electrodes (the smallest size of electrode diameter considered), when compared with 5.0 mm diameter electrodes. Furthermore, 1.5 mm diameter electrodes produced less reaction by-products, such as $N_2O$, $HNO_2$, $HNO_3$ and CO, thus making this electrode most suitable for the hybrid system. In addition, the $BaTiO_3$ pellets with a diameter of 3.0 mm (the largest size considered) provided the best results on the hybrid $NO_x$ control system. The decomposition of the air alone for both reactors was also studied, along with the effects of power supply voltage. However, the power supply frequency was not considered.

In 2011, Rajanikanth and Rout (Rajanikanth and Rout, 2001) studied the dielectric packed bed reactor for the removal of $NO_x$ from simulated gas, and compared this with a conventional DBD. Gas cylinders of NO in $N_2$, $N_2$, $CO_2$ and $O_2$ were used to simulate the vehicle exhaust gas at room temperature, and changes in the concentration of NO, CO, $CO_2$ and $O_2$ were also considered. Three types of catalyst were used as dielectric pellets: alumina ($Al_2O_3$), alumina coated with palladium as catalyst ($Al_2O_3$-Pd), and barium titanate ($BiTiO_3$). The voltage source for this study was a single-phase AC supply, and the range of voltage and pulse frequency of the supplier was 15-28.6 kV and 50-125 Hz, respectively. The pulse rise time was 34 ns. It was shown that the presence of a packed dielectric bed increased the discharge power. Therefore, for a given reactor size and set of operating conditions, higher NO removal efficiencies at lower voltages could be achieved. Barium titanate pellets showed better removal efficiency than the other proposed pellets. For example, DeNO was 76% for DBD alone. It was 84%, 72% and 100% for DBD with alumina, alumina coated with palladium, and barium titanate pellets, respectively. The major contribution of this paper was its comparability with conventional catalytic converters, which operate at an exhaust gas temperature around 300ºC or above. In addition, the effects of pulse frequency and pulse voltage were also studied. It was shown that the NO removal ratio increased with an increase in the pulse repetition ratio, and an increase in the peak of applied voltage. This effect was due to the higher discharge power resulting from the higher pulse repetition rate and higher peak voltage.

In 2003, Ravi et al. (Ravi et al., 2003c) considered the effect of temperature on NO conversion using simulated gases consisting of NO, $O_2$, and $N_2$ in the presence of various hydrocarbons: ethylene, acetylene and n-hexane. They also studied acetylene with the presence of $H_2O$ in the simulated gas. A packed bed DBD reactor with glass beads as pellets was used. The concentration of NO and $NO_2$ was measured at different temperatures, from

room temperature up to 200ºC. A 60 Hz AC high voltage was applied, ranging from 8 kV to 16 kV. It was found that the discharge power increased with increased temperature. NO conversion in the presence of ethylene and n-hexane was better than that of acetylene at all temperatures. The adding of acetylene at room temperature showed no better conversion of NO than when there were no additives. At higher temperatures, the conversion of NO was enhanced. A little enhancement in NO and $NO_x$ removal was observed in the presence of water vapour, due to the effect of OH and O radicals for NO removal.

***Combined DBD reactor with catalyst or absorber***

In 2003, Ravi et al. (Ravi et al., 2003b) investigated the conventional DBD reactor when combined with a catalytic reactor at different temperatures. Three different reactors were studied: DBD alone, catalyst alone, and a cascaded plasma catalyst reactor. The catalyst used was a commercially available SCR catalyst ($V_2O_5 – WO_3$ / $TiO_2$). The simulated gas was the composition of NO, $O_2$, and $N_2$ in the presence of ethylene and ammonia only for the cascaded reactor. A 60 Hz AC 14 kV high voltage power supply was used. It was shown that the rate of oxidation of NO to $NO_2$ decreased with temperature. In addition, it was shown that by using cascaded plasma catalyst reactors, the $NO_x$ removal efficiency was more pronounced, especially at low temperatures, and this was labelled as a "synergy effect". However, clear reasons for this synergy effect were not given. Also, it was also claimed that this behaviour may not be common to all types of catalysts at various temperatures, and one must choose the optimal operating energy density, depending on the characteristics of the individual catalyst.

In 2004, Mok et al. (Mok et al., 2004) studied $NO_x$ removal by using a packed bed plasma reactor assisted with monolith $V_2O_5/TiO_2$ catalyst using AC and pulse voltage. Various effective parameters such as initial NOx concentration, gas flow rate, gas humidity and reaction temperature were studied. The simulated gas was the composition of $N_2$, $O_2$, NO balanced with $N_2$ and ethylene. It was claimed that ethylene helped NO oxidation to $NO_2$. It was shown that increasing the initial concentration of $NO_x$, decreases the removal efficiency for the same energy density; however, if the $NO_2$ fraction keeps constant, the $NO_x$ removal efficiency is similar for different initial concentrations of $NO_x$. This was an important finding in this paper and its discussion is rare in other studies. Furthermore, from their paper, it is seen that increasing the gas flow rate decreases the efficiency of $NO_x$ removal. According to the effect of water vapour, it was shown that for the plasma-catalyst system, by increasing the humidity from 0 to 3%, the $NO_x$ removal efficiency was decreased by almost 10%, and

further increase in humidity did not have a significant effect on $NO_x$ removal efficiency. It was also shown that for the catalyst alone reactor, increase in the reaction temperature enhances the $NO_x$ removal efficiency; however, the reaction temperature is hardly influenced by the $NO_x$ removal efficiency.

***Surface plasma discharge reactor***

In 2011 and 2012, Jolibois et al. (Jolibois et al., 2012a, Jolibois et al., 2011) studied a wet-type reactor featuring a surface discharge. This system was studied, with a coil inserted in the electrical circuit during the treatment process, and also with a catalyst ($\gamma$-$Al_2O_3$). The simulated gas examined was a mixture of NO and air. Sodium sulfite ($Na_2SO_3$) was used to obtain the wet condition required. With wet conditions, the $NO_x$ removal efficiency is improved by dissolving $NO_2$ into the liquid as $NO_2$- and $NO_3$-ions (Thagard et al., 2010). However, the continuous absorption of nitrogen oxides causes saturation and acidification of the liquid, and results in the inhibition of further absorption. By adding $Na_2SO_3$, the nitrite and nitrate ions are reduced to $N_2$, and therefore gas absorption is facilitated (Yamamoto et al., 2000). A comprehensive study was made of variations in voltage and frequency, and it was shown that the $NO_x$ removal efficiency was higher in relation to the signal frequency variations, rather than voltage variations. Furthermore, they showed that the removal efficiency was improved by inserting a coil between the power supply and the surface, and was also improved by using a catalyst. It was claimed that the inductance influenced the power consumed by the plasma.

***Complex unique types of reactors***

In 2009 and 2010, Matsumoto et al. (Matsumoto et al., 2009, Matsumoto et al., 2010b) developed a new pulse generator: the nanosecond pulsed generator. This can produce 80 kV high voltage, with 2 ns rise and fall time, 5ns pulse width and a pulse frequency of 0-100 pps. The authors claimed that this generator could achieve 100% removal efficiency. The simulated gas examined was a mixture of $N_2$ and NO. The nanosecond pulsed discharge was shown to have a distinct advantage in energy efficiency for NO removal when compared with sub-micro-second pulse discharge and other discharge methods. The effects of repetition ratio and applied voltage were studied, and it was shown that the NO removal ratio increased with an increase in the pulse repetition ratio, and by increasing the peak of applied voltage due to the more discharge energy. In addition, it was shown that the positive pulse voltage gave a higher NO removal ratio than the negative pulse voltage when delivered at the same repetition rate in the case of lower applied peak voltage. On the other hand, there were no

changes between the NO removal via positive and negative pulse voltage in the case of the higher applied peak voltage. Unlike previously mentioned studies, in this case, the authors studied the effects of reactor geometry. They showed that the NO removal ratio was increased by using a smaller reactor internal diameter. In addition, the NO removal ratio was increased by using a longer reactor, since the gas residence time in the reactor was also increased. Another important result of this study was that the NO removal ratio was increased considerably with the presence of $O_2$ and water fed by bubbling into the gas stream. This result demonstrated that the introduction of $O_2$ and water in this way is more effective for NO removal due to the effectiveness of the OH radicals or O radicals. In the 2010 study (Matsumoto et al., 2010b), it was shown that the nanosecond pulse discharge had more advantages than DBD and corona discharge as regards NO energy efficiency and the NO removal ratio.

In Table 2-3 is an overview of the papers studied, considering NTP for $NO_x$ removal from simulated gases.

Table 2-3: Overview of published papers featuring NTP for NOx removal from simulated gases

| Authors | Year | Reactor type | Gas type | Catalyst/ adsorbent type | Reactor inlet temperature | Flow rate | Power generator | Peak voltage | Peak pulse frequency | The range of studied energy density |
|---|---|---|---|---|---|---|---|---|---|---|
| Mizuno et al. (Mizuno et al., 1998) | 1999 | DBD reactor | Simulated gas ($N_2O$/ $O_2$/$N_2$/$CO_2$/H2O) | - | 20, -196 °C, -114 °C | 1-8 L/min | Pulses generated by DC voltage supply | 30 kV | 60 Hz | - |
| Yamamoto et al. (Yamamoto et al., 1999b) | 1999 | Packed-bed DBD reactor | Simulated gas ($N_2$/NO) | $BaTiO_3$ | Room temp. | 1-2 L/min | AC high voltage supply | 15 kV | 60 Hz | - |
| Namihira et al. (Namihira et al., 2000, Namihira et al., 2001b) | 2000 2001 | Corona reactor | Simulated gas (NO/$N_2$/$O_2$/$H_2O$) | - | 29.2 °C | 2-12 L/min | Pulses generated by DC voltage supply | 49.2 kV | 13 pps | - |
| Rajanikanth and Rout (Rajanikanth and Rout, 2001) | 2001 | Packed-bed DBD reactor | Simulated gas (NO/$N_2$/$CO_2$/$O_2$) | $Al_2O_3$, $Al_2O_3$-Pd, $BiTiO_3$ | Room temp. | 2 L/min | Pulses generated by DC voltage supply | 50 kV | 125 pps | 10 – 60 J/L |
| Ravi et al. (Ravi et al., 2003c) | 2003 | DBD reactor | Simulated gas (NO/$N_2$/$O_2$/$H_2O$) | - | Room temp. and 200 ºC | 2 L/min | AC high voltage supply | 16 kV | 60 Hz | 0 – 160 J/L |
| Ravi et al. (Ravi et al., 2003b) | 2003 | Combined DBD reactor with catalyst | Simulated gas (NO/$NO_2$/$O_2$/$N_2$/ ethylene, ammunia) | $V_2O_5$-$WO_3$/$TiO_2$ | 100, 150 and 200 ºC | 2 L/min | AC high voltage supply | 14 kV | 60 Hz | 0 – 160 J/L |
| Arai et al. (Arai et al., 2004) | 2004 | Corona reactor | Simulated gas ($N_2$/$O_2$/NO) | - | - | 1 L/min | DC high voltage power supply | 15 kV | - | 0-1500 J/L |
| Saito et al. (Saito et al., 2006) | 2006 | Corona reactor | Simulated gas ($N_2$/$O_2$/NO/$H_2O$/$CO_2$/$C_2H_4$) | - | - | 1 L/min | DC high voltage power supply | 15 kV | - | 0-2500 J/L |
| Matsumoto et al. (Matsumoto et al., 2009, | 2009 2010 | Pulsed streamer discharge reactor | Simulated gas ($N_2$/ NO) | - | - | 2 L/min | Nanosecond pulsed generator | 80 kV | 50 pps | - |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Matsumoto et al., 2010a) | | | | | | | | | | |
| Jolibois et al. (Jolibois et al., 2012a) | 2012 | DBD / Surface plasma reactor | Simulated gas ($N_2$/NO) | $\gamma$-$Al_2O_3$ | Room temp. | 1 L/min | AC high voltage supply | 20 kV | 5 kHz | 0 – 190 J/L |
| Wang et al. (Wang et al., 2012) | 2012 | DBD reactor | Simulated gas ($N_2$/NO) | - | - | 10 L/min | AC high voltage supply | 30 kV | 1 kHz | 100 – 800 J/L |
| Vinh et al. (Vinh et al., 2012a, Vinh et al., 2012b) | 2012 | DBD reactor | Simulated gas ($N_2$/NO/$O_2$/PM) | - | Room temp. | 0.5, 1 and 2 L/min | Alternative high voltage supply | 15 kV | 50 Hz | 0 – 300 J/L |

### 2.4.2 NOx removal from diesel engines exhaust gas

***Corona reactor***

In 1998 and 1999, Puchkarev et al. (Puchkarev et al., 1999, Puchkarev et al., 1998, Slone et al., 1998) investigated the effect of a transient, non-equilibrium plasma on $NO_x$ removal. They developed a pulsed corona discharge with peak voltage of 49 kV, frequency of 1 kHz, pulse rise time of 20 ns and pulse duration between 50 and 100 ns. They studied the effects of diameters of inner and outer electrodes, reactor length, annular dielectric inserts to prevent arcing, flow rates, pulse repetition rates, plasma volume, and pulsed and mean energy deposition into the gas on NO removal. These parameters were studied in order to determine the optimum conditions for cost effective $NO/NO_x$ removal. They showed that short pulses are more effective for efficient energy usage rather than longer pulses. In addition, the energy cost using positive corona is 1.5-2 times higher than that for negative corona for the same $NO_x$ removal. Note that the energy cost defined in this study was calculated as follows:

$$\varepsilon = \frac{250 \cdot E \cdot f}{\dot{V} \cdot \Delta NO_x} \quad (eV / molecule) \qquad 2.24$$

where $\varepsilon$ is the energy cost, $E$ is the energy deposition into the gas, $f$ is the frequency and $F$ is the flow rate. $\Delta NO_x$ is the $NO_x$ removal in ppm.

The researchers realised that a high energy density generated a lower energy cost than a low energy density. They also showed that the energy cost for NO removal varied very little by varying the plasma volume. However, it changed more significantly for $NO_x$ removal. Moreover, they gave evidence that the energy cost and $NO/NO_x$ removal depended on the initial concentration of different species, such as NO, HC, particulate matter and also the gas temperature.

Koga et al. (Koga et al., 2006) compared the effect of corona discharge for $NO_x$ removal in engine exhaust gas and simulated gas. They considered a mixture of $N_2/O_2/NO/NO_2/H_2O/CO_2/C_2H_4$ as the test gas. It was shown that the $NO_x$ removal characteristics in real exhaust and simulated gas were similar if the composition were the same. Effect of flow rate and residence time has been studied as well. The flow rate was changed in the range of 0.5 to 20 L/min. By increasing the residence time, $NO_x$ removal has been increased. Furthermore, the energy density for $NO_x$ removal depends on initial $NO_x$ concentration. When initial concentrations were 160 ppm and 24 ppm, the required energy densities for 90% $NO_x$ removal were 200 J/L and 700 J/L, respectively.

In 2007, Vinogradov et al. (Vinogradov et al., 2007) investigated the DC corona discharge technology for $NO_x$ removal from diesel engine exhaust. Various geometrical parameters of a rectangular corona reactor were studied in order to find the optimum parameters for the best reactor performance. A high voltage DC system with a peak voltage of 50 kV was used in this study. Comprehensive research was performed on a polarity of the corona discharge, and this showed that as regards both cleanness (mass of $NO_x$ removed relative to its initial mass), and efficiency, negative polarity is preferable. It was shown that the cleanness was almost independent of the engine load; in other words, it did not depend on the initial $NO_x$ concentration. However, the efficiency is relatively low for 0kW and twice as high for 2.5, 4.5, and 7.5 kW diesel engines. Therefore, it was concluded that this type of corona reactor is more suitable for higher engine loads. In addition, a comprehensive study was presented on the effective parameters of the reactor, which influenced the residence time. In 2008 (Vinogradov et al., 2008), the authors studied the same corona reactor, but with a pulsed discharge. It was shown in this case, that the cleanness and efficiency are independent of the polarity of the electrodes; however, the positive polarity provided a more stable discharge, and a lower concentration of ozone than negative polarity.

***DBD reactor***

In 2008, Rajanikanth et al. (Rajanikanth and Sinha, 2008) studied two different types of dielectric barrier discharge reactors (wire-cylinder and pipe-cylinder) using simulated gas and real diesel engine exhaust. It was shown that, due to a shorter discharge gap, the pipe-cylinder reactor had more $NO_x$ removal efficiency than the wire-cylinder reactor. This is due to the consumed power of the plasma discharge in the discharge gap which depended inversely on the gap length. These researchers claimed that the average electric field in their pipe-cylinder reactor with 1.625mm discharge gap was about 140 kV/cm and the corresponding electron energy was about 13eV, which is higher than the chemical bond energy of NO (6.50 eV), $NO_2$ (3.11 eV), and CO (11.12eV) molecules. They showed that for an energy density of higher than 30 J/L, NO removal efficiency for the pipe-cylinder is about 20-25% greater than that of the wire-cylinder reactor. However, for the $NO_x$ removal efficiency, it is almost the same as the energy density of 120 J/L. In this year, in another paper (Rajanikanth et al., 2008), they performed this experiment on cascaded plasma adsorbent and achieved the same results - the pipe-cylinder reactor had superior $NO_x$ removal efficiency when compared with the wire-cylinder reactor.

In 2011, Mohapatro et al. (Mohapatro and Rajanikanth, 2011a) studied a crossed flow dielectric barrier discharge reactor on the removal of $NO_x$ from a 3.75 kW diesel engine. This reactor consisted of nine electrodes with the gas flowing radially rather than axially toward the electrodes. This unique feature of the new DBD reactor improved the performance of $NO_x$ removal from diesel engine exhaust, due to the higher discharge and longer residence time. Since their results were obtained without using any catalysts/adsorbents, the authors claimed that by using a cross flow DBD reactor they could remove a significant amount of $NO_x$ from diesel engine exhaust with less energy. For example in one case, with nine electrodes, the DeNO was 100% and $DeNO_x$ was 95% with an energy efficiency of almost 3.5 g/kWh NO. However, with one electrode, the DeNO was 74% and $DeNO_x$ was 45% with an energy efficiency of almost 23.1 g/kWh NO. The voltage source in this study was a pulse generator with a peak voltage of 25 kV and frequency of 75 pps. The pulse rise time was 20ns and the pulse duration was 13 ms.

***Packed bed DBD reactor***

In 2002, Rajanukanth et al.(Rajanikanth and Ravi, 2002) compared the results for filtered real diesel engine exhaust and simulated gas. They used a DBD reactor alone, plus a packed bed DBD reactor (a hybrid adsorber plasma reactor-HAPR) with three different molecular sieves as adsorbent beads: MS-3A, MS-4A and MS-13X. Their experiments were conducted at room temperature and also 200ºC (the average exhaust temperature in urban driving cycles). A 6 kW diesel engine was used to study the effect of different NTP reactors on filtered real diesel engine exhaust and the concentration of NO, $NO_2$, CO, $CO_2$ and aldehydes was considered during all the experiments. A single-phase AC supply with a high voltage range from 15 kV to 25 kV and a frequency of 100pps was employed. It was claimed that the hybrid adsorber plasma reactor (HAPR) successfully demonstrated $NO_x$ removal from diesel engine exhaust. It was shown that the $NO_x$ removal efficiency when using a plasma reactor alone is 36%. This efficiency increased with the HAPR to 73% at room temperature and 78% at 200ºC. It was also determined that MS13X was the superior adsorbent for $NO_x$ removal.

In 2003, Yamamoto et al. (Yamamoto et al., 2003b) investigated the effect of non-thermal plasma on a filtered 2 kW diesel engine exhaust at different loads. Three plasma reactors were evaluated: pulse driven DBD reactor, pulse driven dielectric packed bed reactor and AC driven dielectric packed bed reactor. $BaTiO_3$ ferroelectric pellets were used for the packed bed DBD reactor. The characteristics of the power supply were: a peak voltage of

25 kV, 1.2 ms pulse width, with 13.7 ns pulse rise time for the packed bed DBD reactor and 6.1 ns for the DBD reactor. The frequency of the AC supply was 60 Hz and pulse supply was 210 Hz. It was found that the AC packed-bed reactor and pelletless pulsed reactor showed better performance in terms of discharge power and $NO_x$ removal efficiency, with minimum reaction products for a given power at zero engine load. When the engine load exceeded 50%, there was only a limited decrease in NO reduction and all the reactors performed more or less equally. It is claimed that the total operating cost of the plasma-chemical hybrid system can be one-third to one-fifth of the conventional selective catalytic process. The key finding of this study is the amount of power consumption required for various configurations. Power consumption for the pulsed corona reactor without pellets is less than the pulsed corona with $BaTiO_3$ pellets, and both are less than the 60 Hz AC packed bed plasma reactor.

In 2006, Rajanikanth et al. [41] studied the injection of nitrogen radicals into the real diesel engine exhaust for the technique of $NO_x$ removal by plasma. $N_2$ gas was passed through a separate plasma reactor in order to produce N radicals which were then injected into the treatment zone. Both the NTP reactor and the reactor which produced N radicals are DBD reactors. The removal efficiency without the injection of N radicals has been compared, considering the injection of N radicals. The pulse generator was used in this study as a high voltage generator in the range of 14 kV to 25 kV, and the pulse frequency was 130 pps. It was shown that by injecting N radicals, there was quite a significant improvement in $NO_x$ removal efficiency. However, the specific energy density, which is defined as the division of power to flow rate, increased considerably. It is claimed that this increment in removal efficiency without the use of catalysts or adsorbents is an important step toward NO removal by a plasma reactor alone.

In 2009, Srinivasan et al. (Srinivasan et al., 2009) studied three different voltage energisations (AC/DC/pulse) on the removal of $NO_x$ from both filtered and unfiltered diesel engine exhaust. A packed bed DBD reactor was used, with dielectric beads. It was claimed that the performance of pulse power was better than AC and both were better than the DC energisation. The average electric field in the AC case is not as high as that observed in the pulse energised reactor or for the DC case; the average energy gained by the electrons under DC is insufficient to generate any radicals. In other words, the same removal efficiency could be achieved with less specific energy density in the pulse power than with AC power or with DC power.

***Combined DBD reactor with catalyst or absorber***

In 2003, Rajanikanth et al. (Rajanikanth et al., 2003) investigated a cascaded system of plasma and adsorption process for $NO_x$ and total hydrocarbon (THC) removal from a 6 kW real diesel engine's exhaust. A part of the exhaust was passed through a particulate filter first to filter out solid particulates and then fed to the reactors. Three different systems were evaluated: a DBD reactor, an adsorbent reactor and a cascade system. The cascade system consisted of a DBD reactor upstream of an adsorbent reactor. Three different adsorbent beads were used: activated alumina, MS-13X and activated charcoal. The concentrations of NO, $NO_2$, $NO_x$, CO, THC and aldehydes were measured at different temperatures. A high voltage AC system with a peak voltage of 25 kV and frequency of 100 pps was used in this study. It was shown that the $NO_x$ removal efficiency was higher with the plasma-associated adsorption (cascaded) process when compared with the individual processes, and the removal efficiency was found to be almost invariant in time. For example, in one special case, $DeNO_x$ was 10% for SED 52 J/L, however, for an adsorbent reactor alone, it was 14% and for a cascaded system, it was 25% for SED 52 J/L. In addition, activated charcoal and MS-13X were more effective for $NO_x$ and THC removal, respectively. It was also shown that $NO_x$ removal efficiency decreases with an increase in temperature for all the three adsorbents. However, the temperature was more effective for MS-13X and it proved less effective for the two other adsorbents. For example, with MS-13X, the $NO_x$ removal efficiency was almost 65% at 25ºC and 45% for 140ºC.

In 2004, Rajanikanth et al. (Rajanikanth and Ravi, 2004) again studied the cascaded plasma catalyst; however, they used a filtered diesel engine exhaust at a different load and also used SCR ($V_2O5/TiO_2$) as a catalyst. It was shown that the NO removal efficiency decreased with an increase in exhaust temperature. In addition, the DeNO decreased when increasing the engine load, due to an increase in the initial concentration of NO. They showed that with the catalyst alone under 200ºC, $NO_x$ removal was not affected. However, the plasma-assisted catalytic reactor was successfully employed to remove $NO_x$ from diesel engine exhaust at different loads of the engine. In one particular instance, the $NO_x$ removal efficiency was 33%, 27% and 87% respectively for a plasma reactor, a catalyst reactor and a plasma-assisted catalyst reactor.

In 2007, Rajanikanth et al. (Rajanikanth and Srinivasan, 2007) performed the same experiment as (Rajanikanth et al., 2004) (cited previously), but this time in a more detailed fashion. The researchers examined a plasma reactor with an adsorbent and then a catalyst

reactor, while using different kinds of adsorbent and catalyst materials. They showed that between three different adsorbent materials (activated charcoal, MS-13X, activated alumina), the activated charcoal cascaded with plasma, exhibited superior adsorption properties. Furthermore, MS-13X cascaded with plasma gave higher $NO_x$ removal efficiency when compared to activated alumina cascaded with plasma. It was shown that the performance of the cascaded process at high temperatures was poorer than that at room temperature, due to the poor performance of plasma and adsorbent processes at higher temperatures. A four-stage cascaded plasma catalyst was also examined. When comparing the four-stage cascaded plasma catalyst with the two-stage model, the four-stage catalyst showed superior performance. It was claimed that the cascaded plasma-adsorbent reactor could be a viable option for low temperature (< 200 ºC) stationary diesel exhaust $NO_x$ treatment. However, the cascaded plasma-activated catalytic reactor could also be a better option for non-stationary diesel exhaust $NO_x$ treatment, since it is not significantly affected by the plasma reactor temperature.

In 2009, Rajanikanth et al. (Rajanikanth et al., 2009) presented a novel way for generating high voltage for the plasma reactor in diesel engine exhaust. A solar powered high frequency electric discharge was developed to improve the size and specific energy density required in comparison with the traditional repetitive pulse or AC energisation. This generator can produce up to 16 kV high voltage with a high frequency of 12.2 kHz and a pulse rise time of 24 ns. This new high voltage generator was employed with DBD reactors, and different systems were examined, such as cascaded plasma-adsorbent and cascaded plasma-catalyst reactors. It was shown that under this solar-powered high-frequency AC application, there was a considerable improvement in the $NO_x$ removal, when compared with other generators. For example, in the DBD reactor, $NO_x$ removal efficiency was 22%, 27% and 46% respectively for the 50 Hz ordinary AC power supply, repetitive pulse power supply and 12.2 kHz AC power supply energised by a solar powered battery. In addition, the cascaded system of a solar-powered generator with adsorbent had superior performance, when compared with other systems. It was claimed that this solar-powered high voltage power supply could be designed for a possible retrofit in vehicles. It could be used on top of a vehicle with appropriate mechanical fixtures. However, it would need modification to the reactor and the plasma in order to accommodate the actual exhaust flow-rate and temperature.

***Effect of carbonaceous soot oxidation on NOx removal***

Rajanikanth et al. (Rajanikanth et al., 2004, Rajanikanth et al., 2005, Srinivasan and Rajanikanth, 2007b, Srinivasan and Rajanikanth, 2007a, Rajanikanth and Sinha, 2008) studied the effect of carbonaceous soot oxidation on $NO_x$ removal. They used unfiltered diesel engine exhaust, which contains carbonaceous soot, and measured the concentration of $CO_2$, CO, NO, $NO_2$, THC and aldehydes. These were compared using six different reduction systems: a DBD alone, an adsorbent alone, a cascaded plasma-adsorbent reactor (PRAR), a pellet bed catalyst reactor, a honeycomb catalyst reactor and a cascaded plasma-catalytic reactor (PRCR). A high voltage AC system with a peak voltage of 25 kV and a frequency of 130 pps was employed on a 4.4 kW diesel engine exhaust at no load condition. Three different temperatures were examined: 24ºC, 100ºC and 150ºC.

It was shown that the $NO_x$ removal efficiency using the plasma technique was improved with the presence of carbonaceous soot in the diesel engine raw exhaust, due to the reactions with $NO_2$. Taking as an example one case, for a specific energy of 50 J/L, $NO_x$ removal efficiency was 45% for an unfiltered diesel engine; however, $DeNO_x$ was 30% for filtered diesel exhaust gas (Rajanikanth et al., 2004). In Table 2-4, the initial concentrations of the main substances in a diesel engine exhaust that participate in plasma $NO_x$ removal for a 2.6 kW diesel engine at 40% load, have been tabulated (Rajanikanth and Sinha, 2008, Rajanikanth et al., 2008).

Table 2-4: Initial concentrations of the main substances in diesel engine exhaust.

| Substance | Concentration (ppm) or volume fraction (%) |
|---|---|
| $O_2$ | 12.5% |
| $CO_2$ | 4.9% |
| CO | 1770 ppm |
| NO | 600 ppm |
| $NO_2$ | 66 ppm |
| $NO_x$ ($NO+NO_2$) | 666 ppm |

In addition, different adsorbent beads were tested, such as activated charcoal, molecular sieves, MS-13X and activated alumina. Adsorbent reactor and PRAR appeared to show good performance in $NO_x$ removal; however, they did not exhibit efficient CO removal. They used

various catalysts, such as conventional two-way and three-way catalysts, but only studied CO removal with the catalyst reactor. It was shown that generally, catalysts have a positive effect on CO removal. Although the two-way catalyst exhibits a more effective CO removal than the three-way catalyst, the problem is that the catalyst did not show effective results on $NO_x$ removal, due to a high oxidising environment in the diesel engine exhaust.

In Table 2-5, an overview of the studies considering NTP for $NO_x$ removal from diesel engine exhaust is schematized.

Table 2-5: Overview of the published papers considering NTP for NOx removal from diesel engine exhaust

| Authors | Year | Reactor type | Gas type | Catalyst/adsorbent type | Reactor temperature | Flow rate | Power generator | Peak voltage | Peak pulse frequency | The range of studied energy density |
|---|---|---|---|---|---|---|---|---|---|---|
| Puchkarev et al. (Puchkarev et al., 1998, Slone et al., 1998, Puchkarev et al., 1999) | 1998 1999 | Corona reactor | Diesel exhaust gas | - | - | 1-10 L/min | Pulse supply | 49 kV | 1 kHz | - |
| Rajanikanth and Ravi (Rajanikanth and Ravi, 2002) | 2002 | DBD reactor / Combined DBD reactor with adsorbent | Simulated gas (NO in $N_2$, $O_2$, CO) / Diesel engine exhaust at no load | MS-3A, MS-4A, MS-13X | Room temp. and 200ºC | 2 L/min | AC high voltage supply | 25 kV | 100 pps | - |
| Yamamoto et al. (Yamamoto et al., 2003b) | 2003 | DBD reactor / Packed bed DBD reactor | Diesel engine exhaust at various loads | $BaTiO_3$ | Room temp. | 3 L/min | AC high voltage supply / pulse supply | 25 kV | 60 Hz for AC / 210 Hz for pulse | - |
| Rajanikanth et al. (Rajanikanth et al., 2003) | 2003 | DBD reactor / Combined DBD reactor with adsorbent | Diesel engine exhaust at no load and load 50% | Activated alumina,MS-13X, activated charcoal | Room temp. | 2 L/min | AC high voltage supply | 25 kV | 100 pps | 0 – 100 J/L |
| Rajanikanth and Ravi (Rajanikanth and Ravi, 2004) | 2004 | DBD reactor / Combined DBD reactor with catalyst | Diesel engine exhaust at various loads | SCR (V205/Ti02) | 100, 150 and 200ºC | 2 L/min | Pulse supply | - | 80 pps | 0 – 100 J/L |
| Rajanikanth et al. (Rajanikanth et al., 2005, Srinivasan and Rajanikanth, | 2004 2005 2007 | DBD reactor / Combined DBD reactor with catalyst and adsorbent | Diesel engine exhaust at various loads | Adsorbent: activated charcoal, molecular sieves MS-13X, activated alumina / catalyst: conventional 2-way and 3-way catalyst, non-conventional activated Alumina ($A1_2O_3$) | 24, 100, 150ºC | 4 L/min | AC high voltage supply | 25 kV | 130 pps | 0 – 100 J/L |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2007b, Srinivasan and Rajanikanth, 2007a, Rajanikanth et al., 2004) | | | | | | | | | | |
| Rajanikanth and Sushma (Rajanikanth and Sushma, 2006) | 2006 | DBD reactor / Combined DBD reactor -adsorbent | Diesel engine exhaust at various loads | $BaTiO_3$ | Room temp. | 4 L/min | Pulse generator | 25 kV | 130 pps | - |
| Koga et al. (Koga et al., 2006) | 2006 | Corona reactor | engine exhaust gas and Simulated gas ($N_2/O_2/NO/NO_2/H_2O/CO_2/C_2H_4$) | - | - | 0.5-20 L/min | DC high voltage power supply | 15 kV | - | 0-2500 J/L |
| Rajanikanth and Srinivasan (Rajanikanth and Srinivasan, 2007) | 2007 | DBD reactor / Combined DBD reactor with catalyst and adsorbent | Diesel engine exhaust at various loads | Adsorbent: activated charcoal, molecular sieves MS-13X, activated alumina / catalyst: alumina | 24, 100, 150ºC | 4 L/min | AC high voltage supply | 25kV | 130 pps | 0 – 100 J/L |
| Vinogradov et al. (Vinogradov et al., 2007, Vinogradov et al., 2008) | 2007 2008 | Corona reactor | Diesel engine exhaust | - | 25ºC | 8 L/min | DC high voltage supply / pulse supply | 50 kV | 1000 Hz | 0 – 140 J/L |
| Rajanikanth and Sinha (Rajanikanth and Sinha, 2008, Rajanikanth et al., 2008) | 2008 | DBD reactor / Combined DBD reactor with adsorbent | diesel engine exhaust at various loads and Simulated gas ($NO/N_2/O_2$), | MS-13X/carbon molecular sieves (CMS)/activated charcoal | Room temp. | 2 L/min | Pulse supply | 25 kV | 130 pps | 0 – 190 J/L |
| Srinivasan et al. (Srinivasan et al., 2009) | 2009 | Packed bed DBD reactor | Diesel engine exhaust at various loads | - | Room temp. | 2 L/min | DC/ AC high voltage supply /pulse supply | 25 kV | 130 pps | 0 – 190 J/L |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Rajanikanth et al. (Rajanikanth et al., 2009) | 2009 | DBD reactor / Combined DBD reactor with catalyst | Diesel engine exhaust at various loads | Commercially available catalytic converter | Room temp. | 2-4 L/min | AC high voltage supply /AC high voltage supply (solar powered battery) / pulse supply | 16 kV for AC, 25 kV for pulse | 50 Hz for AC, 12.2 kHz for AC (solar), 87pps for pulse | 90 J/L |
| Mohapatro et al. (Mohapatro and Rajanikanth, 2011a) | 2011 | Cross-flow DBD reactor | Diesel engine exhaust at load 27% | - | - | 2-25 L/min | Pulse supply | 20 kV | 75 pps | 0 – 550 J/L |

## 2.5 CONCLUSION

As presented in this chapter, non-thermal plasma has been shown to have promising potential for the removal of $NO_x$ from exhaust gases. Many studies have been conducted in order to improve the existing technologies and to develop new ways to increase the performance of NTP. DBD reactor was found to be more common in emission reduction applications due to scalability, effectiveness and low operational cost. Surface plasma reactor has shown greater energy efficiency for NO removal compared to DBD and corona discharge reactors. However, there is still controversial to compare NTP reactors with the same physical properties, regardless of the mode of the application and gas composition. If the energy consumption of about 3% of the engine output power can be achieved, this technique can reach to practical level. Various combinations of NTP with a catalyst and adsorbent have also been initiated in order to increase the $NO_x$ removal efficiency. Study of the published papers indicates that pulse power technology is more efficient for generating plasma, and has increasingly been applied in recent years. Furthermore, combining NTP with a catalyst or adsorber while using a packed bed reactor, can be more effective than NTP alone. The $NO_x$ removal efficiency from the exhaust emission in a diesel engine is higher than simulated gases, due to the presence of carbonaceous soot in the emission gas. Most of the presented studies do not cover that beyond a laboratory scale. There are also some contradictions in some aspects of NTP, such as what polarity is optimum for $NO_x$ removal. Regarding the existing publications, energy consumption is the main challenge of using this technology. More comprehensive research should be considered in order to improve the electrical aspects and also the reactor design. Additionally, a few studies investigated the economics of NTP technology. In view of global health and environmental concerns and increasingly stringent emission regulation restrictions, NTP technology is predicted to become commercially viable in the future, and therefore, more research is necessary in order to make this technology widely available.

# Chapter 3: Particulate matter removal using non-thermal plasma technology: A review

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Publication: Paper in preparation

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| Md. M. Nabi | Extensively revised the manuscript |
| Z. Ristovski | Supervised the project, aided with the development of the paper and extensively revised the manuscript |
| H. Rahimzadeh | Supervised the project, aided with the development |
| R. Brown | Supervised the project, aided with the development of the paper and extensively revised the manuscript |

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|---|---|---|
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**Abstract**

This paper provides an overview of the current literature on non-thermal plasma (NTP) emission treatment of diesel engine exhaust focusing especially on particulate matter (PM). NTP treatment of exhaust is believed to be a potentially promising technology for both $NO_x$ and PM reduction and the significance of exploring concepts of plasma emission treatment held by various researchers is considered. The main argument presented in this paper suggests that there is a strong correlation between mechanical, chemical and electrical parameters involved in plasma production and exhaust treatment, which will ultimately result in improvement of diesel engine emission treatment. The lack of research on the concept of PM reduction by using NTP compared to the number of the papers about NOx has been highlighted; while the focus of the research about the PM has been recognised to be on PM mass reduction only. It is found that the PM removal mechanism by using NTP is in early stages yet and different existing theories in this area should be evaluated and completed in future research. Moreover, the energy consumption is identified as the main challenge of NTP emission reduction applications.



**Keywords:** Non-thermal plasma (NTP); Diesel particulate matter (DPM); Particle mass reduction; Particle size distribution; Diesel engines

## 3.1 INTRODUCTION

Diesel engines offer numerous advantages such as high fuel economy, excellent combustion efficiency, low operating cost, durability and low carbon monoxide and hydrocarbon emissions. However, on a mass basis, diesel engines emit 30-100 times more particulate matter (PM) and about 2-20 times more NOx emissions than gasoline engines (Saiyasitpanich et al., 2007, Song et al., 2009). Therefore, because of the large number of diesel engine applications, they continue to emit significant amounts of pollutants (Brinkman et al., 2005).

Diesel particulate matter (DPM) has been considered as the most complicated component of diesel exhaust. DPM consists basically of elemental carbon with minor fractions of volatile organic components from lubricant oil and unburned fuel, and inorganic components such as ash and sulfur compounds. Nuclei mode particles with a diameter of below 0.04 µm and agglomeration mode particles with a diameter up to 1 µm can be found in diesel particles (Majewski, Revision 2013.08b). Therefore, DPM differs in diameter, solubility, composition and therefore in its toxicity and they are implicated in a series of adverse effects on the environment (Ramanathan, 2007 ) and human health (Seaton et al., 1995, Sydbom et al., 2001b, omers et al., 2004). Concerns about health and environmental aspects on one side, and more and more stringent emission legislation on the other side (Rens and Wilde, 2005, Sydbom et al., 2001a, Matti Maricq, 2007), demand increased monitoring and control of diesel emissions, modification of the old emission reduction systems and creation of new, efficient and clean ways to remove DPM.

Until now, various technologies have been applied to meet the stringent standards for DPM control on a global basis. Diesel oxidation catalysts (DOC) (Cooper and Roth, 1991b), diesel particulate filters (DPF) (Kuki et al., 2004, Ohno et al., 2002 -a) and fuel borne catalysts (FBC) (Farrauto and Voss, 1996) have been considered for DPM, HC and CO control in automobile and stationary engines (Prasad and Venkateswara, 2010). Since the emissions of HC and CO from diesel engines are low, these technologies are focused on PM reduction. Most of these technologies are related to the reduction of PM mass while neglecting the number of particles. For example, conventional emission treatment systems such as diesel particulate filters cannot remove nanoparticles, particularly those under 100 nm in diameter (Suzuki et al., 2008). It should be noted that the health impact of DPM is more relevant to particle number and its related characteristics such as particle size distribution,

surface area and chemical composition in contrast to particle mass only (van Setten et al., 2001b).

Negative health effects of PM, severity of emission standards and limitation of conventional after treatment systems have motivated new technologies for diesel exhaust emissions reduction. The NTP technique has been considered as a promising technology for diesel exhaust emission reduction. Plasma is the fourth state of matter, which is an ionised gas containing free electrons, ions and charged particles while it is electrically neutral (Fridman, 2008). Chemical reactions will be started by introducing plasma inside the exhaust; induced atoms and radicals produced by plasma will contribute to numerous plasma-assisted oxidation processes. These reactions can oxidise HC, CO, $NO_x$ and also DPM (Majewski, 2004).

This is the first review paper that provides an overview of the literature concerning PM removal from exhaust. In comparison to the variety of publications on NOx treatment by plasma, very little research has been done to study the effect of plasma on PM. Since NTP technology has only recently been investigated for PM removal, there is no relevant review paper available on this topic, which is the main motivation for this work. The first part of this chapter concerns diesel engine emissions. The second section contains an overview of the harmful effects of DPM and diesel emission legislations. Then, the plasma and NTP technology are presented and conventional after treatment systems are discussed. The final section provides a comprehensive summary of findings to date on the use of plasma for effective PM removal alone and simultaneous removal of PM and NOx from diesel engines, whilst highlighting the significance of contrasting approaches concerning plasma emission treatment that are held by a number of researchers. The main argument presented in this section suggests that there is a strong correlation between mechanical, chemical and electrical parameters involved in plasma production and exhaust treatment, which will ultimately result in the improvement of diesel engine emission treatment systems. This chapter seeks to bring together, in a systematic way, the disparate material on the use of NTP for PM removal, and address the lack of research on the mechanisms of PM reduction from diesel emissions.

## 3.2 DIESEL PARTICULATE MATTER (DPM) STRUCTURE

Diesel exhaust is different from gasoline exhaust in two main ways: First, the amount of PM and nitrogen oxides emitted by diesel engines is much higher than gasoline engines. Furthermore, the diesel exhaust is leaner and the amount of unburned hydrocarbon and carbon monoxide is lower compared to the petrol engine exhaust. Therefore, most of the research

about emission reduction of diesel engines is mainly focused on PM and NOx reduction (Prasad and Venkateswara, 2010).

Complete combustion of a hydrocarbon fuel, which has been basically composed of carbon and hydrogen, would only generate $CO_2$ and $H_2O$ without formation of any other harmful products. However, due to the existence of several parameters such as short time of the chemical oxidation inside the combustion chamber, the non-homogeneity of the air fuel mixture inside the cylinders, and the heterogeneity and quick change of the temperature the ideal thermodynamic equilibrium cannot be achieved. Therefore, an incomplete combustion will occur inside the combustion chamber, which results in formation of different gaseous, semi-volatile and particle phase emissions (Prasad and Venkateswara, 2010, Stratakis, 2004b).

DPM formation during the combustion and DPM evolution process is a very complicated field in literature (D'Anna, 2009, Abid et al., 2008, Desgroux et al., 2013). For the sake of simplicity, DPM can be formed due to the incomplete combustion of hydrocarbons and it is composed mostly of elemental carbon (soot) with the approximate formula of $C_8H$ (Hall-Roberts et al., 2000) and a fraction of organic components (Burtscher, 2005). Different components in the DPM structure originate from four different sources including fuel, lubrication oil, air and material breakdown. The typical composition of DPM has been shown in Figure 3.1.

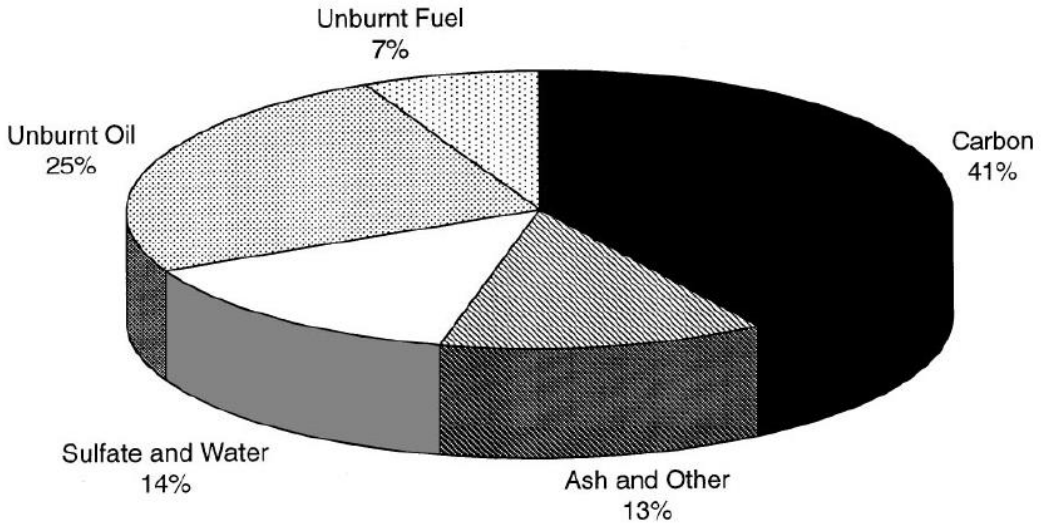


Figure 3.1: Composition of a typical PM for a heavy-duty diesel engine tested in a heavy-duty transient cycle (Kittelson, 1998b)

Diesel particles are composed basically from two main components, including semi-volatile or soluble materials and non-volatile or insoluble materials. The soluble fraction will dissolve in certain solvents while it undergoes evaporation by heating as well (Eastwood, 2008). The soluble or volatile fraction has three main components including organic, sulfate and the nitrate components. A soluble organic fraction (SOF) of DPM is present in the form of fine droplets and it has been formed due to the absorption of different hydrocarbons on the surface of carbon particles. At high diesel exhaust temperature, most of the SOF components are in the gas phase; however, they can become liquid on lower temperatures in a laboratory dilution tunnel (Majewski, Revision 2013.08b). The sulfate fraction is formed due to the interaction between molecules of $H_2SO_4$ and $H_2O$ which comprises of hydrated sulfuric acid and it can be found mostly in liquid phase. Research indicates that sulphate particulates are separated from carbon particles and are present in the exhaust as nucleation mode particles (Majewski, Revision 2013.08b). Nitric acid ($HNO_3$) is the main contributor to the nitrates fraction of DPM. Nitric acid is formed due to the reaction between water and nitrogen oxide ($NO_2$), and if it transfers into the particulate phase after formation, it will be quantified as nitrates fraction.

The non-volatile or insoluble part of DPM includes two main fractions, carbonaceous and ash, which are known as solid fractions. The carbonaceous fraction has been composed mostly of elemental carbon (soot). The black smoke emitting from some diesel engines is mostly due to this finely dispersed soot substance inside the diesel exhaust. The primary soot fraction is formed in both diffusion and premix combustion inside the combustion chamber. Then, these primary carbon atoms will form a pallet-like structure and these pallets will form a leaf-shaped crystallite structure (Majewski, Revision 2013.08b). These primary soot particles in (nuclei mode) will agglomerate while traveling from the cylinder through the exhaust system to form a chain-like, elongated structure before discharging into the environment (Majewski, Revision 2013.08b, Eastwood, 2008).

As mentioned previously, metallic ash is another component of the DPM solid fraction. This ash fraction is mainly responsible for filter choking in vehicles with diesel particle filters (DPF), which increases filter pressure drop and increases the fuel consumption. The ash fraction contains zinc, sulphates, magnesium and phosphates, which originate from burning fuel and lubrication oil additives inside the combustion chamber. Furthermore, metal oxide impurities, such as oxides of iron coming from the corrosion of engine wear and the engine exhaust manifold, can also be found in the ash fraction (Eastwood, 2008).

## 3.3 NEGATIVE EFFECTS OF DPM

DPM is suspected of having a series of negative health effects on human (Seaton et al., 1995, Sydbom et al., 2001b, omers et al., 2004, Ristovski et al., 2012), air, water, soil, buildings, visibility, agriculture, global climate change and the environment in general (Bauner et al., 2009, Ramanathan, 2007 ). Particles vary in composition, size, mass, and surface area and their toxicity depend on these characteristics. Particle mass measurement is the most common criterion in the literature for PM control studies. In PM mass applications, usually PM below a certain value of aerodynamic diameter has been collected and the measured mass has been considered as a criterion for total PM emission. However, the particle size distribution of PM from compression ignition engines has become of increased concern. It was recognised that fine particles from industrial processes and automobiles have more negative environmental and health effects than large particles (Darcovich et al., 1997). Regarding the particle size distribution, DPM can be categorised in four main groups as follows (Majewski, 2002b):

- Large particles > 10 μm
- Coarse particles 2.5 – 10 μm ($PM_{10}$)
- Fine particles 0.1 - 2.5 μm ($PM_{2.5}$)
- Ultrafine particles < 100 nm

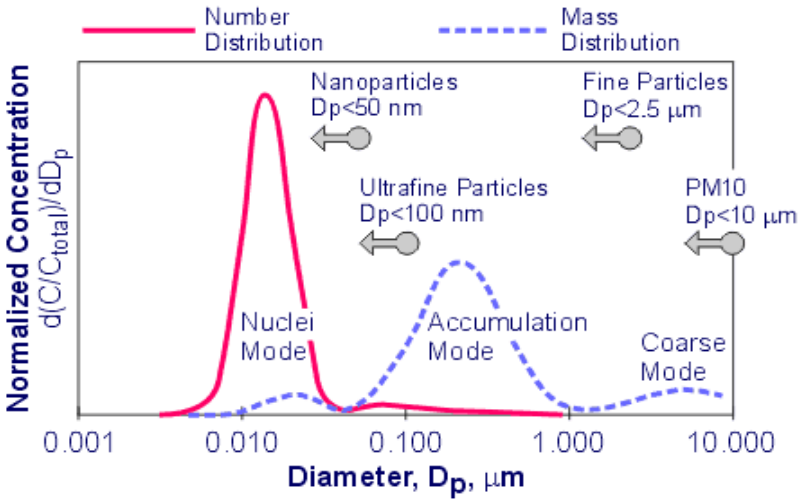


Figure 3.2: Illustration of a typical particle mass and particle size distribution (Majewski, 2002b)

The time in which particles remain in the atmosphere, depends on the particle size directly. For example, coarse particles will be removed from the atmosphere by sedimentation and precipitation in a few hours, while fine particles remain in the atmosphere even for days and can travel for long distances (Prasad and Rao Bella, 2011). As displayed in Figure 3.2, more than 90% of diesel exhaust-derived PM number is smaller or equal to 100 nm (nucleation mode) (McClellan, 1989), while most of the mass is in the range of 0.1–1.0 μm (accumulation size fraction) (Seinfeld, 1975, Kittelson, 1998a). As it is shown in Figure 3.3, the nose and throat are able to remove large particles only, while $PM_{10}$ can get into the trachea and upper bronchi. The smaller the particles are, the more penetration they achieve. For example, ultrafine particles can reach all areas of the lung and can even enter the bloodstream and reach the brain (Zhua et al., 2007). Some other negative effects of DPM on human health are: respiratory mortality and morbidity, inflammation in the lungs, eyes irritation, light-headedness and headache, asthma, irritation of the eyes, lung function decrements, lung cancer, cardiovascular disease, premature death and sudden infant death syndrome (Pope et al., 2002, Ristovski et al., 2012, Prasad and Rao Bella, 2011).

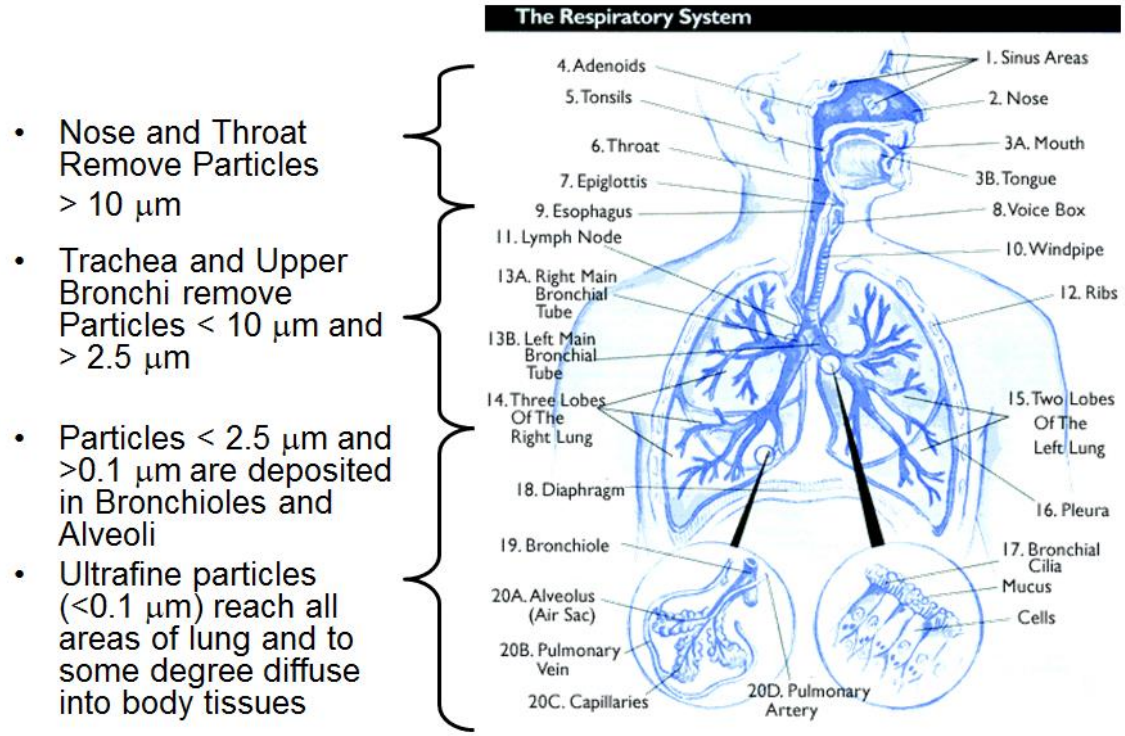


Figure 3.3: Penetration of different size of particles into the respiratory system (Stewart, 2011)

Table 3-1: Emission standards over time for diesel cars in Japan, EU, and the USA

| Country | Standard | Date | CO | HC | HC +NOx | NOx | PM | PN |
|---|---|---|---|---|---|---|---|---|
| | | | g/km | | | | | #/km |
| Japan | Emission Standards for Diesel Passenger Cars | | | | | | | |
| | Vehicle weight | | | | | | | |
| | < 1250 kg | 2002 | 0.63 | 0.12 | | 0.28 | 0.052 | |
| | | 2005 | 0.63 | 0.024 | | 0.14 | 0.013 | |
| | | 2009 | 0.63 | 0.024 | | 0.08 | 0.005 | |
| | > 1250 kg | 2002 | 0.63 | 0.12 | | 0.3 | 0.056 | |
| | | 2005 | 0.63 | 0.024 | | 0.15 | 0.014 | |
| | | 2009 | 0.63 | 0.024 | | 0.08 | 0.005 | |
| EU | Emission Standards for Diesel Passenger Cars | | | | | | | |
| | Euro 4 | 2005.01 | 0.5 | | 0.3 | 0.25 | 0.025 | |
| | Euro 5a | 2009.09 | 0.5 | | 0.23 | 0.18 | 0.005 | |
| | Euro 5b | 2011.09 | 0.5 | | 0.23 | 0.18 | 0.005 | 6E+11 |
| | Euro 6 | 2014.09 | 0.5 | | 0.17 | 0.08 | 0.005 | 6E+11 |
| US | LEV II Emission Standards for Passenger Cars and LDVs < 8500 lbs; 50,000 miles/5 years | | | | | | | |
| | | | NMOG | CO | NOx | PM | HCHO | |
| California | | | g/mile | | | | | |
| | LEV | | 0.075 | 3.4 | 0.05 | | 0.015 | |
| | ULEV | 2004-2010 | 0.04 | 1.7 | 0.05 | | 0.008 | |
| | SULEV | | | | | | | |

Note: PN - Particle Number, NMOG - non-methane organic gases, HCHO – formaldehyde, LEV-Low Emission Vehicles, ULEV-Ultra Low Emission Vehicles, SULEV-Super Ultra Low Emission Vehicles

## 3.4 DIESEL EMISSION LEGISLATIONS

Considering the negative effects of DPM on health and environment, the regulation of exhaust emissions is becoming increasingly stringent by the day. The first standard for exhaust emission regulation was introduced in both the USA and Europe in 1982 for light duty vehicles (Van Setten et al., 2001a), and this standard has been modified several times. Table 3-1 indicates the emission standards for diesel passenger cars in the USA, Europe and Japan. Note that the emission standards are usually introduced in mass per distance (g/km or g/mile of light-duty vehicles or passenger cars) over a defined test cycle. As it can be seen, PM legislations have been gradually tightened since 2000, and more recently, PM number limitation has been added to emission legislation.

Euro VI regulation will come into play in 2013-14, which will enable the harmonisation of the European standards with those of the USA and Japan. The legislations are advancing with consideration of particle number monitoring for Euro VI, and SULEV (super ultra-low emission vehicle) fleet average light-duty (LD) emissions (Johnson, 2009, Johnson, 2012). So, there is a major challenge for diesel engine manufacturers to meet the emission standards while achieve a high level of engine performance and fuel efficiency. The trend of diesel particle standards presented in the above table make it clear that effective PM control technologies should be introduced to enable the manufacturers to meet the stringent diesel emission standards (Bauner et al., 2009).

## 3.5 PLASMA TECHNOLOGY

Plasma is known as the fourth state of matter where both electrons and cathode ions coexist together. Plasma can be formed in two different ways. First, by using thermal energy and heating the molecules to extremely high temperatures (more than 2000 °C), which is called thermal or hot plasma. The second type is called non-thermal plasma (NTP) and can be generated by exposing the molecules of the gas to a highly strong electrical field. The minimum required voltage to maintain the plasma is called the breakdown voltage. At a voltage level higher than the breakdown voltage, the rate of electron production surpasses the loss rate. In the NTP variety, the temperature of the background gas does not change during the plasma formation while the temperature of its electron is much higher than the background gases (EPA, 2005). For a special gas species, NTP reactor configuration and material, the breakdown voltage depends only on gas pressure and discharge gap (Paschen, 1889).

NTP, which employs an electrical field to breakdown the gas molecules in a plasma state requires much lower energy and power compared to thermal plasma. Having a high energy content, NTP has been used in many environmental applications by producing ionised gas through the electric current discharge and providing enough energy to free electrons and allow the electrons and ions to coexist (Mizuno, 2007). These energised electrons can also dissociate the chemical bonds of different components, which results in production of free radicals and recombination of them in plasma state. Basically, the chemical reactions in plasma state can be divided into the primary and secondary processes. The primary process mainly consists of the electron impact reactions including excitation, dissociation, ionisation, dissociative attachment, dissociative ionisation, etc. (Phelps, 1985). Electron impact reactions take place in the plasma state due to the reaction of energised electrons with atoms or molecules up to a certain energy threshold, which results in the production of positive and negative ions, free radicals and excited and metastable species. On the other hand, the secondary process will happen due to the reactions between the products of primary reactions (Hsin-Liang, 2008).

Different reactors have been designed to introduce plasma inside the exhaust for emissions reduction applications (Chae, 2003). Among them, dielectric barrier discharge (DBD) and corona discharge reactors have been used more than others for diesel exhaust treatment. In DBD at least one dielectric layer exists between the anode and cathode electrodes. The dielectric layer is usually made of glass, quartz or ceramic. It prevents the occurrence of the arc discharge inside the DBD and also spreads the micro discharges uniformly along the DBD surface, which increases the chance of collision between the background gas and electrons (Eliasson et al., 1987). In corona discharge reactors, at least one electrode is a needle or wire shape. When voltage approaches are applied to the breakdown voltage, a crown-like discharge inside the reactor will be formed, while the electric field closer to the needle electrode will be much higher than the other places (Van Veldhuizen and Rutgers, 2001). Comparing the DBD and corona discharge reactor, DBD has shown a better performance than corona discharge for pollution abatement. DBD has more specific input energy (SIE) than the corona reactor for the same gas residence time (Rosocha and Korzekwa, 1998, Rosocha, 2005) and shows more removal efficiency (Kim et al., 2005a).

## 3.6 CONVENTIONAL TECHNOLOGIES FOR CONTROLLING DIESEL PARTICLES

Diesel particulate filters (DPF) have been widely used for PM removal in diesel engines. DPF are generally made of a honeycomb structure containing multi membranes with several small pores that can remove PM by filtration (Yao, 2009a). However, there are some drawbacks in using DPF as an after treatment system (Prasad and Venkateswara, 2010). DPF has a good efficiency at the exhaust temperatures greater than 300 °C; however, in urban and suburban areas, the temperature of diesel exhaust is often lower than 300 °C, which results in PM accumulation within the DPF (Yao, 2009a). Furthermore, deposition of PM increases pressure drop in the DPF. This deposition can cause DPF choking and thus regeneration is required. For regeneration, high temperatures of about 600 °C should be provided (Zelenka et al., 1996, Hiranuma et al., 2003). These effects increase fuel consumption, which is not desirable for emission reduction and fuel economy. For example, increased fuel consumption as a result of using a DPF with 42% porosity is estimated as high as 6-11% and cannot be economically viable (Ohno, 2006).

Diesel oxidation catalyst (DOC) was initially used as the first contribution to the reduction of PM mass emission (Cooper and Roth, 1991a) in 1996 in the USA and 1998 in Europe (Prasad and Venkateswara, 2010). It is actually a non-filtered channel resembling the conventional catalytic converters for gasoline engines. DOC reduces DPM by 20-40%, which is relatively low compared to that for gaseous emission catalysts. There is also a risk that the fuel sulfur will be oxidised and form sulfate and thus increases the total PM concentration (Prasad and Venkateswara, 2010).

In fuel-burn catalyst (FBC), metals such as iron, cerium and platinum have been added into the fuel to approach a more complete and efficient combustion. These additives can improve the combustion quality and reduce the amount of soot emitted from diesel engines (Howard and Kausch Jr, 1980). However, the implementation of this technique can also cause the formation of extra metal nanoparticles (Jung et al., 2005). These metallic nanoparticles have a great potential to penetrate deeply inside the human inhalation system and enter the blood stream, which can cause serious neurological disease (Brewer, 2009).

## 3.7 PARTICULATE MATTER (PM) REMOVAL BY PLASMA

NTP technology has shown a good potential for PM removal applications. NTP oxidation of PM can be operated through low temperature reaction pathways. Low

temperature removal is quite important in diesel engine applications because the mean temperature of diesel exhaust is below 200 °C for 70% of the diesel operating cycle.

The literature about PM removal by using NTP technology can be divided into three main categories including: NTP application for DPF regenerating, NTP application for direct removal of PM from exhaust emission and simultaneous removal of PM and $NO_X$.

### 3.7.1 NTP application for filter regeneration

Diesel particulate filter (DPF) has been extensively used for reduction of PM (Kojetin et al., 1993, Ichikawa et al., 1995, Suzuki and Matsumoto, 2004, Finoa, 2007). DPF choking can occur due to the deposition of PM on the porous wall of DPF. Therefore, PM incineration, or DPF regeneration is the main challenge in DPF applications. Oxygen incineration by using a heater, or $NO_2$ oxidation techniques such as CRT (continuous regeneration trap) or CSF (catalysed soot filter), have been already used for incinerating the trapped carbon particles in DPF (Kong et al., 2005, Kuenstler et al., 2003). On the other hand, NTP technology can convert NO to $NO_2$ and also produce different active oxygen species in the diesel exhaust. Both $NO_2$ and oxygen can oxidise deposited soot in a plasma state at low temperature. Therefore, this technique has been considered by different scientists for DPF regeneration in literature (Okubo et al., 2007, Kim et al., 2002, Okubo et al., 2009, Kuwahara et al., 2011, Okubo et al., 2004, Okubo et al., 2002, Okubo et al., 2008).

Direct plasma regeneration of a diesel particulate filter is the concept of an effective regeneration method (Kupe et al., 2000). In this method, the oxidation catalyst is replaced by an NTP reactor. The method is to employ plasma for NO to $NO_2$ oxidation inside the exhaust and use $NO_2$ and induced free radicals by plasma for burning the deposited carbon soot on DPF. Regeneration of diesel particulate filter, using NTP without using any catalyst has been studied in (Okubo et al., 2002). A barrier-type pulse corona plasma reactor has been used (Yamamoto et al., 2001a, Yamamoto et al., 2001b, Kuroki et al., 2002) while the maximum peak voltage was 45 kV and the applied frequency was 210 Hz. A simulated gas (2% NO balanced with $N_2$ mixing with dry air) was passed through the plasma reactor which oxidised 70% of NO to $NO_2$. Then, the produced $NO_2$ by plasma and other induced radicals (such as O, N, and OH) flowed in-to the cordierite DPF. The temperature was kept constant at 250 °C during the experiments. A soot removal efficiency of 75% on energy efficiency of 40 J/L was achieved, while the regeneration time was about eight hours, which is very slow. $NO_2$ and

other active species such as O, $O_2$*, $O_3$, etc. are proposed for oxidation of carbon based particles through the following equations:

$$\begin{cases} C + 2NO_2 \rightarrow CO_2 + 2NO \\ C + NO_2 \rightarrow CO + NO \\ C + O_3 \rightarrow CO_2 + \frac{1}{2}O_2 \end{cases} \quad 3.1$$

Kim et.al (Kim et al., 2002) compared the effect of pure $NO_2$ injection and a plasma-treated gas containing NO, $NO_2$, $O_2$ and HC for soot oxidation. They employed a simulated diesel exhaust and found that pure $NO_2$ was not so effective for DPF regeneration when temperature was below 250 °C. However, in the case of the plasma treated gas, the soot oxidation was much higher than that of the pure $NO_2$ even in lower temperatures about 230 °C. In plasma treated gas, $NO_2$ and other by-products of NTP react as the carbon oxidants, which can deliver higher removal efficiency. In both pure $NO_2$ and plasma-treated gas techniques, the effect of temperature on DPF regeneration was clear. They reported the plasma-treated gas to be more effective and faster than pure $NO_2$ for DPF regeneration. The results have been obtained based on a simulated diesel exhaust ($NO_2$/He, NO/He, $O_2$ and $C_3H_6$ gas cylinders), thus the effectiveness of this technique in real operating conditions may be varied.

Regeneration of DPF using indirect or remote NTP has been considered by a few researchers (Li and Liu, 2000, Chang, 2001, Kanazawa et al., 1998, Urashima et al., 1998). In this method, instead of producing plasma inside the exhaust directly, the NTP-treated air is injected into the exhaust. NO fraction of diesel exhaust will be oxidised to $NO_2$ and the induced $NO_2$ with other activated oxygen species will incinerate deposited carbon soot on the DPF. For direct plasma methods (Okubo et al., 2003b), plasma will be formed directly inside the exhaust gas at high temperature. Therefore, the residence time of gas decreases by about 50% and as a result the conversion efficiency of NO to $NO_2$ decreases by about 50%. Furthermore, additional $NO_x$ may also be produced, due to the occurrence of plasma reactions on high temperature (Okubo et al., 2003b).

Okubo et.al (Okubo et al., 2004) employed a needle-to-plane barrier plasma reactor (Takaki and Fujiwara, 2001) for remote plasma experiments. The peak voltage was more than 35 kV and the pulse frequency was changed from 9 to 1000 Hz. The exhaust gas has been simulated by mixing 2% NO balanced with $N_2$ in a cylinder with dry air. They kept

temperature constant at 300 °C during the experiments. An NO component of 91% was oxidised to $NO_2$ and ozone was considered as the main parameter in the oxidation process. Furthermore, CO and $CO_2$ concentrations, which were high at the beginning of the experiments, were reduced during the experiment. This occurred due to the reduction of soot concentration over the time period and hence there was a reduction of carbon oxidation by $NO_2$. This trend was the same as the trend reported by Kim et.al (Kim et al., 2002). The specific energy density (SED) was 78 J/L and they mentioned that if the SED of 10 J/L (for a 3-L-class diesel engine) can be achieved (which is around 3% of automotive diesel engine power output over the United States Federal Test Procedure), the plasma SED will be at a practical level (Hoard et al., 2000b).

The application of remote NTP for PM removal from actual diesel exhaust, by developing a new after treatment system using NTP desorption and reduction, has been studied in (Okubo et al., 2008). It has been confirmed that DPF regeneration is possible by using remote surface discharge plasma through the oxidation of PM by ozone. On the other hand, $NO_x$ reduction by NTP technique is also possible for oxygen-lean exhaust. To control the concentration of oxygen in the exhaust, they proposed controlling the incineration state of the engine or injecting oxygen poor gas into the combustion chamber. Around 10% oxygen is generally included inside the diesel exhaust in normal operation loads. So, by using NTP technology, NO is oxidised to $NO_2$ and cannot be reduced to $N_2$ in this condition. This means that plasma alone cannot be effective for total $NO_x$ reduction in normal engine operation conditions. Therefore, two different NTP reactors were proposed: one for DPF regeneration and the other one for $NO_x$ reduction, instead of using a conventional catalyst converter. The first one was a surface discharge reactor to produce ozone and free radicals for filter regeneration. Ozone and free radicals were injected upstream of DPF which oxidised NO to $NO_2$. Then, $NO_2$ and ozone incinerated the deposited particles inside the DPF. The second reactor was a barrier-type packed bed NTP reactor (Okubo et al., 2001a, Okubo et al., 2001b) which was employed for $NO_x$ adsorption downstream of the DPF. 1.87g soot in 47min with SED of 9.8 J/L was removed and NOx removal efficiency was 80% at SED of 78 J/L. In the NTP $NO_x$ reactor, a Zeolite adsorbent has been used inside the NTP reactor, so it is hard to decouple the effect of NTP and Zeolite for $NO_x$ reduction.

The effect of remote NTP by using a needle-to-plane plasma reactor (Okubo et al., 2002) for DPF regeneration in actual exhaust has also been studied by Okubo et al. (Okubo et al., 2007). Temperature was kept constant at 280 °C during the regeneration process. High

efficient regeneration, by injecting a small amount of activated gas (injecting-flow-rate/main-flow-rate =1%-10%) at peak voltage of 34.7 kV and the pulse frequency of 840 Hz, has been reported. They also monitored THC (total Hydrocarbon), $N_2O$, NO, $NO_2$, CO, $CO_2$ and $O_3$ concentrations at the DPF outlet. Injecting activated species was effective in the oxidation of NO to $NO_2$ and $NO_2$ can be used for incineration of the deposited soot. $NO_2$ concentration decreased in the reactor outlet and CO and $CO_2$ concentration increased during the experiments. This shows the NTP regeneration has been effective for oxidising soot to CO and $CO_2$. On the other hand, $NO_x$ and THC concentrations have been reduced under the NTP condition. Most of the PM incineration has occurred at the beginning of the NTP start time. Ozone concentration was zero at the DPF outlet, which shows that all ozone produced by plasma has been consumed for DPF regeneration.

In 2009, Okubo et.al (Okubo et al., 2009) studied the characteristics of filter regeneration by NTP induced ozone injection. They injected induced $O_3$ in to the flue pipe in a direction opposite to the flow of the actual exhaust upstream of the DPF. The temperature in their experiments was constant at approximately 250 °C. By injecting ozone, NO was oxidised to $NO_2$ and both ozone and $NO_2$ incinerated deposited PM. The concentration of injected ozone was 1.45% and the flow rate was 12.6 L/min. During the regeneration process, the PM decreased from 787 to 297 over 28 minutes. Their energy efficiency was 3.5g (PM)/kWh. By injecting ozone, the concentration of NO decreased from 247 ppm to 97 ppm and the concentration of total $NO_x$ was decreased from 263 ppm to 127 ppm due to the oxidation of $NO_x$ to the other components such as $HNO_3$. They also studied the effect of different $O_3$ injection flow rates. The highest energy efficiency was about 6.47 g (PM)/kWh, which was obtained for an ozone injection flow rate of 5 L/min. They reported that the required energy for continuous regeneration is only 0.25% of the engine power.

### 3.7.2 NTP application for direct PM removal from exhaust emission

Thomas et.al (Thomas et al., 2000a), considered NTP for PM treatment of exhaust in 2000. This research was one of the first studies that investigated the effect of NTP on PM removal and particle size distribution. They used a complex packed bed reactor containing packing material, which increased the residence time within the plasma region. They claimed that by increasing the residence time selectively, the level of oxidation of emissions may be decoupled from the energy deposition into the exhaust. Their packed plasma system removed 99.9% of PM with average diameters of about 60 nm. The performance was reduced to 90% removal for ultrafine particles. A complicated reactor was used in their research and limited

information was provided about electrical and mechanical design parameters. Due to the existence of pellets, the high deposition is really probable, which should be considered for PM removal by plasma.

Ye et.al (Ye et al., 2005) used a plasma reactor combined with a catalyst to reduce PM emission. In their experiments, a discrete range of PM diameter between 0.3 μm to 5 μm has been considered. They studied the effect of plasma energy density, reaction temperature and exhaust flow rate on PM removal. Improvement of PM removal by filling the discharge gap with catalyst pellets has been studied as well. The plasma reactor consisted of a 2 mm diameter stainless steel rod electrode, a grounded plate type electrode and a piece of glass on the surface of the plate as a dielectric barrier. The discharge gap was about 3 mm and effective discharge length was 70 mm. Pulsed voltages with a frequency of 15 kHz and adjustable voltages ranging from 0 to 15 kV were applied. PM removal was increased gradually with increasing energy density until reaching a maximum value and then decreased with further increase of energy density. The same trend has been observed for HC removal in their paper. The reason is the high value of the electric field at high voltage levels, which causes local arc formation and electrical energy loss. Based on their experiments, NTP was more effective at higher temperatures and lower flow rates. They also showed that the enhanced packed bed catalyst reactor has higher PM removal efficiency. Depending on the operating conditions, PM removal efficiency ranged approximately from 25 to 75%.

Yao et al. (Yao et al., 2006b) studied the effect of uneven DBD reactors for PM emission reduction. The main novelty of this research is the modification in the plasma reactor design. They tested six different types of uneven DBD reactors with discharge gaps ranging from 0.4 to 1.0 mm. In this research, a PM removal of 67% has been achieved for a 0.4 mm reactor gap. The energy efficiency has been increased by decreasing the gap distance, while the PM deposition rate inside the reactor increased. Their energy efficiency was typically in the range of 3-10.6 g/kWh at an energy density of 2-16 J/L depending on the applied voltage or frequency. An uneven electrode shape has been chosen to avoid corona discharge inhibition due to the PM deposition on the surface of the dielectrics. This uneven reactor has many sharp corners that induced efficient corona discharges in each gap. In these experiments, the peak voltage was 10 kV and pulse repetition was 10-500 Hz. To design the uneven DBD reactor, 30 pairs of alumina and stainless steel plates have been used. The reactor inlet temperature was 170-180 °C. Also reported, was the achievement of a continuous

energy efficiency reduction by increasing energy injection, no matter whether the energy injection has been increased by pulse voltage or pulse repetition.

In 2006, Fushimi et.al (Fushimi et al., 2006) studied the effect of the number of pairs of electrodes for the above uneven dielectric barrier discharge reactor. They defined the energy consumption of less than 100 W and pressure drop of less than 2 kPa for PM removal to be in a practical range. They compared 20, 30 and 50 pairs of electrodes for PM removal, while the range of injection energy in their experiments was 840-340 W. By choosing 20 pairs, the PM removal and energy efficiency were found to be 47-84% and 2.9-0.25 g/kWh respectively. For 30 pairs, these values were 74-93% and 6-1.8 g/kWh. When 50 pairs were used, energy efficiency was increased further to 13.7-3.6 g/kWh. By increasing the number of pairs, the discharge area and residence time increased, which corresponds to more PM removal. In their tests, residence time increases from 4.5 ms to 11.2 ms by increasing the number of pairs. Also the Reynolds number for 20, 30 and 50 pairs was equal to 584, 390 and 234 respectively. The pressure drop increases with time, indicating the accumulation of PM on the surface of aluminium and/or stainless steel reactor plates.

Fushimi et.al (Fushimi et al., 2008) also employed an uneven DBD reactor for their experiments and studied the effect of polarity and the rise time of pulse voltage waveforms for PM removal. They studied different wave forms (positive, negative, positive-negative and negative-positive). The width and rise time of the pulse are two main parameters for studying the wave forms and energy efficiency of the plasma driven reactors and the cost of the power supply depends on these two parameters. They reported O atoms generated by plasma, as the main component for PM oxidation. O atoms unzip the C-C bonds and forms epoxy groups, which result in oxidation. As mentioned before, in NTP application for DPF regeneration $O_3$ and $NO_2$ have been introduced as the main oxidant and the contribution of $O_3$ and $NO_2$ for PM incineration was approximately 50:50 based (Okubo et al., 2009). On the other hand, in this paper the $NO_2$ and $O_3$ contribution in PM removal was considered to be very small due to the slow rate of PM oxidation by $O_3$ and $NO_2$, O and OH radicals were proposed as the main oxidants of PM. In their experiments, the peak voltage changed from 7 to 10 kV. Pulse repetition frequency was 580 Hz for positive and negative pulse and 340 Hz for positive-negative and negative-positive pulse. They found that PM removal is almost the same in the range of 65-80% for all kinds of wave forms. When the peak voltage of the negative pulse was below 8 kV, the PM removal was lower than other wave forms. They observed that PM removal increases with increasing energy injection and is saturated at energy injection more

than 200W. The saturation of PM removal is due to the limitation of PM deposition. They also calculated the energy efficiency for PM removal. It was in the range of 3.9-11.6 g/kWh. It was concluded that the energy efficiency for PM removal is just a function of energy injection and there is no obvious relationship between PM removal and energy efficiency with the voltage wave forms, except for negative pulse voltage with the peak value below 8 kV. However, a contrast trend has been reported by Smulders et.al (Smulders et al., 1998) for dependency of NTP application on discharge wave form, as they found pulse plasma with a very short rise time to be more effective for removing volatile organic components (Smulders et al., 1998).

In 2007, Yao et.al studied particle size variations and by-products of particle oxidation under plasma treatment by using an uneven DBD. The reactor was set up in the tail pipe and actual diesel exhaust was passed through the reactor (Yao et al., 2007). They used a particle size spectrometer for monitoring the particle size distribution. The exhaust flow rate was 33.7 L/s and reactor inlet temperature was 430 K for actual exhaust experiments. They also conducted some research about the simulated exhaust. For simulating the exhaust, an atomiser was utilised to generate PM at a feeding rate of 3 mg/h. This amount of PM was mixed with 2.4 L/min $N_2$ and 0.6 L/min $O_2$ before entering the NTP reactor. For actual exhaust experiments, PM concentration at reactor outlet without plasma (0 J/L) was found to be less than PM concentration at reactor inlet due to the particle deposition on the surface of the DBD reactor plates. By starting the plasma, PM concentration has not been changed considerably at reactor outlet, especially for particles smaller than 22 nm. They also demonstrated PM removal as a function of particle size. PM deposition in the reactor outlet was not the same for all particle sizes before starting the plasma. By introducing plasma inside the exhaust, particle removal increased by the increment of particle size and the maximum of PM removal was obtained for particle size of between 30-100 nm. When energy density was about 1.1 J/L, the PM removal of about 60% was obtained for PM size ranging from 30-300 nm. As noted previously, PM removal using the model exhaust was also considered. NTP for PM removal especially for PM size less than 22 nm has not been so effective, while there is no unique trend in the results.

Suzuki et.al (Suzuki et al., 2008) used 110 g of carbon dispersed in 25 $m^2$ of water and 6 L/min gas mixture of nitrogen and oxygen to simulate the diesel engine particles. Their carbon black particles (CBP) had an average size of 30 nm. They changed the ratio of nitrogen to oxygen to investigate the effect of oxygen in PM removal. They found that about

80% of the CBP were removed, irrespective of the gas mixture ratio. They also observed that by increasing oxygen ratio, $CO_2$ production increased due to the increase in activated oxygen production. They also tested their reactor for exhaust emission of a real diesel engine. They got an average removal of 43% under plasma condition, while this trend was different from that of Yao et. al (Yao et al., 2007). Furthermore, the removal efficiency for real exhaust was lower than the removal efficiency of simulated gas. They also observed the dependency of PM removal to engine load.

Some other specifications of PM removal have been studied in different literature, especially by Yao et.al (Yao, 2009b, Yao et al., 2009a, Yao et al., 2008). They mainly used an uneven dielectric barrier discharge reactor for their experiments. They found that discharge property does not change very much with PM deposition inside the reactor and PM removal increases by increasing energy injection. Pressure loss can be produced due to the PM deposition inside the reactor. But if flow rate is high enough, it can blow off the deposited particles (Yao et al., 2008). In 2009, they characterised the catalyst – supported DBD reactor for PM removal (Yao et al., 2009b). They used two different kinds of catalyst layers: $Fe_2O_3$ and $TiO_2$ and found that these two kinds of catalyst layers do not obviously influence plasma discharge. They reported that an $Fe_2O_3$ layer on an alumina surface promotes PM oxidation. They also observed the particulate matter combustion in pulsed discharge duration by using a dynamic range streak camera (Yao et al., 2009a). They visualised the luminescence from discharge gap fed with PM and oxygen under plasma discharge. This luminescence was due to the presence of $CO_2$ and CO, which has been excited by energised electrons. Yamamoto et.al (Yamamoto et al.) studied seven different metal oxide catalysts ($TiO_2$, ZnO, $V_2O_5$, $Fe_2O_3$, $CO_3O_4$, $MnO_2$ and CuO) for diesel PM removal under plasma discharge. They also confirmed that $Fe_2O_3$ is the most desirable catalyst for PM oxidation removal.

### 3.7.3 Simultaneous removal of PM and NOx

The focus of different studies in the area of NTP application for diesel exhaust emissions reduction is more on PM or $NO_X$ removal separately. However, in real applications, the simultaneous reduction of PM and $NO_X$ should be considered. Thomas et.al (Thomas et al., 2001) presented one of the first studies in this area. They evaluated the potential of combining different NO selective catalysts with plasma systems. It has been found that 2% Ag-$Al_2O_3$ is an effective catalyst for NO removal, and then this catalyst has been assessed for PM and $NO_X$ removal. Plasma DPF trapping has been combined with NO catalyst and it has been confirmed that, in addition to trapping and oxidising PM by plasma, the plasma DPF

stage can be operated to generate a highly reactive reactant mixture (containing HC*), which can subsequently enhance the catalytic reduction of NO to $N_2$.

Mok et.al (Mok and Huh, 2005) employed an NTP technique with a catalysts system to remove $NO_X$ and PM simultaneously. The plasma reactor has been used for converting a part of NO to $NO_2$ while a $V_2O_5$ / $TiO_2$ catalyst downstream of the DBD reactor reduced NO and $NO_2$ to $N_2$. They evaluated the effect of temperature and input power in their experiments. The reactor consisted of nine uncovered steel rods and four covered steel rods by ceramic tube. They applied high voltages (AC 400 Hz) in the range of 8-15 kV to produce plasma. The exhaust flow rate in their system was 10 L/min. In this study, ammonia has been used as the reducing agent, and was added to the exhaust before entering the reactor. NO concentration decreased with the increase of energy density at all temperatures, while NO oxidation was slower at higher temperatures. Ozone has been introduced as the key parameter in oxidation of NO to $NO_2$. The amount of ozone and the rate of reaction between NO with O and OH, decreased with the increase of temperature. They also found a small decrease in the total $NO_x$ ($NO+NO_2$) level due to the reaction of NO and OH which produces some $HNO_3$. When a catalyst alone was used, 35-60% reduction in total $NO_x$ level was observed depending on reaction temperature. On the other hand, by using a catalyst DBD system, $NO_x$ removal efficiency was improved and was about 80%. $NO_x$ removal efficiency has been achieved. They also assessed the PM removal by proposed hybrids system through the flowing reaction pathway for PM removal:

$$NO \xrightarrow{O,O_3,OH} NO_2 \qquad 3.2$$

$$PM + NO_2 \rightarrow CO_2 + N_2 \qquad 3.3$$

Besides these reactions, it is believed that the oxygen atom, ozone and hydroxyl radical can also be involved in PM oxidation. PM removal efficiency for the hybrid system was 50% and 80% at energy efficiency of 20 and 40 J/L respectively. These values show the effectiveness of the hybrid system for PM removal as well.

Song et.al studied the PM, hydrocarbons (HC) and $NO_x$ abatement characteristics of diesel exhaust in 2009 (Song et al., 2009). They studied the effect of peak voltage, frequency and engine load on contaminant removal. They used a DBD reactor, consisting of two concentric quartz tubes for dielectric barrier layers with the discharge gap being 4mm. Flow

rate kept constant at 5 L/min and a high frequency AC power supply with peak voltage of 0-14 kV and frequency of 10-27 kHz has been used for producing plasma. They collected PM samples by using filters and evaluated the effect of NTP on PM gravimetrically. By increasing voltage at each frequency level, discharge power increased continuously. Generally, PM, HC and $NO_x$ removal increased with an increase of the applied voltage while the trends of PM and HC abatements were different from the one for $NO_x$. They also changed frequency from 10 to 20 kHz at different voltage levels and studied the effects on discharge power and removal efficiency. Approximately for all voltage levels, the maximum of discharge power and consequently maximum of removal efficiency was obtained at about 15 kHz, which is the resonance frequency of the DBD system. Based on their experiments, the maximum of PM, HC and $NO_x$ could reach 80%, 70% and 65% respectively.

In 2010, Okabo et.al [25] used packed pellets of $BaTiO_3$ for simulation of exhaust to study the effect of non-thermal plasma for PM and $NO_x$ removal. They considered the $NO_x$ molecules to be induced by N radicals and particulate matter to be incinerated by oxygen radicals produced either by $NO_x$ or $O_3$. They showed simultaneous removal of PM and NOx is possible under oxygen poor conditions. Furthermore, an optimum value for mass of loaded PM has been reported. When mass of loaded soot is higher than a threshold value, NTP is not effective for PM and $NO_x$ removal. Under an optimised plasma condition, the energy efficiency was 2.2 g/kWh for PM removal and 4.3 g $(NO_2)$/kWh for $NO_x$ reduction. Combination of NTP and catalyst for simultaneous PM and $NO_x$ removal also needs comprehensive study, specially dealing with the particle size distribution.

## 3.8 CONCLUSION

In this chapter, application of non-thermal plasma for particulate matter removal from diesel exhaust in different studies has been reviewed. NTP technology has been considered as a promising technology for filter generation, PM removal from the exhaust and simultaneous removal of PM and $NO_x$. For filter regeneration applications, high efficiency of about 75% has been reported in literature. Moreover, supreme value of PM removal from the exhaust, even more than 90% PM removal efficiency has been achieved in some experiments. This technique can be employed even at low exhaust temperatures with a very fast start-up time. Moreover, NTP performance for PM and $NO_x$ removal can be improved by using it in combination with a catalyst or DPF. However, this technology is in its early stages yet. Several parameters, such as discharge voltage and frequency, reactor configuration, flow rate, temperature and gas composition, should be taken into the account simultaneously for

evaluating the NTP application for PM removal. Most of the research in this area is conducted from an electrical point of view only and is mostly based on simulated gas. In real diesel exhaust applications due to the complexity of exhaust, formation of extra harmful by-products is possible. Furthermore, the mechanism of PM removal is not clear yet and contradictory explanations can be found in literature. Discharge power has remained as the main challenge for development of this technology for mobile applications. If the energy consumption can reach below 3% of the engine output power, this would be in practical range. Furthermore, most of the research in this area has monitored the particle mass only. Regarding the new stringent standard and negative health effects of ultrafine particles, further studies are still required to evaluate the effect of NTP on particle size distribution as well. NTP reactor modification, not only from the electrical side, but also by considering mechanical and physical design parameters to increase PM residence time and PM deposition rate inside the reactor, should be developed in future research in this area.

# Chapter 4: Effect of pulsed power on particle matter in diesel engine exhaust using a DBD plasma reactor

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Publication: Plasma Science, IEEE Transactions on 41 (8), 2349-2358

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| Md. Mostafizur Rahman | Assisted with conducting the experiment |
| Firuz Zare | Supervised the project, aided with the development of the paper |
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**Abstract**

Non-thermal plasma (NTP) treatment of exhaust emission is a promising technology for both nitrogen oxides ($NO_X$) and particulate matter (PM) reduction by introducing plasma into the exhaust. This study considers the effect of NTP on PM mass reduction, PM size distribution and PM removal efficiency. The experiments have been performed on real exhaust from a diesel engine. The NTP is generated by applying high voltage pulses using a pulsed power supply across a dielectric barrier discharge (DBD) reactor. The effects of the applied high voltage pulses up to 19.44 kVpp with repetition rate of 10 kHz are investigated. In this paper, it is shown that PM removal and PM size distribution need to be considered together, as it is possible to achieve high PM removal efficiency with an undesirable increase in the number of small particles. Regarding these two important factors, in this research, 17 kVpp voltage level is determined to be an optimum point for the given configuration. Moreover, particle deposition on the surface of the DBD reactor was found to be a significant phenomenon, which should be considered in all plasma PM removal tests.



**Keywords:** Particle size distribution, particle mass reduction, diesel exhaust gas, dielectric barrier discharge (DBD), pulsed power, push-pull converter.

## 4.1 INTRODUCTION

There is a continuous increase in the number of diesel engines in both stationary and mobile application due to the lower operating cost, higher thermal efficiency and longer durability, as well as lower hydrocarbons (HC) and carbon monoxide (CO) emissions (Song et al., 2009). However $NO_X$ and particulate matter (PM) emissions still remain the two main environmental concerns in diesel engine applications. Studies focused on risk assessment have shown that high outdoor $NO_X$ concentration observed in residential areas contributes to increased respiratory and cardiovascular diseases and mortality (Chaloulakou et al., 2008a). Moreover, the health effects of diesel particulate matter have been an area of concern for many years, due to both the chemical composition and the particle size distribution (Mayer et al., 1995, D'Anna, 2009). The small particles are inhalable and penetrate deep into the lungs, where they are able to enter the bloodstream and even reach the brain (Zhua et al., 2007, Oberdörster G et al., 2004).

Up to now, several technologies have been applied for $NO_X$ and particulate treatment of diesel engines. In recent years, application of non-thermal plasma (NTP) in exhaust gas treatment has gained lots of interest (Matsumoto et al., 2010a, Takaki et al., 1999, Mizuno, 2007, Saito et al., 2010). The NTP treatment of exhaust gas is a promising technology for both $NO_X$ and PM reduction by introducing plasma inside the exhaust gases. In non-thermal plasma, electrons have a kinetic energy higher than the energy corresponding to the random motion of the background gas molecules. The intent of using non-thermal plasma is to selectively transfer the input electrical energy to the electrons, which would generate free radicals through collisions and promote the desired chemical changes in the exhaust gas. These reactions can be accomplished at a fraction of the energy that is required in the thermal plasma system (Majewski, 2004). $NO_X$, unburned hydrocarbons, carbon monoxide and PM will be oxidised due to oxidation processes which happen by introducing plasma in the exhaust gas.

Applying pulsed power is one of the efficient ways to generate NTP. Pulsed power is the rapid release of stored energy in the form of electrical pulses into a load, which can result in delivery of large amounts of instantaneous power over a short period of time. Recently, solid-state pulsed power has gained more interest as it is compact, reliable, has a long lifetime and high repetition rate. In the last decade, research and studies established the advantage of using power electronics topologies in pulsed power applications (Davari et al., 2012c, Zabihi

et al., 2010). In this research a bipolar pulsed power supply based on push-pull topology is implemented.

Generally, a pulsed power supply is employed to generate NTP using a dielectric barrier discharge (DBD) reactor. A DBD is essentially a multilayer capacitor which has been extensively used for various applications (El-Deib et al., 2010, Tao et al., 2010, Rahmani et al., 2009, Takaki et al., 2004, Osawa and Yoshioka, 2012, Ghomi et al., 2011, Ayan et al., 2008, Piquet et al., 2010). Also it can be a packed bed DBD reactor (Yamamoto et al., 1999a, Rajanikanth and Rout, 2001, Ravi et al., 2003c, Rajanikanth and Ravi, 2002, Yamamoto et al., 2003b, Rajanikanth and Sushma, 2006, Srinivasan and Rajanikanth, 2007a, Srinivasan et al., 2009) or assisted by another catalyst or adsorbent (Yamamoto et al., 1999a, Ravi et al., 2003b, Rajanikanth et al., 2003, Rajanikanth et al., 2004, Rajanikanth and Ravi, 2004, Rajanikanth and Srinivasan, 2007, Srinivasan and Rajanikanth, 2007b, Srinivasan and Rajanikanth, 2007a, Rajanikanth et al., 2008, Rajanikanth et al., 2009). Here, a conventional DBD reactor with multipoint-to-plane geometry is developed.

Diesel particulate matter (DPM) consist mostly of carbonaceous soot with minor components of volatile organic fraction (VOF) from unburned fuel, lubricating oil, inorganic compounds such as ash and sulfur compounds and metals including zinc from lubricating oil (Stratakis, 2004b). DPM are the cause of a series of adverse effects on environment (Ramanathan, 2007 ) and human health (Seaton et al., 1995, Sydbom et al., 2001b, omers et al., 2004). Particulate formation begins with nucleation in the engine cylinder and dilution tunnel, and is followed thereafter by agglomeration (Majewski, 2002a). Most of the diesel particulate matter mass is in the accumulation mode, whereas in terms of particle number, most particles are found in the nucleation mode. More than 90% of diesel exhaust-derived PM is smaller than 1 μm in diameter (McClellan, 1989). Most of the mass is in the 0.1–1.0 μm "accumulation" size fraction, while most of the particle numbers are in the < 0.1 μm "nano-particle" fraction (Seinfeld, 1975, Kittelson, 1998a). Ultrafine particles have an aerodynamic diameter less than 100 nm and are emitted in high number by compression ignition engines. Whilst ultrafine particles do not contribute much to the total mass of particulate matter emitted from an engine, they contribute greatly to the total number of particles. The particle size distribution of particulate matter from compression ignition engines has become of increased concern since a study by the Health Effects Institute demonstrated an increased number of nanoparticles emitted from a 1991 Cummins engine, despite a reduction in overall particle mass, relative to an older 1988 Cummins engine (Majewski, 2002c).

Ultrafine particles can penetrate deep into the lungs where they are able to enter the bloodstream and even reach the brain (Zhua et al., 2007). The respiratory health effects (in particular asthma) from particle emissions correlate strongly with particle number, rather than particle mass emissions (Peters et al., 1997) . In 2014 the Euro VI regulation will be implemented and the number of particles emitted by compression ignition engines (in addition to a new particle mass limit) will be regulated. This demonstrates that particle number emissions are becoming a very prominent issue in engine design and research (Surawski et al., 2012, Ristovski et al., 2012).

The main concern of this paper is to analyse the effect of pulsed power on PM mass reduction and PM size distribution considering the pulsed power effects on ultrafine particles emitted from real diesel engine exhaust emission. In this research, a pulsed power supply based on the push-pull inverter is developed to generate up to 19.44 kVpp across the DBD load. The tests were conducted at different voltage levels with fixed repetition rate of 10 kHz. PM mass reduction, PM removal efficiency and PM size distribution are investigated by evaluating the results obtained.

## 4.2 EXPERIMENTAL METHOD

### 4.2.1 Experimental setup

A schematic diagram of the experimental setup is shown in Figure 4.1. Experiments were conducted on a modern turbo-charged 6-cylinder Cummins diesel engine (ISBe22031) at the QUT Biofuel Engine Research Facility (BERF). The engine has a capacity of 5.9 L, a bore of 102 mm, a stroke length of 120 mm, a compression ratio of 17.3:1 and maximum power of 162 kW at 2500 rpm. Particle number distributions are measured with a scanning mobility particle sizer (SMPS) consisting of a TSI 3080 classifier, which pre-selects particles within a narrow mobility (and hence size) range and a TSI 3025 condensation particle counter (CPC) which grows particles (via condensation) to optically detectable sizes. The SMPS software increases the classifier voltage in a pre-determined manner, so that particles within a 10-500 nm size range are pre-selected and subsequently counted using the CPC. The software also integrates the particle number distribution to enable calculation of the total number of particles emitted by the engine at each test mode. Each SMPS measurement takes 180 s and in this paper, the results are presented based on the average of three consequent measurements for each operating condition. Gaseous emissions are measured with CAI 600 series gas

analyses. $CO_2$, $NO_x$ and CO concentrations can be measured by this gas analyser, whereas particulate mass emissions are measured with a TSI 8530 Dust-Trak II.

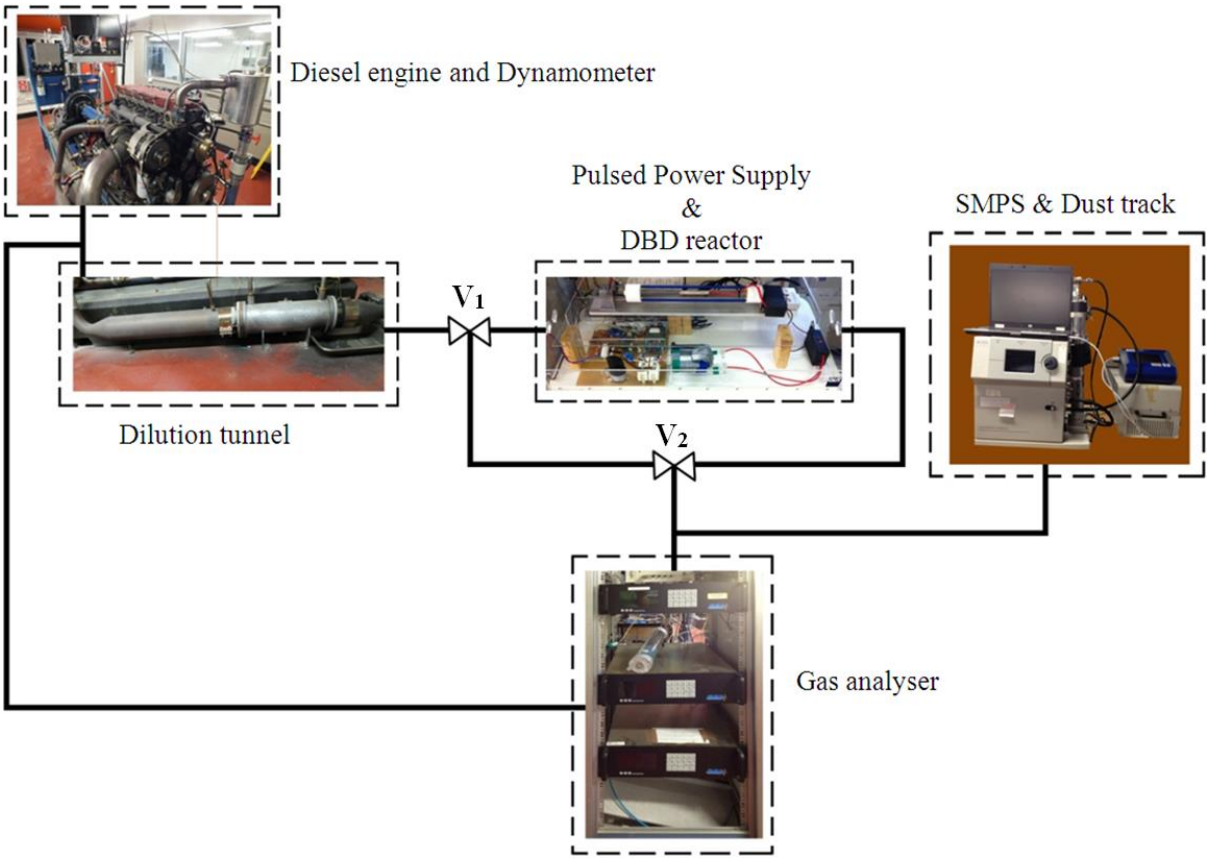



Figure 4.1: Schematic diagram of plasma treatment system developed at QUT engine lab

As depicted in Figure 4.1, three way-valves to control the exhaust path-ways are employed. With this configuration, it is possible to measure both gaseous emissions and particles before entering the reactor and after leaving it, by changing the three-way valve directions. $CO_2$ was used as a tracer gas in order to calculate the dilution ratio. $CO_2$ was measured from the dilution tunnel with dilution ratios being calculated using the following equation:

$$Dilution\ ratio = \frac{CO_{2,exhaust} - CO_{2,background}}{CO_{2,diluted} - CO_{2,background}} \qquad 4.1$$

Laboratory background $CO_2$ measurements were made before the commencement of each test session. Every concentration measured after dilution should be modified by using a dilution ratio. Based on the above formula, dilution ratio of about 11.5 has been calculated for these experiments.

### 4.2.2 DBD reactor

A conventional dielectric barrier discharge reactor was designed for the experiments. Figure 4.2 shows a schematic of the reactor. As illustrated in Figure 4.2, it consists of two concentric quartz tubes. Both tubes are 400 mm long and have a wall thickness of 1.5 mm. The outside diameters of inner and outer quartz tubes are 20mm and 25mm, respectively. Exhaust passes through the gap between these two quartz tubes. Based on pre-designed geometry, the discharge gap is 1 mm. The DBD is connected to the pulsed power supply using internal and external electrodes. The internal electrode is a copper cylinder and the external electrode is made by a copper coil that wraps the exterior part of the DBD. The electrodes are placed in the middle of the DBD load with a length of 100 mm. Both tubes are fixed by two Teflon caps at each end. DBD reactor was cleaned by using the compressed air before starting the experiments. Exhaust enters the reactor at the angle of 45 degrees and flows through the gap and leaves the reactor at the same angle. The exhaust flow rate passing through the DBD reactor was 9 L/min for all the experiments. The system has been precisely checked to avoid any leakage before starting the experiments. All instruments are calibrated based on their standard calibration protocols and all has been checked prior to each experiment to make sure the measurements are precise.

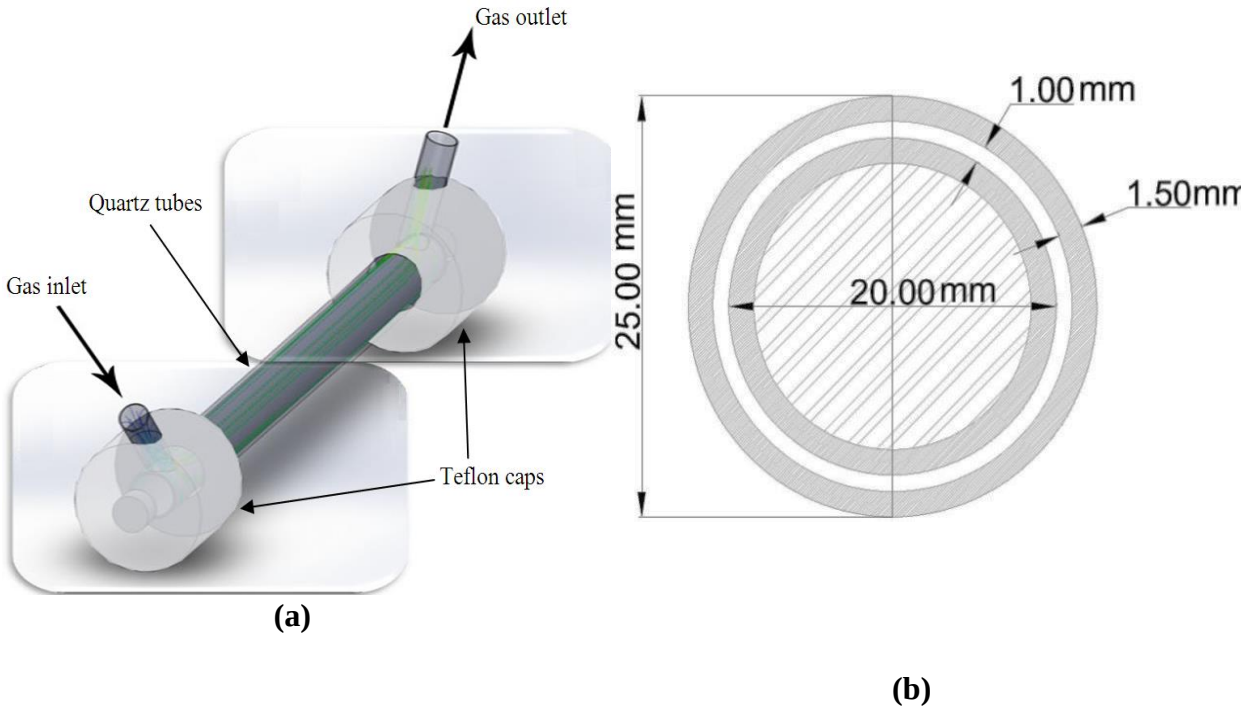



Figure 4.2: DBD reactor in Solidworks: a) schematic, b) cross-section

### 4.2.3 Bipolar pulsed power supply

Figure 4.3 shows a circuit schematic diagram of the pulsed power supply. As illustrated, it is based on the push-pull inverter topology. The push-pull inverter contains two switches that are driven with respect to ground. This is the main advantage of the inverter. This topology uses a centre-tapped transformer, which is excited in both directions. A step up transformer is used to boost the voltage and achieve galvanic isolation.

The main reason for using a push-pull topology is to generate bipolar output voltage. Applying voltage periodically builds-up charges across the electrodes, which can result in arcing. In order to sustain the non-thermal plasma and prevent it from arcing, bipolar pulse generation can be employed for clearing charges [50]. Employing a lower number of switches is another advantage of the push-pull inverter. The two switches $S_1$ and $S_2$ are switched alternately with a controlled duty ratio to convert input DC voltage into high frequency AC voltage, suitable for exciting the DBD load. Hence, the generated output voltage is bipolar.

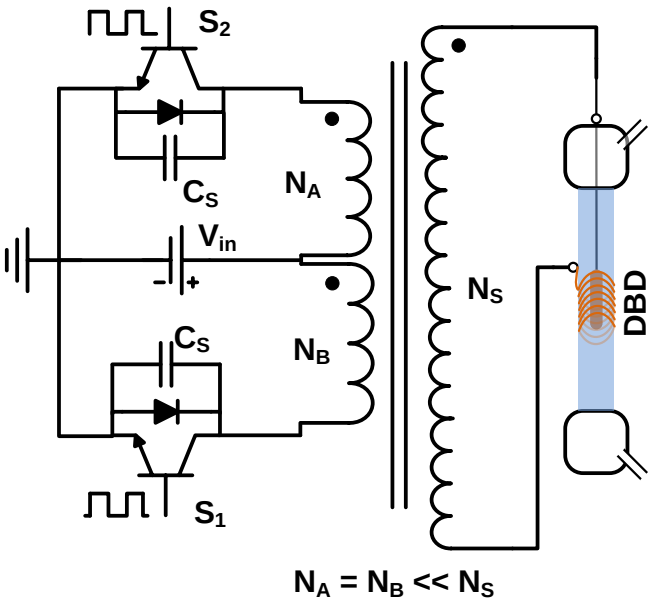



Figure 4.3: Pulsed power supply circuit schematic diagram (push-pull inverter)

Adding a DBD load turns the push-pull inverter into a resonant stage with approximately sinusoidal output. The frequency of the semi-sinusoidal shape signal is determined by an L-C circuit, comprised of the transformer inductance and capacitances of DBD and the transformer. The repetition rate can be used to adjust the power, and by optimising the resonance it is possible to obtain a high frequency, semi-sinusoidal waveform.

A typical measured output voltage of the employed pulsed power supply is depicted in Figure 4.4.

The first portion of the output voltage waveform is the resonant circuit dominated by the magnetising inductance of the transformer and the capacitances of the transformer and DBD. The period of this signal is approximately 11.2 µs. The second one is the resonance happening during the switches' off-state, between the leakage inductance and the capacitances of the transformer and DBD. The period of this signal is equal to 34.8 µs. As can be seen from the figure, the repetition rate is set to 10 kHz. It is quite important to generate a symmetrical waveform for clearing charge purpose and avoiding transformer saturation.

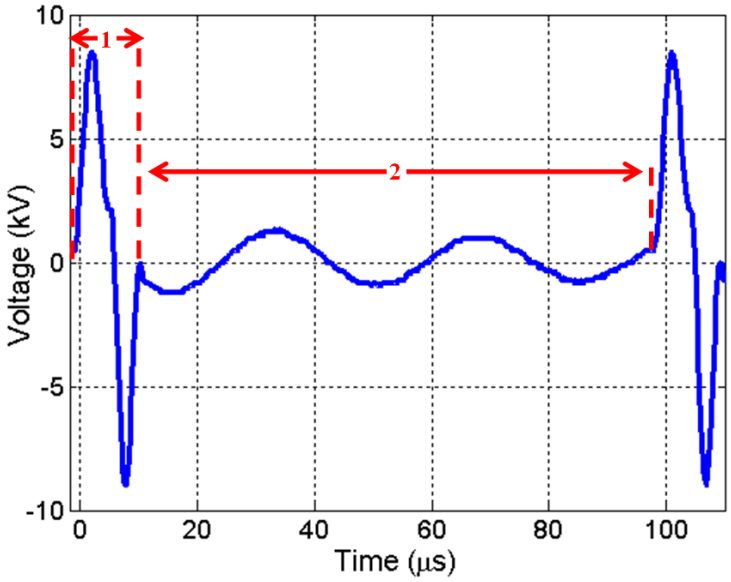



Figure 4.4: A typical measured output voltage of the employed pulsed power supply

Figure 4.5 shows the experimental hardware setup for the pulsed power supply. Here, 1200V IGBT modules, SK75GB123, are used as power switches. Semikron Skyper 32-progate drive modules are utilised to drive the IGBTs and provide the necessary isolation between the switching-signal ground and the power ground. A Texas Instrument TMS320F28335 DSC (Digital Signal Controller) is used for PWM signal generation. A centre-tapped step-up transformer with a UU100 core 3C90 grade material ferrite from Ferroxcube, is designed with $N_A = N_B = 5$ and $N_S = 293$. Here, a 470 pF capacitor ($C_S$) is placed across each switch to protect them against the voltage spikes. The output voltage is measured and captured using a Pintek DP-22Kpro differential probe and RIGOL DS1204B oscilloscope, respectively.

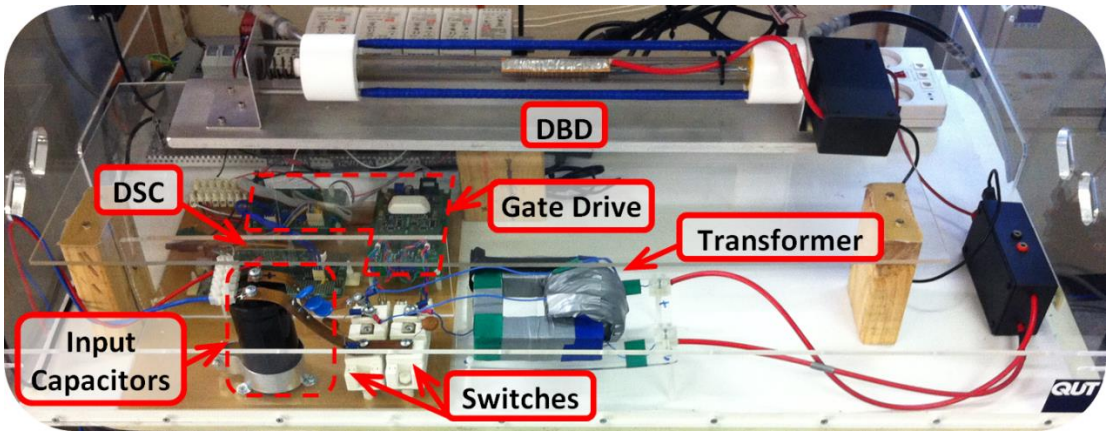



Figure 4.5: Electrical Hardware setup with the DBD load

## 4.3 RESULTS AND DISCUSSION

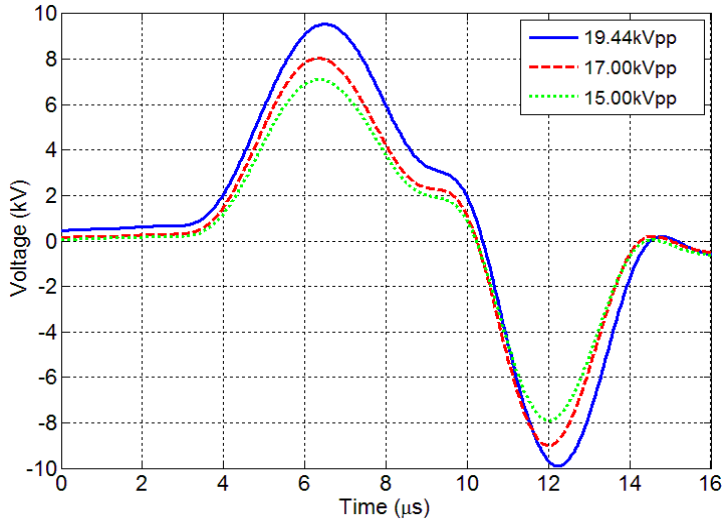
### 4.3.1 Plasma effect on PM size distribution

The effect of plasma on emission treatment is considered for various experiments based on the aforementioned Cummins diesel engine. In all experiments, engine speed and load are kept constant at 40 kW (25% load) and 2000 rpm, respectively. A portion of raw exhaust directly from an iso-kinetic sampling port of the tailpipe was diluted with air and passed through the reactor. Emission concentration is measured before and after applying the pulse to study the plasma effects. In addition, the median particle diameter, which is another useful parameter used to study the effect of the plasma technique, is also measured. It is to be noted that all illustrated results in each experiment have been obtained as an average over three consecutive measurements.

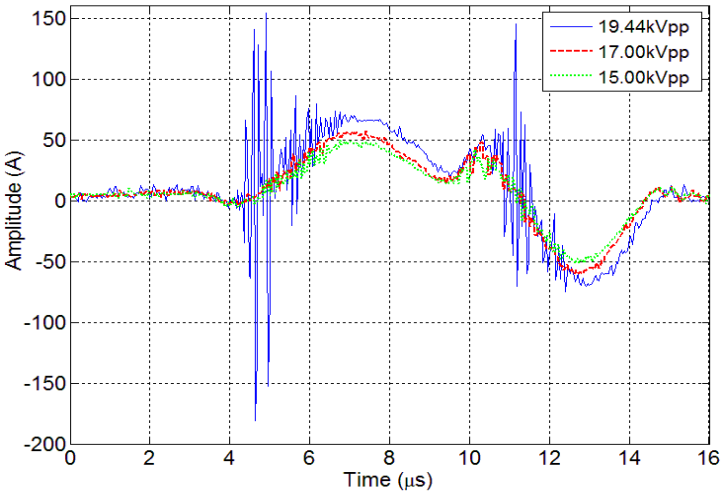
The experiments were made by applying output voltage from 10 kVpp up to 19.44 kVpp. However, the first effects of plasma appeared at 15 kVpp, following with optimum operation at 17 kVpp and finally a high amount of small particle generation at 19.44 kVpp. Hence, the measurements are reported in this section regarding the mentioned three applied voltage levels. Figure 4.6 illustrates the measured results. The applied output voltages across the DBD load for three different voltage levels of 15 kVpp, 17 kVpp, and 19.44 kVpp are depicted in Figure 4.6A. As shown in this figure, at the beginning both switches are turned off and they are switched alternately during the experiments. When one of the switches is turned on, the voltage and consequently the current started to increase. The measured output voltages show the rate of voltage rise of 2840 V/µs. After about 10 µs, the first switch is turned off and the second one will change to on. The measured load currents are illustrated in Figure 4.6B, which shows many narrow pulsed current spikes occurring in each

half-cycle of the applied voltage. The measured current at 19.44 kVpp, compared with the other applied voltages, shows higher number of the micro-discharges in the gap with much higher amplitude. This is due to the fact that the applied voltage has reached the value of the breakdown voltage, which depends on the gap distance, dielectric material, repetition rate, etc. Controlling the amplitude of current discharges is quite important as it can directly affect the plasma reaction, which will be discussed later. Figure 4.6C shows the voltage stress across the switch during the switching transition. As can be seen, due to employing a centre-tapped transformer, the peak-to-peak voltage stress across the switch in a push-pull inverter is approximately twice the input voltage.

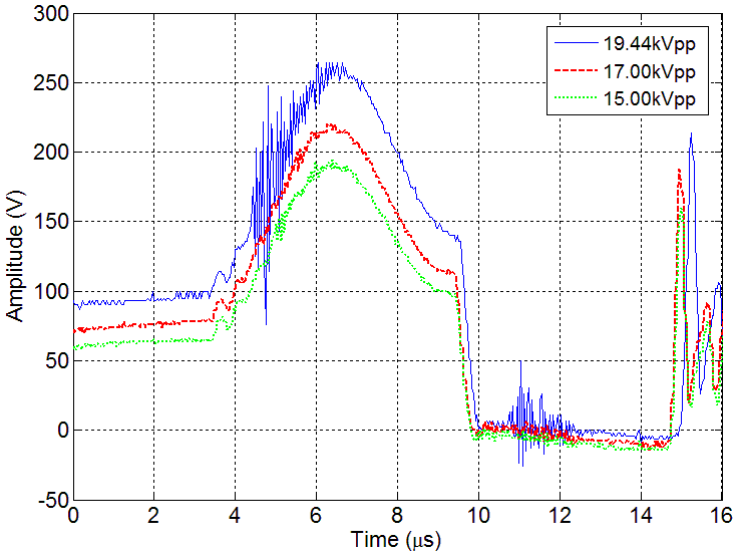
In these experiments, the output voltage amplitude is controlled by changing the input DC voltage between 72.4 V, 84.4 V, and 94.8 V. Under the same conditions, Figure 4.7 shows an image of DBD recorded at 19.44 kVpp. As can be seen, NTP is clearly occurring between the two electrodes.




(A)




(B)




(C)

Figure 4.6: The measured electrical parameters: A) output voltages across the DBD load, B) output current, and C) voltage stress across the switch

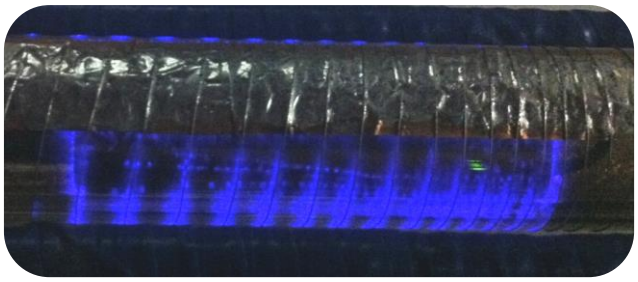


Figure 4.7: DBD image

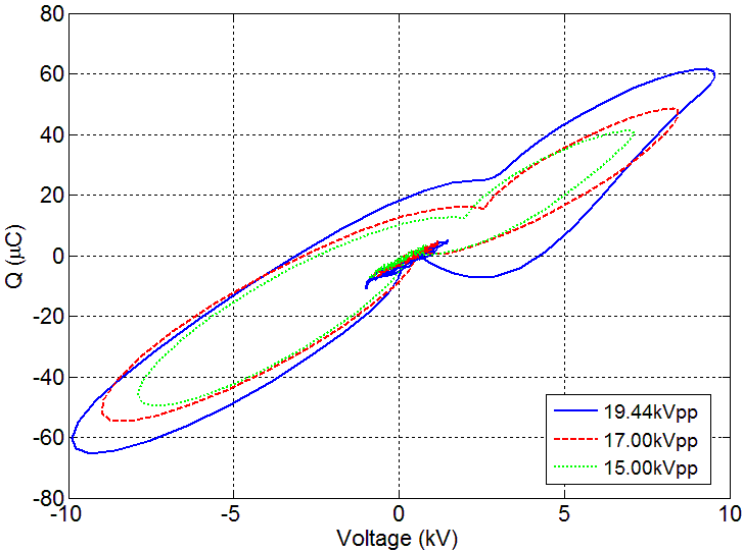



Figure 4.8: V-Q cyclogram of the DBD load as a basis of power consumption calculation

To measure the power consumption of the DBD load, the energy transferred to the DBD load has been calculated by employing the Lissajous (V−Q) diagram (Kriegseis et al., 2011, Mildren and Carman, Jan. 2001).To measure Q, a 4nF capacitor is placed in series with the DBD reactor. Thus, by measuring the voltage across the capacitor and multiplying it by its capacitance value, it is possible to calculate Q. The energy consumed by the DBD reactor for one cycle is calculated from the area of V−Q curve for different experiments, where V is the measured voltage across the DBD reactor (see Figure 4.8). Hence, by considering the employed repetition rate (frequency) it is possible to calculate the average consumed power by the DBD load. It is to be noted that the series connected capacitor is selected large enough so as not to affect the DBD reactor capacitance. The relevant equations are:

$$W = \oint Q(t)dv \tag{4.2}$$

$$C(t) = \frac{dQ(t)}{dV(t)} \tag{4.3}$$

By substituting 4.3 in 4.2:

$$W = \oint \frac{Q(t)}{C} dQ = \frac{1}{2} CV^2 \tag{4.4}$$

Therefore, considering 4.2 to 4.4 the averaged consumed power can be calculated as below:

$$P_A = f \times W = f \oint Q(t)dv = f \frac{1}{2} CV^2 \tag{4.5}$$

The illustrated data in Figure 4.8 clearly indicate that the DBD reactor power consumption correspondingly increases with the applied voltage level. This can be also realised from Eq. 4.5, which shows the relation between the power and the applied voltage. The calculated averaged power consumption ($P_A$) for the applied voltages of 15 kVpp, 17 kVpp, and 19.44 kVpp are 27.37 W, 36.54 W, and 55.17 W respectively. The higher averaged power at 19.44 kVpp can be realised through the measured discharged current as it has occurred at higher amplitude and higher number of the micro-discharges.

In the first experiment, the maximum voltage level (19.44 kVpp) is applied. To estimate the deposition rate on the reactor surface, emissions in the reactor inlet (reactor inlet no pulse) and reactor outlet (reactor outlet no pulse) without applying any pulse voltage are measured. Finally, the pulsed power supply is applied across the DBD and the emissions in

reactor outlet are measured (reactor outlet with pulse). The same process is employed in all the following experiments.

Figure 4.9 illustrates the particle size distribution at 19.44 kVpp. There is a considerable amount of PM deposition on the reactor surface, which is likely related to the small gap between the tubes (1 mm). The median diameter in the reactor inlet is 70 nm, while in the reactor outlet, it is decreased to 66 nm. This shows that larger particles are deposited more on the reactor surface. By applying pulsed power, as shown in this figure, the median diameter decreases remarkably to 35 nm. This implies that lots of big particles have been oxidised or broken into small particles by producing plasma inside the exhaust emissions at this voltage level.

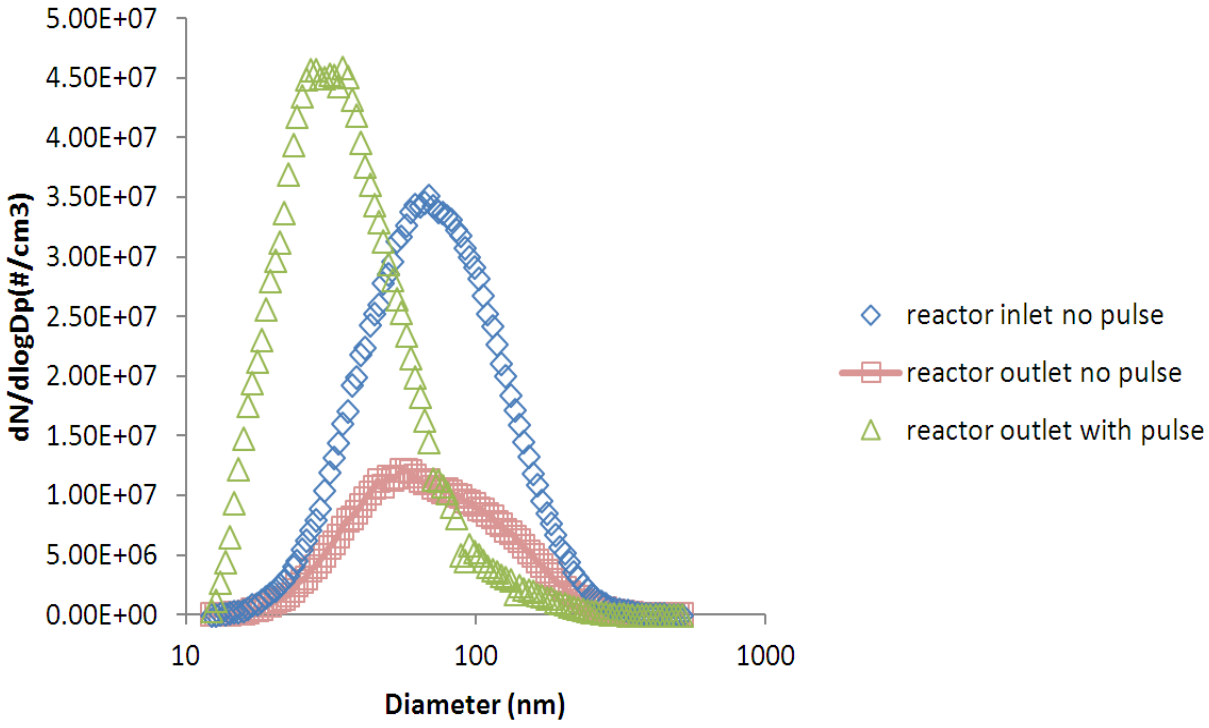



Figure 4.9: Particle Size Distribution (2000 rpm, 25% Load, 19.44 kVpp)

The peak value of particle number at the reactor inlet is around $3.5\times10^{7}\ particle/cm^{3}$. This value declines to $1.2\times10^{7}\ particle/cm^{3}$ at the reactor outlet due to deposition. By applying pulsed power, the graph peaks to $4.5\times10^{7}\ particle/cm^{3}$, which is approximately four times bigger than the particle number at the reactor outlet without any pulse. The number of particles with a diameter of less than 70 nm in the reactor outlet with applying pulse is higher than the particle numbers at the reactor outlet without any pulse. This effect increases even more at particle diameters less than 50 nm. At this level, the particle number at reactor outlet

surpasses the number of particles at reactor inlet. These findings imply that the 19.44 kVpp pulse power at 10 kHz, increases the number of small particles considerably. The origin and nature of these particles is still not clear and will be of interest in future investigations. However, the effect of 19.44 kVpp on particle size can be understood, with regard to the high level of micro-discharges in the discharged current, as depicted in Figure 4.6B.

The effect of voltage level with 17 kVpp is considered in the second experiment. The results obtained have been summarised in Figure 4.10. The figure shows the median diameter changes from 70 nm at reactor inlet to 78 nm at reactor outlet without any pulse, and then falls to 75 nm at reactor outlet with applying pulse. This shows that the larger particles are deposited and also removed by plasma selectivity compared to smaller particles. As can be seen, at this voltage level (17 kVpp) the number of small particles has not increased. This is an important feature when compared with the previous experiment (19.44 kVpp).

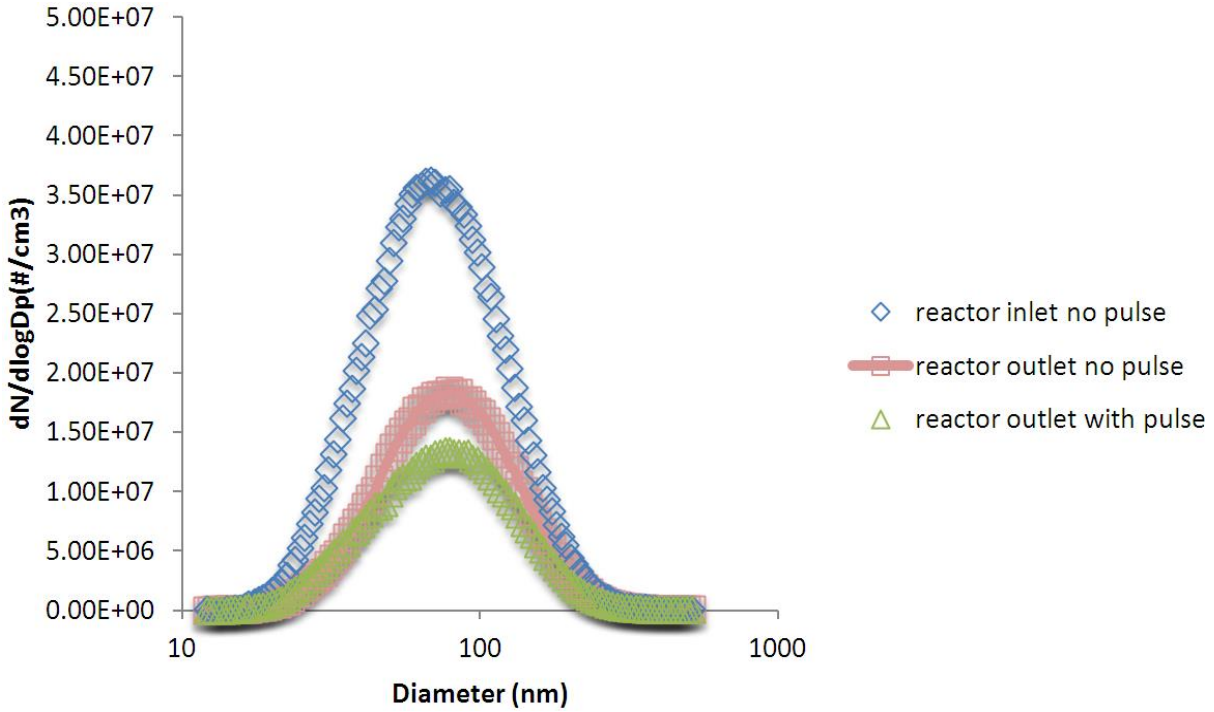



Figure 4.10: Particle Size Distribution (2000rpm, 25% Load, 17 kVpp)

The last experiment is conducted by applying 15 kVpp pulses. The measured results are depicted in Figure 4.11, which shows no growth in the number of small particles same as the second experiment (17 kVpp). The maximum of PM concentration took place at around 71 nm. There is a small difference between PM concentrations with and without applying plasma. Therefore, this level of voltage can remove particles at the same rate of deposition.

Comparing the values of median diameter in the reactor inlet and outlet shows that the smaller particles are more likely to be deposited inside the reactor under the no pulse condition. On the other hand, by applying the pulse, the median diameter is in the same range as the reactor inlet. There is no increase in the number of small particles at this voltage level. This trend in median diameter variation is almost in complete agreement with the voltage of 17 kVpp.

Careful comparison of the reactor outlet particle size distribution when there is no pulse, indicates that the distribution in Figure 4.9 shows a reduction in particle median diameter, whereas Figure 4.10 shows a slight increase in particle median diameter. Experiments for Figure 4.10 were conducted approximately 30 min after that for Figure 4.9. Therefore, there is a possibility that wall initial deposition occurred with larger particles; the later experiments for Figure 4.10 favoured slightly smaller particles due to the larger surface area of the wall and the attraction of particles to deposited particles, rather than the quartz wall alone.

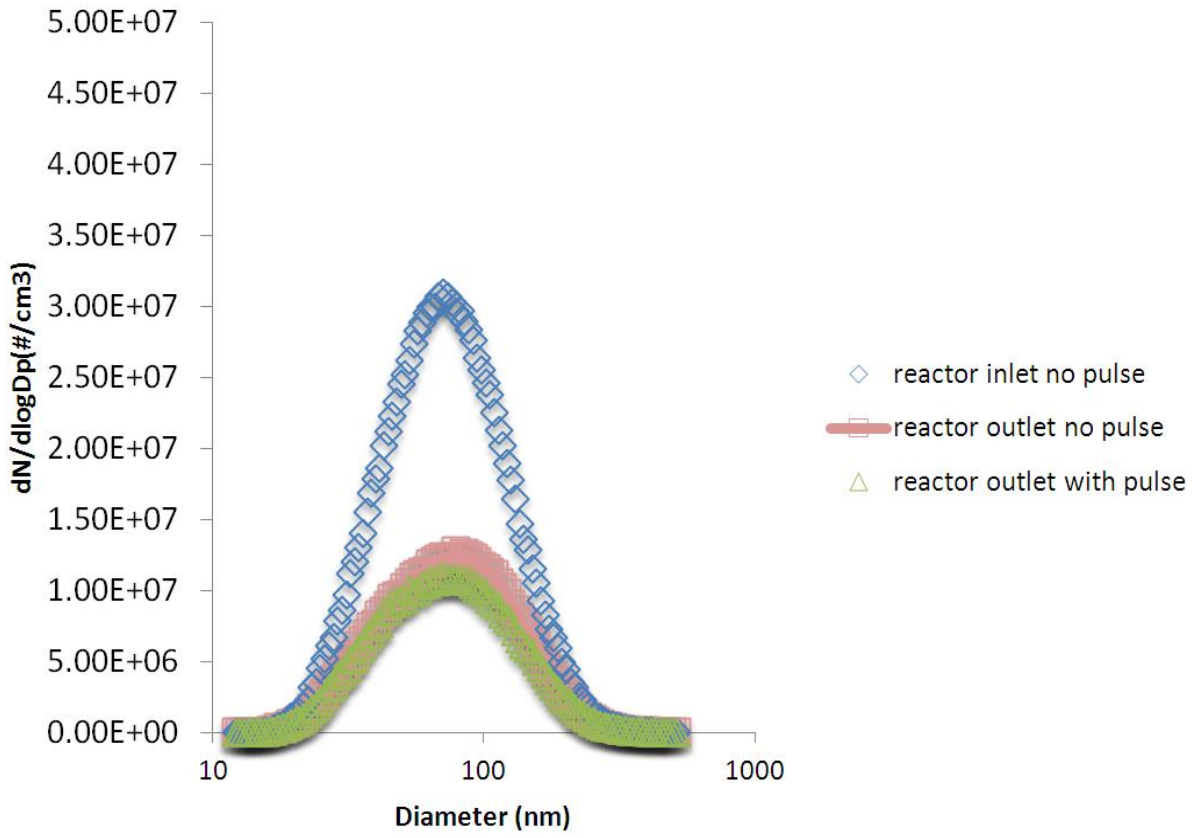



Figure 4.11: Particle Size Distribution (2000 rpm, 25% Load, 15 kVpp)

### 4.3.2 PM removal efficiency

PM removal can be calculated based on the following equation:

$$PM\ removal = \frac{inlet\ PM\ concentration - outlet\ PM\ concentration\ (with\ pulse)}{inlet\ PM\ concentration} \times 100 \qquad 4.6$$

Where the PM concentration unit is (particle/cm$^3$) and PM removal is calculated for all PM diameters. This equation has been used for calculation of PM removal efficiency when the PM concentration at reactor inlet is greater than the outlet. Figure 4.12 illustrates the PM removal at 19.44 kVpp. PM deposition on the reactor surface increases with the PM size and gets to the maximum value of 70% removal at around 80 nm. But after 80nm, PM removal decreases again. For most of the particle sizes, PM deposition on the reactor surface is more than 40%. When a 19.44 kVpp voltage is applied to the reactor, PM removal efficiency reaches the value of 90% for larger particles. Removal efficiency for particulate matter less than 80 nm is less than PM removal without applying any pulse. This indicates undesirable operation of the plasma within this particle size range. Also, there is no removal for particles smaller than 50 nm. There is a high possibility that this increase in particle numbers can be related to the following two factors: firstly, fragmentation of larger particles by electron impact reactions or incomplete oxidation and secondly, oxidation of gaseous exhaust emissions to particles by plasma generated ozone.

Figure 4.13 shows the PM removal at 17 kVpp, which shows that PM removal by plasma is more effective than deposition removal. This means that at this level of voltage, all deposited particles and also some large particles inside the flow can be removed or oxidised. For particles smaller than 35nm, PM removal percentage by deposition is higher than PM removal by plasma. Apparently, smaller particles cannot be removed by plasma within this range (< 35 nm). However, another possibility can be dissociation of larger particles to smaller ones by electron impact reactions.

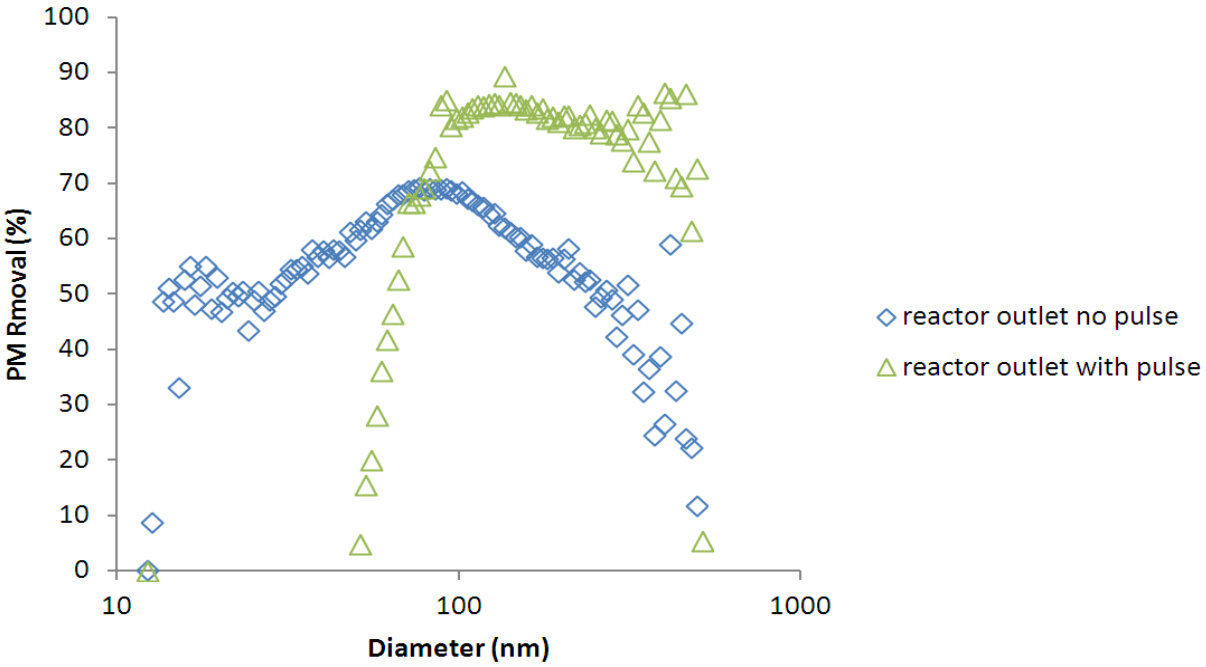



Figure 4.12: PM removal as a function of PM size (2000 rpm, 25% Load, 19.44 kVpp)

PM removal efficiency at 15 kVpp is illustrated in Figure 4.14. As can be seen, the PM removal for both graphs increases to an optimum value and then decreases. The maximum PM removals in the reactor outlet with and without the pulse are 61% and 69% respectively. For particles larger than the 60 nm diameter, PM removal when applying pulse voltage is slightly higher than PM removal without any pulse. However, for particles with smaller diameters, these values are in the same ranges.

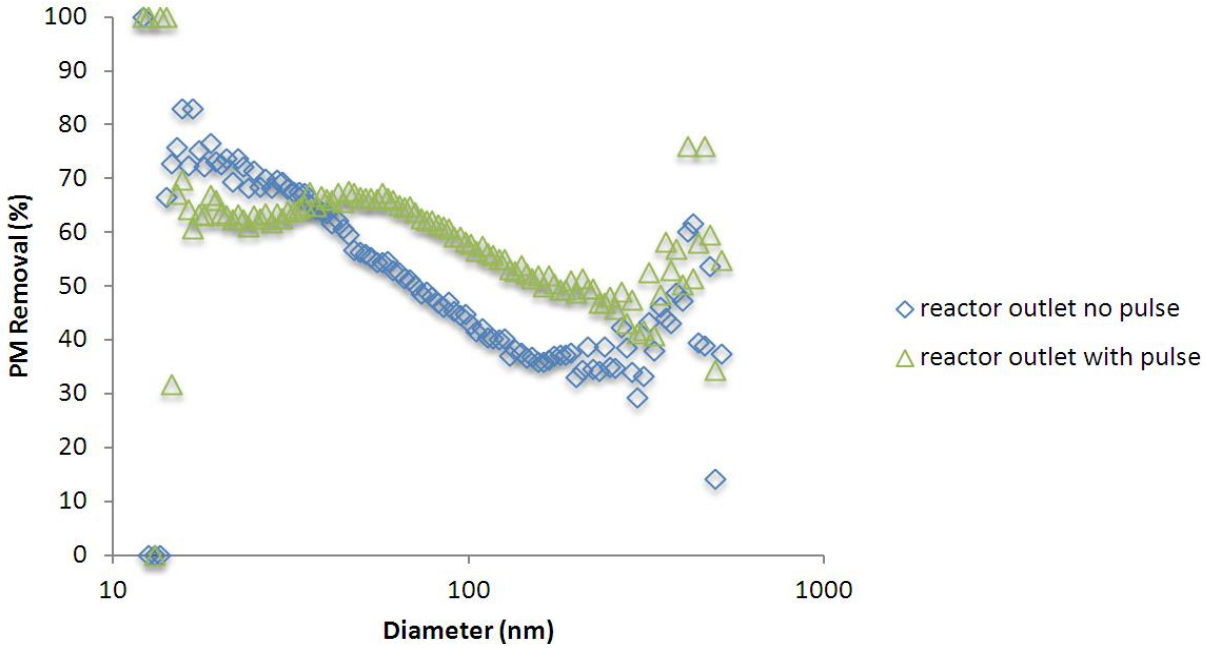



Figure 4.13: PM removal as a function of PM size (2000 rpm, 25% Load, 17 kVpp)

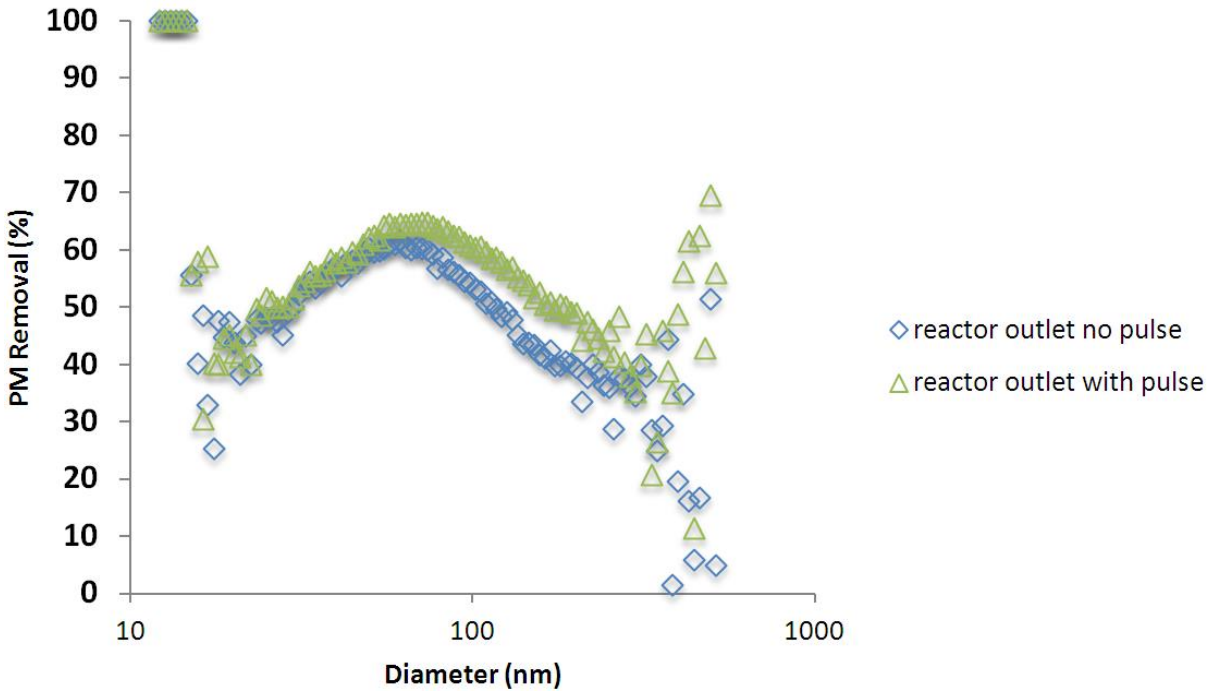



Figure 4.14: PM removal as a function of PM size (2000 rpm, 25% Load, 15 kVpp)

Regarding the results obtained, it can be concluded that the voltage level has an important role in size dependent removal efficiency. At 15 kVpp, the particle size distribution has been affected slightly. The PM removal without producing small particles can be improved as the voltage increases to 17 kVpp. The increase in the number of small particles has been noticed when the voltage level goes up to 19.44 kVpp, while larger particles have been reduced considerably. By taking into account all the above mentioned features, the 17 kVpp experiment shows better efficiency in terms of particle size distribution for the given configuration.

### 4.3.3 Plasma effect on PM mass reduction

After studying the effect of different voltages on particle size distribution, in this section, the effect of plasma on particle mass reduction is considered. In a similar way to the previous sections, three different voltage levels have been applied to the DBD load. All results obtained have been summarised in Table 4-1. PM mass concentrations in the reactor inlet were 4.56 mg/m$^3$, 4.26 mg/m$^3$ and 5.14 mg/m$^3$ respective to the variation of engine operating conditions for the three tests conducted. These values decreased to 2.48 mg/m$^3$, 3.68 mg/m$^3$ and 4.37 mg/m$^3$ at the reactor outlet in the no pulse condition, respectively. This shows a significant particle deposition inside the reactor. When the pulsed power is applied,

plasma PM removal occurrs. This causes the PM mass concentration reduction of 43.9%, 38.6% and 27.1% at 19.44 kVpp, 17 kVpp and 15 kVpp respectively.

Table 4-1: PM Mass Reduction at Different Voltage Levels

| **Applied Voltage / Measurement** | **19.44 kVpp** | **17 kVpp** | **15 kVpp** |
|---|---|---|---|
| **Reactor Inlet PM Concentration (**$mg/m^3$**)** | 4.56 | 4.26 | 5.14 |
| **Reactor Outlet No Pulse PM Concentration (**$mg/m^3$**)** | 2.84 | 3.68 | 4.37 |
| **Reactor Outlet By-Pulse PM Concentration (**$mg/m^3$**)** | 2.56 | 2.62 | 3.74 |
| **Plasma PM Mass Removal Efficiency (%)** | 43.9 | 38.6 | 27.1 |

The maximum PM mass reduction has been obtained when the voltage level is 19.44 kVpp. However, according to the particle size distribution measurements, this voltage level increases the number of small particles, which is not a desirable feature. The 17 kVpp applied voltage shows a more suitable performance with good mass reduction of around 40% without any increase in ultrafine particle numbers. The 15 kVpp voltage level is found to be almost the threshold breakdown voltage for the given configuration, below which there is no significant PM mass reduction, PM removal, and PM size distribution, all of which have not been affected too much.

## 4.4 CONCLUSION

In this study the effect of non-thermal plasma, obtained by applying high voltage pulses on PM size distribution and PM mass reduction, was investigated. It was found that NTP plasma not only affects the PM mass concentration, but also changes the PM size distribution. At very high voltage levels (here 19.44 kVpp), NTP was very effective for PM mass reduction. However, PM mass reduction is not the only concern. It became clear that at high

voltage levels, the number of ultrafine particles increases significantly. Regarding the negative health effects of tiny particles, the performance of plasma at such high voltage levels is not desirable. Considering the PM mass reduction and PM size distribution simultaneously, an optimum voltage level of 17 kVpp at 10 kHz was found for the given configuration and operating condition. Moreover, the wall attachments of particulates are another important parameter, which should be considered in all experiments. It was found that wall attachments are variable even without introducing any plasma. Therefore, particle deposition inside the reactor and its effect on plasma PM removal should be considered in more detail in the future.

# Chapter 5: Study of particulate matter removal mechanism by using non-thermal plasma technology

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Publication: ICESP 2013-XIII International Conference on Electrostatic Precipitation being held in Bangalore, India.

**Author Contribution**

| Contributor | Statement of Contribution |
|---|---|
| M. Babaie<br>Signature | Conducted the experiments, performed the data analysis and drafted the manuscript |
| P. Davari | Assisted with conducting the experiment and revised the manuscript |
| P. Talebizadeh | Assisted with preparing the manuscript |
| Z. Ristovski | Supervised the project, aided with the data analysis and development of the paper |
| H. Rahimzadeh | Supervised the project and aided with the development of the paper |
| R.J. Brown | Supervised the project, aided with the data analysis and development of the paper and extensively revised the manuscript |

**Principal Supervisor Confirmation**

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

| Name | Signature | Date |
|---|---|---|
| Associate Professor Richard Brown | R. J. Brown | 30/09/2014 |


**Abstract**

The number of diesel engines in both stationary and mobile applications today is steadily increasing. Diesel engines emit lower hydrocarbon (HC) and carbon monoxide (CO) than gasoline engines. However, they can produce more nitrogen oxides ($NO_x$) and have higher particulate matter (PM). On the other hand, emissions standards are getting more stringent day-by-day, due to considerable concerns about unregulated pollutants and most particularly, the deleterious effect of ultrafine particles on human health. Non-thermal plasma (NTP) treatment of exhaust is known as a promising technology for both $NO_x$ and PM reduction by introducing plasma inside the exhaust emission. Vehicle exhaust emissions undergo chemical changes when exposed to plasma. In this study, the PM removal mechanism, using NTP by applying high voltage pulses of up to 20 $kV_{pp}$ with a repetition rate of 10 kHz, are investigated. It is found that voltage increase does not necessarily have a positive effect on PM removal in diesel engine emissions.



**Keywords:** Non-thermal plasma, Particulate matter removal, Dielectric barrier discharge, Pulsed power supply

## 5.1 INTRODUCTION

Diesel engines have been employed in a variety of industries and their applications are growing rapidly. Despite the large number of diesel engine applications, little has been done to reduce the large amounts of pollutants caused by diesel engines. According to the negative effects of $NO_x$ and PM on health, governmental legislations for permissible exhaust emission standards are becoming more and more stringent day-by-day.

Up to now, several technologies have been applied for $NO_x$ and particulate treatment of diesel engines. For example, the selective catalyst reduction (SCR) method is one of the common technologies for $NO_x$ reduction of automobile and stationary engines (Narula et al., 2005). There are some problems in using SCR catalysts, such as the possibility of ammonia leakage, catalyst poisoning, catalyst discharge under high temperature condition or under the influence of sulphur, and the need for construction of urea solution stations. Diesel particulate filters (DPF) have been used widely for particulate matter removal in diesel engines (Johnson, 2012). However, there are some drawbacks in using DPF, such as pressure drop inside the exhaust due to the PM deposition. This deposition can cause filter choking so filter regeneration at a high temperature of about $600^{\circ}C$ is required. These effects cause more fuel consumption, which is not appropriate for emission production and fuel economy.

The electrical discharge plasma technique appears to be a very promising method for both $NO_x$ and PM reduction (Thomas et al., 2000b). It is composed of free electrons, ions, radicals, atoms, and molecules in various states of excitation. In non-thermal plasma, the majority of electrical energy goes into the production of high-energy electrons rather than into gas heating (Penetrante, 1994). The discharge achieves non-thermal conditions through the production of short-lived micro discharges. The short lifetime of the micro-discharges is achieved by applying very-short high-voltage pulses (Yan et al., 1998). The intent of using non-thermal plasma is to selectively transfer the input electrical energy to the electrons, which would generate free radicals through collisions and promote the desired chemical changes in the exhaust emission (Majewski, 2004). In other words, when plasma is introduced in the exhaust, oxidation processes will be started. $NO_x$, unburned hydrocarbons, carbon monoxide and particulate matter (PM) will be oxidised. In spite of $NO_x$ reduction to $N_2$ and $O_2$, plasma treatment of exhaust emissions is more related to NO oxidation to $NO_2$ (Rajanikanth et al., 2004). The plasma is believed to show potential to improve catalyst selectivity and removal efficiency. Moreover, plasma can oxidise PM in diesel exhaust emissions.

The majority of studies in this area are related to the effect of plasma on $NO_x$ removal (Mohapatro and Rajanikanth, 2010, Vinh et al., 2012c, Jolibois et al., 2012b). However, PM removal

efficiency of plasma has not been fully investigated. In 2000,Thomas et.al (Thomas et al., 2000b), considered NTP for emission treatment of exhaust. They used a packed bed reactor and found that by increasing the residence time selectively, when using a packing material into the NTP reactor, the level of oxidation of species may be decoupled from the energy deposition into the exhaust. Their packed plasma system removed 99.9% of PM of average diameters around 60 nm. Ye et al. (Ye et al., 2005) used a plasma reactor with a catalyst to treat exhaust emission from a gasoline engine to reduce PM emissions. In their experiments, they considered PM diameter ranges of 0.3 to 5 μm in a discrete manner. Their results indicated that PM removal efficiency ranged approximately from 25 to 75%. Suzuki et al. (Suzuki et al., 2008) used carbon black particles (CBP) to simulate the diesel engine particles in their experiments. They could remove about 80% of the CBP by introducing plasma. Song et al. considered the PM, hydrocarbons (HC) and $NO_x$ abatement characteristics in 2009 (Song et al., 2009). They studied the effect of peak voltage, frequency and engine load on contaminant removal by using a dielectric barrier discharge (DBD) reactor consisting of two concentric quartz tubes. They showed that by increasing voltage at each frequency level, discharge power increases. But there is an optimum for frequency of about 15.5 kHz regarding the discharge power. They found PM, HC and $NO_x$ abatements obviously increase with an increase in the applied voltage. Approximately for all voltage levels, the maximum of discharge power and consequently maximum of removal efficiency was obtained at about 15 kHz. In 2010 Okabo et al. (Okubo et al., 2010a) used packed pellets of $BaTiO_3$ for simulation of non-thermal plasma for PM and $NO_x$ removal. They confirmed that carbon soot is removed under oxygen poor conditions and simultaneous removal of PM and $NO_x$ happened.

The aim of this paper is to study the effect of NTP on the PM removal mechanism from the exhaust gases of a real diesel engine. In this regard, the hypothesis of gas to particle change by using NTP technology was evaluated. Regarding the PM after treatment systems, PM mass reduction and PM size distribution was considered simultaneously. The experiments are conducted using a DBD reactor, which has been designed and fabricated for this purpose. Employing a pulsed power supply developed based on the power electronics technology (Davari et al., 2012a, Davari et al., 2012b, Davari et al., 2012c), provided the ability to sustain NTP with-in the DBD reactor and the possibility of applying different voltage levels (Babaie et al., 2013b).

## 5.2 EXPERIMENTAL SETUP

A dielectric barrier discharge reactor was designed for the experiments. It consists of two concentric quartz tubes. Both tubes are 400 mm long and have a wall thickness of 1.5 mm. The outside diameter of the inner and outer quartz tubes are 20mm and 25mm respectively. Diesel

exhaust passes through the gap between these two quartz tubes. Based on pre-designed geometry, the discharge gap will be 1 mm. The internal electrode is a copper cylinder and the external electrode is made by a copper coil that wraps the exterior part of the DBD. The discharge length for primary experiments was 100 mm. Figure 5.1 shows the designed reactor and employed pulsed power supply (Babaie et al., 2013b). By applying high voltage pulses (see Figure 5.2), plasma discharge will happen between these two electrodes. The dielectric has two functions of limiting the charge transferred by an individual

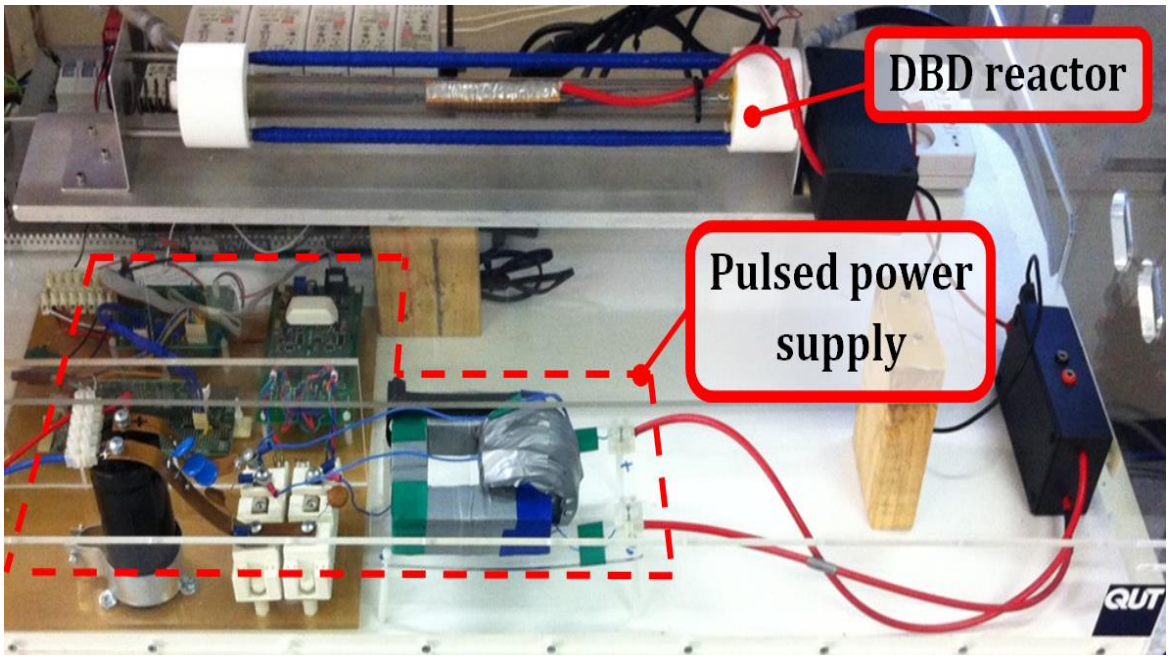


Figure 5.1: Plasma reactor and electrical setup

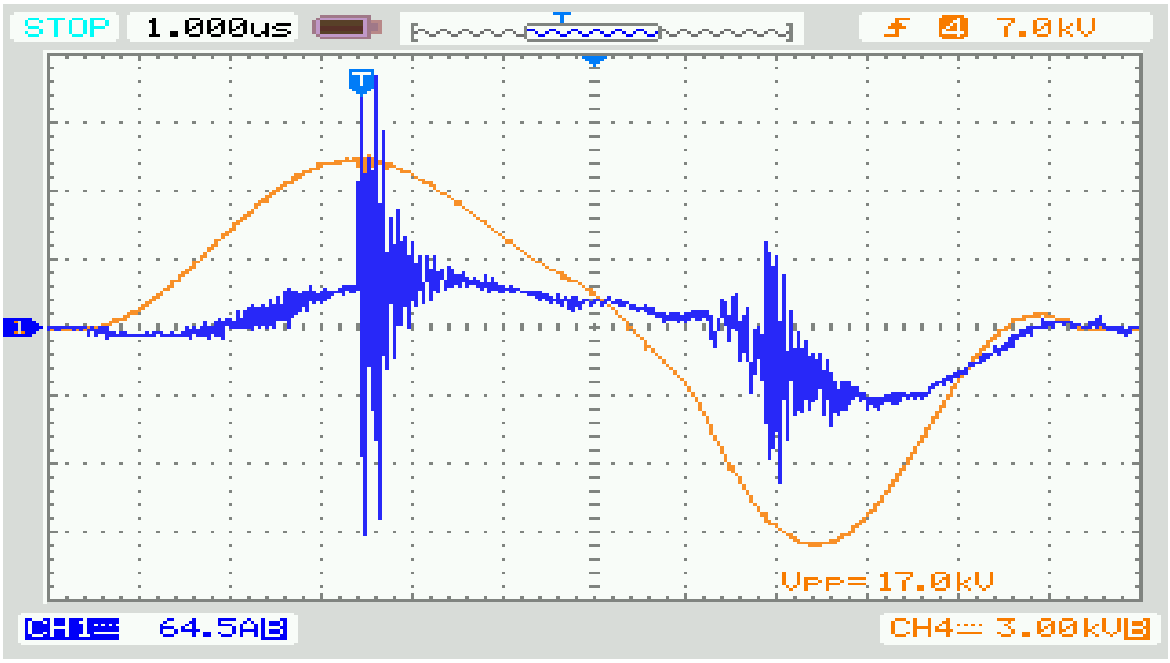


Figure 5.2: Typical measured waveforms of pulsed voltage and current of the DBD reactor

micro-discharge and spreading the micro-discharge over the electrode surface tube (Eliasson et al., 1987). Both tubes are fixed by two Teflon caps at each ends and exhaust enters the reactor by the angle of 45 degree and flow throughout the gap and leave the reactor with same angle.

A schematic diagram of the experimental setup is shown in Figure 5.3. Experiments were conducted on a modern turbo-charged 6-cylinder Cummins diesel engine (ISBe220 31). A pulsed power supply is used to induce high voltage between the two dielectric layers. The applied voltages are in 15-20 $kV_{pp}$ range at frequency of 10 kHz. When the breakdown voltage is reached a discharge will be started and ionisation occurs and an electrical current starts flowing into the gas.

Particle number distributions are measured with a Scanning Mobility Particle Sizer (SMPS) consisting of a TSI 3080 classifier, which pre- selects particles within a narrow mobility. Gaseous emissions are measured with CAI 600 series gas analyser and particulate mass emissions are measured with a TSI 8530 Dust-Trak II.

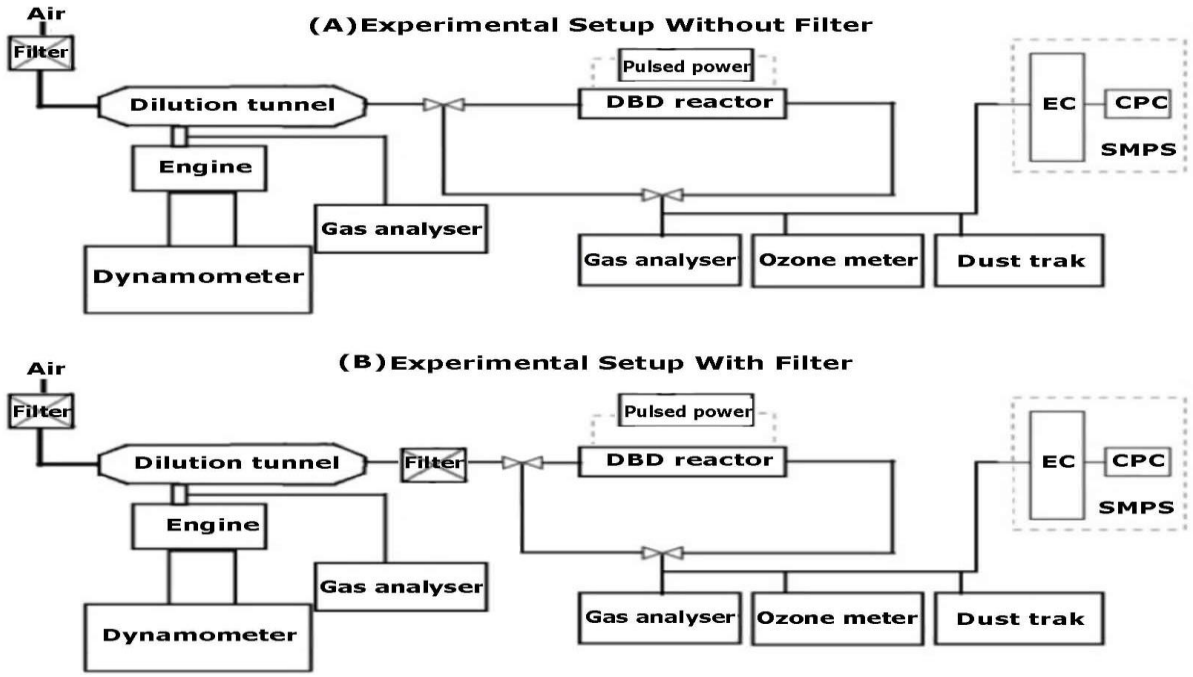


Figure 5.3: Schematic diagram of experimental setup: (A) without filter, (B) with filter

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Plasma effect on particle size distribution

For studying the effect of plasma on the emission treatment of exhaust, some initial experiments have been carried out considering the emissions of the Cummins diesel engine. In all experiments engine speed and load were kept constant at 40 kW (25% load) and 2000 rpm,

respectively. A portion of raw diesel exhaust directly from an iso-kinetic sampling port of the tailpipe has been diluted with air and passed through the reactor. The dilution ratio was constant at about 10 in all experiments. The plasma removal effect was considered at three different voltage levels at 15, 17 and 20 $kV_{pp}$, which correspond to different discharge powers. First, the maximum voltage level has been applied to make sure that the breakdown voltage has been met and plasma has been formed. Emission concentrations were measured at the reactor inlet (reactor inlet no pulse) and the reactor outlet (reactor outlet no pulse) without applying any pulse voltage to see the rate of deposition on the reactor surface. Then, pulse voltage was applied to produce plasma and particle size distribution was measured at the reactor outlet (reactor outlet with pulse). This procedure was repeated for the rest of the measurements. The effect of plasma on particle size distribution has been shown in Figure 5.4, Figure 5.5, and Figure 5.6.

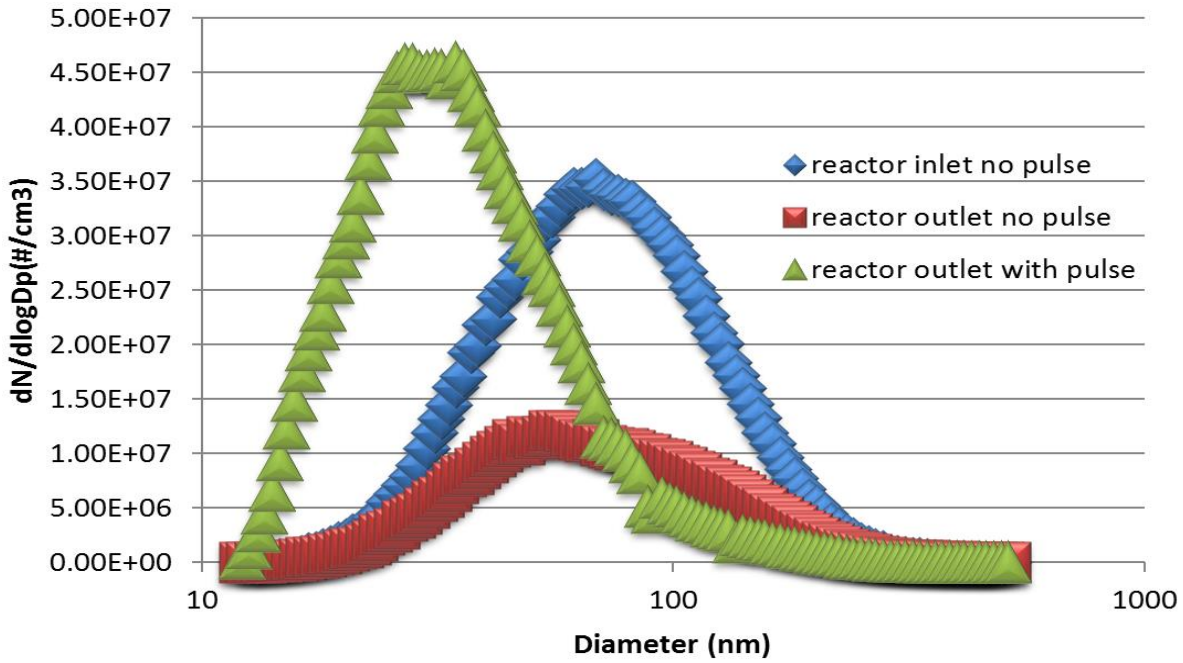


Figure 5.4: Particle size distribution (2000 rpm, 25% Load, 20 $kV_{pp}$ and 10 kHz)

PM diameters, whose removal is being targeted, are in the range of 10 nm to 500 nm. As it is shown, particle size distributions are different under varied voltage levels. Figure 5.6 shows that particle size distribution changes slightly by applying 15 $kV_{pp}$. As depicted in Figure 5.5 the PM removal is improved by increasing the applied voltage up to 17 $kV_{pp}$. When the voltage level goes up to 20 $kV_{pp}$, more larger particles have been removed; however, many smaller particles have been produced. Therefore, regarding the particle size distribution, increasing the voltage level above 17 $kV_{pp}$ has adversely affected the system performance.

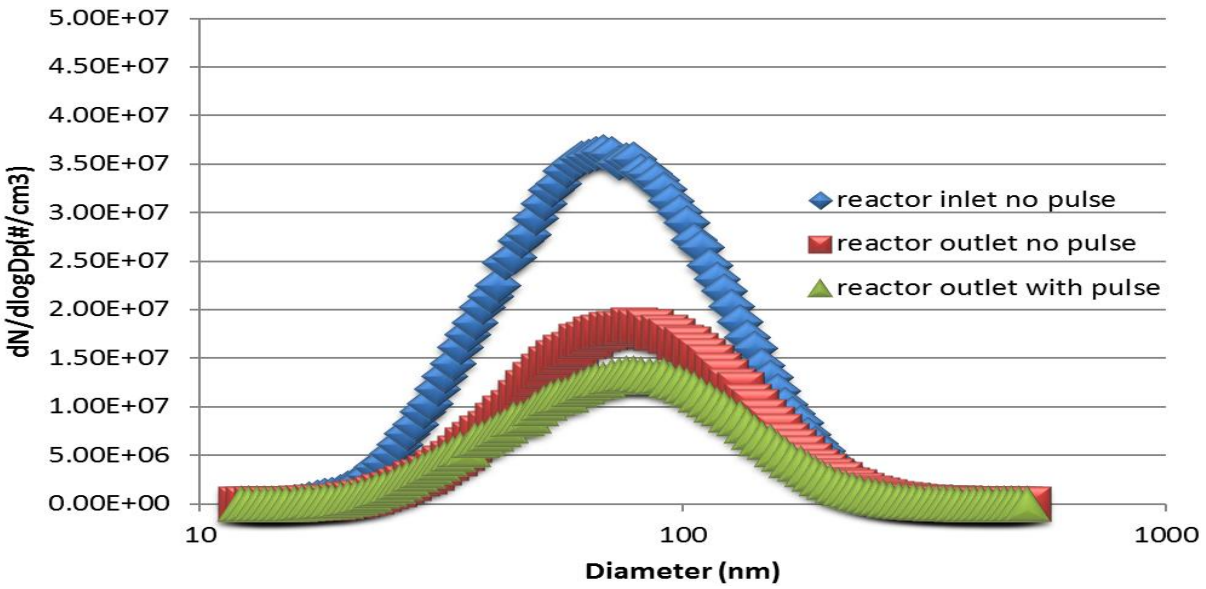


Figure 5.5: Particle size distribution (2000 rpm, 25% Load, 17 $kV_{pp}$ and 10 kHz)

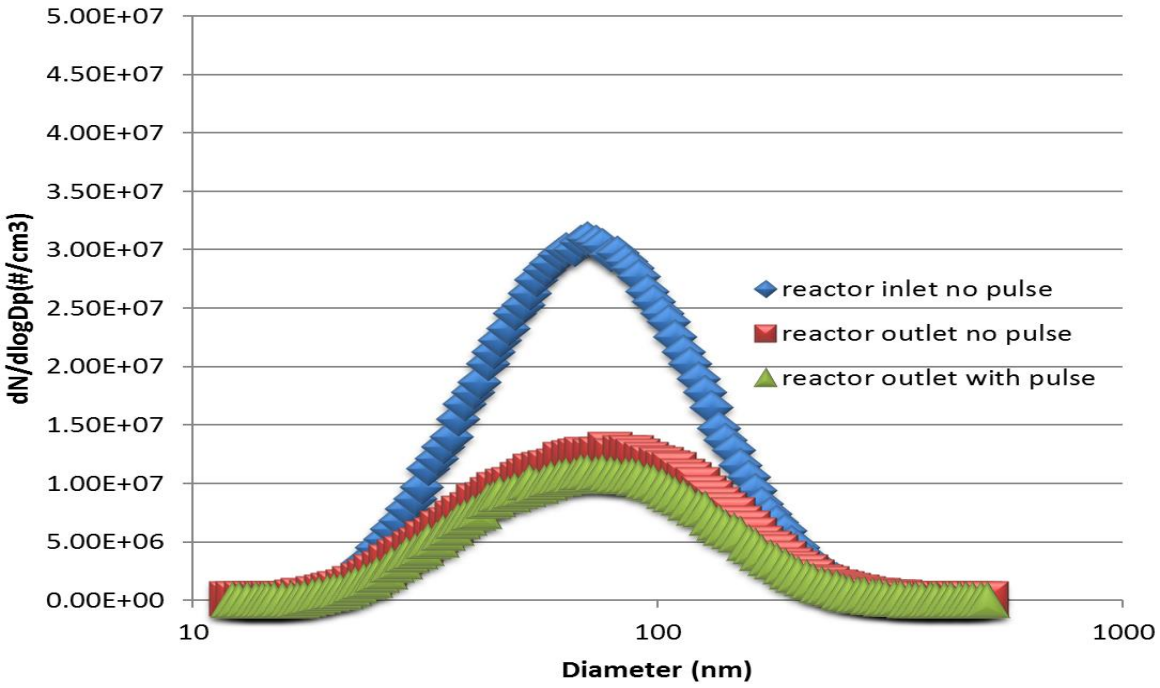


Figure 5.6: Particle size distribution (2000 rpm, 25% Load, 15 $kV_{pp}$ and 10 kHz)

As can be seen at 20 $kV_{pp,}$ the number of tiny particles was increased dramatically. Two possibilities can be considered for this phenomenon:

- Plasma changes some part of the exhaust gas emissions to particles.
- Larger particles break into smaller particles or probably some condensation happens.

For studying the first theory, a PM filter was added in the reactor inlet and diesel exhaust passed through this filter before entering the reactor. The schematic diagram of this setup has been illustrated in Figure 5.3B and the results have been summarised on the three following figures.

As shown in Figure 5.7, Figure 5.8 and Figure 5.9, by adding this filter, almost all particles have been removed from the exhaust gas before entering the DBD reactor. Just a small portion of particles have not been trapped by the filter. After introducing plasma, most of the un-trapped particles are removed when the voltage levels are 15 $kV_{pp}$ and 17 $kV_{pp}$. However, as Figure 5.9 depicted, the effect of plasma at 20 $kV_{pp}$ on particle size distribution is different. Without applying any pulse, the number of particles is very small. But, by applying 20 $kV_{pp}$ and introducing plasma inside the reactor, the number of small particles was massively increased. This result indicates the occurrence of gas to particle reactions at this voltage level. Therefore, some part of increase on PM numbers obtained on Figure 5.4 could be due to the conversion of gas to particles.

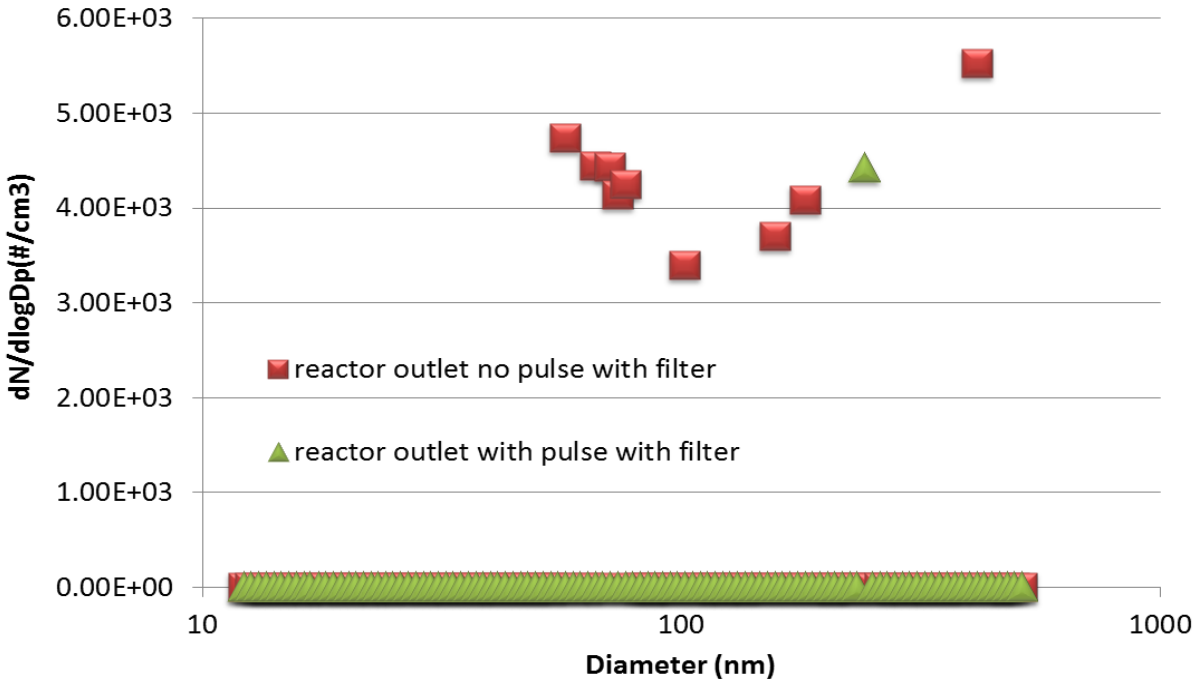


Figure 5.7: Particle Size Distribution with filtering (2000 rpm, 25% Load, 15 $kV_{pp}$ and 10 kHz)

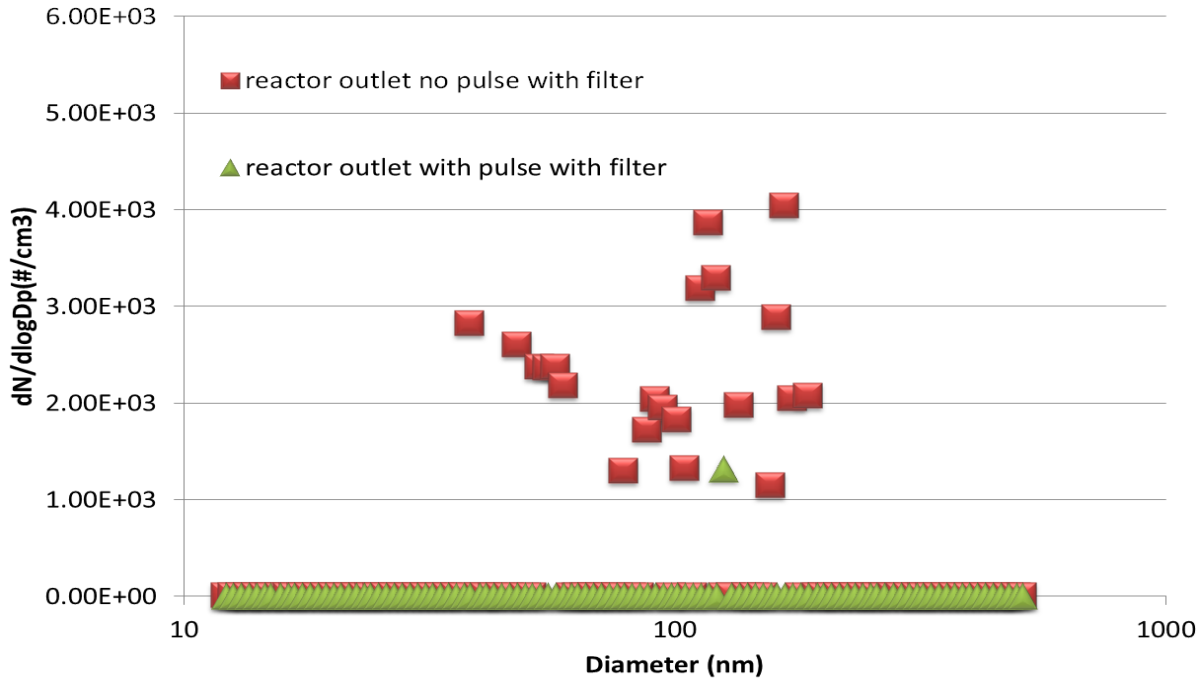


Figure 5.8: Particle Size Distribution with filtering (2000 rpm, 25% Load, 17 $kV_{pp}$ and 10 kHz)

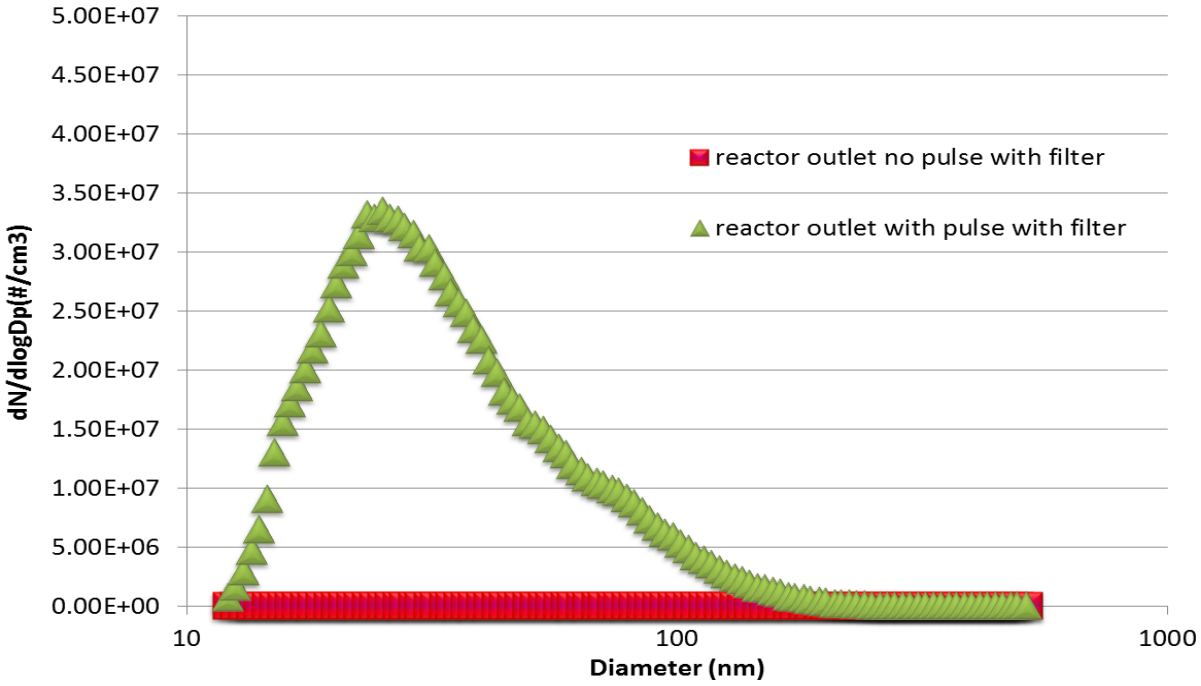


Figure 5.9: Particle Size Distribution with filtering (2000 rpm, 25% Load, 20k Vpp and 10 kHz)

### 5.3.2 Particle mass effect by introducing plasma

In this section, the effect of plasma on particle mass reduction is presented. Three different voltage levels have been considered the same as in the previous section. All results have been summarised in Table 5-1. The PM mass reduction without using any filter for 20 $kV_{pp}$, 17 $kV_{pp}$ and

15 $kV_{pp}$ are 43.9%, 38.6% and 27.1%, respectively. The maximum PM mass reduction has been obtained when the voltage level is 20 $kV_{pp}$. Also, a reasonable mass reduction can be obtained, of around 40% by applying 17 $kV_{pp}$ without any increase in ultrafine particle numbers.

When a filter is added at reactor inlet, the PM concentration is very low due to the filter trapping, compared to the PM concentration without using any filter. Particle mass before and after applying a pulse were measured to clarify the amount of gas to particle changes. Without applying high voltage pulses, the particle mass concentration in the reactor outlet is 0.012 $mg/m^3$, 0.01 $mg/m^3$ and 0.013 $mg/m^3$ for three different measurements. However, by applying 20 $kV_{pp}$ PM mass increases to 0.084 $mg/m^3$. This shows that some part of the gaseous pollutants change to particles due to the plasma effect. At 17 $kV_{pp}$ and 15 $kV_{pp}$, there is no increase in particle mass by introducing plasma. Further studies are required to completely understand this effect.

Table 5-1: The concentration of PM before and after the treatment at different voltages

| **Operating condition** / **Filtering** | **20 $kV_{pp}$ @10 kHz** | **17 $kV_{pp}$ @10 kHz** | **15 $kV_{pp}$ @10 kHz** |
|---|---|---|---|
| | **Yes** | **Yes** | **Yes** |
| **Reactor Inlet PM Concentration** ($mg/m^3$) | - | - | - |
| **Reactor Outlet No Pulse PM Concentration** ($mg/m^3$) | 0.012 | 0.01 | 0.013 |
| **Reactor Outlet By-Pulse PM Concentration** ($mg/m^3$) | 0.084 | 0.01 | 0.013 |

## 5.4 CONCLUSION

In this paper, the effect of non-thermal plasma on the PM removal mechanism and PM size distribution at different voltage levels has been studied. NTP was generated and controlled at different operating points by using a pulsed power supply. A DBD reactor with two dielectrics was employed in order to generate plasma. The results showed the ability of the proposed system to decrease PM concentrations. Furthermore, it was found that voltage increase does not necessarily have a positive effect on PM removal in diesel engine emissions. This has been validated based on the hypothesis of gas to particle change by using NTP technology.

# Chapter 6: Influence of non-thermal plasma after treatment technology on diesel engine particulate matter composition and NOx concentration

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Publication: Under review by International Journal of Environmental Science and Technology

**Author Contribution**

| Contributor | Statement of Contribution |
|---|---|
| M. Babaie<br>Signature | Conducted the experiments, performed the data analysis and drafted the manuscript |
| T. Kishi | Assisted with conducting the experiments |
| Y. Zama | Supervised the experiments |
| M. Arai | Supervised the project, aided with the development of the paper and data analysis |
| T. Furuhata | Supervised the experiments |
| Z. Ristovski | Supervised the project, Aided with the development of the paper and data analysis |
| H. Rahimzadeh | Supervised the project, Aided with the development of the paper |
| R. J. Brown | Supervised the project, aided with the development of the paper, data analysis and extensively revised the manuscript |

**Principal Supervisor Confirmation**

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

| Name | Signature | Date |
|---|---|---|
| Associate Professor Richard Brown | R. J. Brown | 30/09/2014 |


**Abstract**

The effect of non-thermal plasma (NTP) technology for particulate matter (PM) removal and nitrogen oxide emission reduction from diesel exhaust has been investigated. A sample of exhaust was cooled to the ambient temperature and passed through a dielectric barrier discharge (DBD) reactor. The DBD reactor was employed for producing plasma inside the diesel exhaust. A range of discharge powers by varying the applied voltage from 7.5 kV to 13.5 kV at a frequency of 50 Hz have been evaluated during the experiments. Regarding the $NO_x$ emission concentration, the maximum removal efficiency has been achieved at energy density of 27 J/L. Soot, soluble organic fraction (SOF) and sulfate components of diesel particulate matter have been analysed separately and the consequence of NPT exposure on PM size distribution on both the nucleation and accumulation modes has been studied. NTP was found to be very effective for soot removal and it could approach complete removal efficiency for accumulation mode particles. However, when applied voltage approached 12 kV, the total number of nucleation mode particles increased by a factor of 50 times higher than the total particle numbers at the reactor inlet. This increase in nucleation mode particles increased even more when applied voltage was set at 13.5 kV.



**Keywords:** Non-thermal plasma; dielectric barrier discharge; diesel emission reduction; Particulate matter; Nitrogen oxides

## 6.1 INTRODUCTION

Diesel engines emit a lot of pollutants such as carbon monoxide (CO), unburned hydrocarbons (HC) nitrogen oxides ($NO_x$) and particulate matter (PM) due to the incomplete combustion of diesel fuel. Among different components of diesel emission, diesel particulate matter (DPM) is the most complex component. DPM is essentially composed of a solid fraction (soot), soluble organic fraction (SOF), which is heavy hydrocarbon derived from fuel or lubrication oil and sulfate particulates derived from sulfur. The solid fraction generally consists of elemental carbon, which has not formed any chemical bond with any other elements. Furthermore, metallic ash is another component of the solid fraction and it is basically composed of metal oxides, sulfates, phosphates and iron oxides derived from the corrosion of exhaust manifold (Merkel et al., 2001). Sulfate particulates are formed in the process of heteromolecular nucleation, where sulfuric acid chemically reacts with the water fraction presented in the exhaust (Morawska et al., 2008). Sulfate particulates are considered to be separated from carbon particles and they are found as nucleation mode particles in the exhaust (Maricq et al., 2002). The number of sulfate particles depends on the sulfur content of the diesel fuel (Ristovski et al., 2006). The SOF fraction can exist in the form of separated fine droplets in diesel exhaust or can be adsorbed on the surface of carbon particles. The proportion of SOF in the total PM can be different depending on the engine specifications and engine operating conditions. The low SOF content is called 'dry' particulates (less than 10% of the total PM composition) whereas in wet particulates, the SOF content is higher (over 50% of the total PM composition) (Majewski, 2002d).

Regarding particle size, diesel engines show a bimodal particle distribution with a combination of nucleation mode and accumulation mode (Kittelson et al., 2006). Nucleation mode particles are mostly consisting of SOF and sulfate particles that are primarily volatile and unstable with a small amount of solid elemental carbon and other materials. On the other hand in accumulation mode, primary carbon particles and other solid materials agglomerate with each other to form a bigger particle and adsorb some SOF fractions and other vapour components on its surface (Majewski, 2002d). While most of the mass is in the 0.1–1.0 μm “accumulation” size fraction, most of the particle numbers are in the < 0.1 μm “nucleation particle” fraction (Seinfeld, 1975, Kittelson, 1998a). Such small particles are inhalable, able to reach the lower human airways and penetrate deep into the lungs where they can enter the bloodstream and even reach the brain (Zhua et al., 2007, Wang et al., 2013). Therefore, there is a considerable concern about the deleterious effect of diesel particles on human health and DPMs are suspected for a series of adverse effects on the environment (Ramanathan, 2007 ) and human health (Ristovski et al., 2012, Seaton et al., 1995, Sydbom et al., 2001b, omers et al., 2004).

Given the likely health effects of diesel emissions, there is a clear need to consider new technologies to reduce the emissions of diesel engines. Non-thermal plasma (NTP) is believed to be a promising candidate for different emission reduction applications (Zhang et al., 2013, Zhu et al., 2011, Zhu et al., 2009). Plasma is the fourth state of matter composed of free electrons, ions, radicals, atoms, and molecules in various states of excitation, which have a tendency to remain overall electrically neutral over the large length scales (Inan and Gołkowski, 2010). Plasma is divided into thermal or hot plasma and non- thermal or cold plasma. In the thermal variety, the kinetic energy (temperature) of charged particles and the kinetic energy (temperature) of the background gas are similar, while in non-thermal plasma, electrons have a kinetic energy higher than the energy corresponding to the random motion of the background gas molecules (Majewski, 2004). Non-thermal plasma contains many kinds of chemically active species generated by many chemical reaction mechanisms such as electron attachment, dissociation, ionisation, excitation etc. For example, O, $O_3$ , N, N*, $N_2^+$ and OH can be generated by the dissociation and ionisation of the ambient gases caused by the impact of energetic electrons (Akiyama et al., 2007).

Both gaseous and particle emissions of exhaust emissions undergo chemical changes when they are exposed to plasma. In comparison to the numerous publications on $NO_x$ treatment by plasma (Lebouvier et al., 2011, Vinh et al., 2012c, Arai et al., 2004, Jolibois et al., 2012b, Mohapatro and Rajanikanth, 2011b, Chae, 2003, Yoshida et al., 2009), a limited amount of research has investigated particulate matter (Ye et al., 2005, Suzanne E. Thomas et al., 2000, Babaie et al., 2013b) and most of it has emphasized PM mass reduction only (Yao et al., 2006b, Fushimi et al., 2008). In this paper, the effect of plasma technique on particulate matter constituents (soot, SOF and sulfates) and NO, $NO_2$ and $N_2O$ emission concentrations have been studied. A dielectric barrier discharge (DBD) reactor was employed for producing plasma inside the diesel exhaust and a range of discharge power by varying the applied voltage from 7.5 kV to 13.5 kV has been discussed. Moreover, PM size distribution for a different range of voltages was deliberated. PM size distribution results have been considered in conjunction with PM constitute outcomes to obtain a better insight into the plasma effects on diesel particulate matters' structure.

## 6.2 MATERIALS AND METHODS

A schematic diagram of the experimental setup is shown in Figure 6.1. Experiments were conducted on a 0.4-litre, two-cylinder, four-stroke, indirect injection diesel engine with a swirl combustion (Kubota, Z-402E). All the experiments have been conducted under steady state conditions at a constant engine load of 2 kW. The exhaust flow rate passing through the reactor was

kept constant at 3 L/min for all experiments. The heat is removed from the exhaust to cool it down to room temperature before entering the reactor via a water trap.

A dielectric barrier discharge (DBD) reactor was used to create plasma inside the exhaust. DBD is an excellent source of energetic electrons with 1-10 eV and high density (Xu, 2001). It consists of two concentric quartz tubes, each with wall thicknesses of 2 mm. The outside diameter of the inner tube is 12 mm and inside diameter is 8 mm. For the outer quartz tube, the inside and outside diameters are 22 mm and 18mm respectively. Exhaust passes through the gap between these two quartz tubes. Based on designed geometry, the discharge gap is 3 mm. Both bends of the reactor tubes are stoppered by heat-resistant Teflon caps. The centre electrode is a stainless steel rod, having a diameter of do = 6.0mm (SUS304) which is passed through the centre of the inner glass tube. Aluminium foil is used on the outer periphery of the outer glass tube to provide the ground electrode. The effective length of the barrier discharge device in this reactor is 250mm. AC voltage is obtained by boosting a neon transformer (LECIP Inc., 100A-15UHCS) as a commercial power supply (up to 13.5 kV) at 50 Hz is applied between the electrodes to form the plasma. For the experiments, a range of voltages from 7.5 kV up to 13.5 kV has been applied at a constant frequency of 50 Hz. As shown in Figure 6.1, a 0.2 μF capacitor is used between the ground and the outer peripheral electrode to find the discharge power between these two electrodes.

To observe the effect of plasma on particle composition before and after introducing plasma, quartz-fiber filter papers were utilised to collect PM samples at the reactor outlet. At first, the power supply was turned off and the applied voltage was zero. Then voltage was increased up to 7.5 kV, which is just higher than the required breakdown voltage of the proposed configuration for initiating the plasma. Four more voltage levels (9, 10.5, 12 and 13.5 kV) have been applied to produce stronger plasma inside the plasma reactor. Ten different samples have been collected for each voltage level and PM components such as dry soot, soluble organic fraction (SOF), and sulfate are measured using a combustion type PM analyser (Horiba, MEXA-1370PM). On the other hand, the size distributions of particles sampled before and after the DBD reactor are measured by a scanning mobility particle sizer (TSI, SMPS-3034). PM size distribution was measured at reactor inlet and reactor outlet without applying any voltage to find the particle deposition rate inside the reactor. Then, the plasma was introduced inside the DBD reactor at the different aforementioned voltage levels. Size distribution and PM composition results have been analysed in conjunction, to obtain a better understanding of plasma effects on PM composition. Moreover, the effect of NTP on different nitrogen oxides has been considered. To find out the effect of NTP on $NO_x$ concentration, NO, $NO_2$ and $N_2O$ have been measured by the Fourier Transform Infrared (FTIR) Horiba Mexa-4000 FT in the reactor inlet and outlet at different voltage levels.

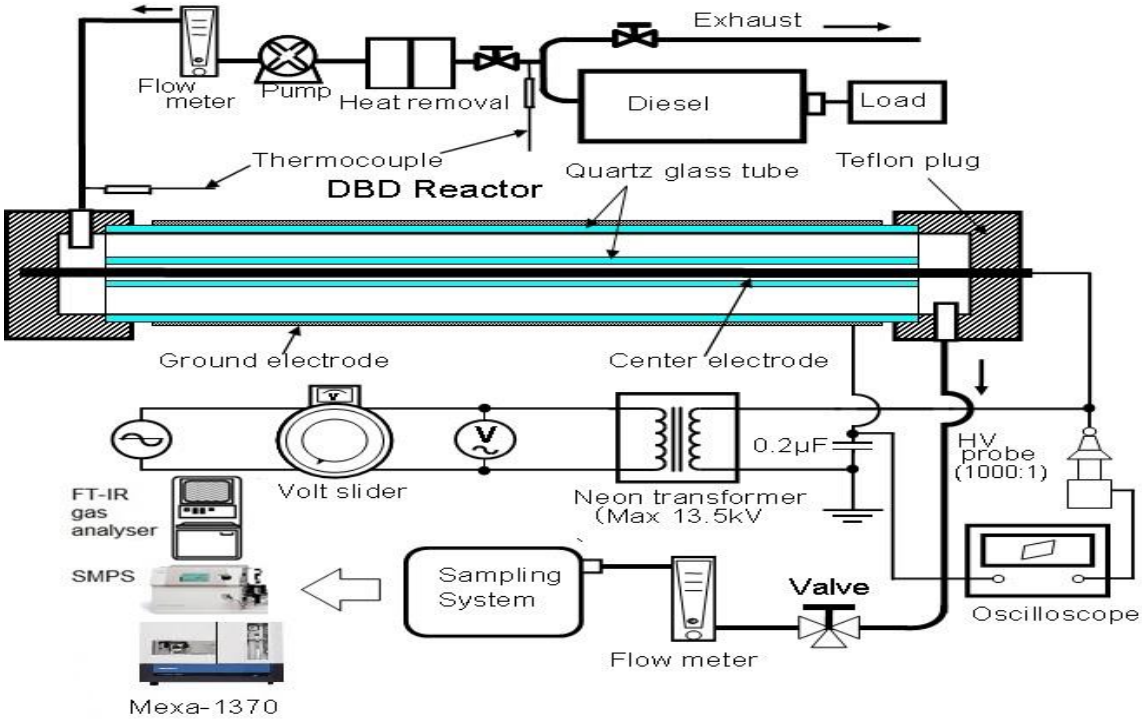


Figure 6.1: Schematic diagram of experimental setup and sampling system

## 6.3 RESULTS AND DISCUSSION

### 6.3.1 Emission characterisation of diesel engine

Before studying the effect of plasma on diesel engine exhaust, the gaseous emissions have been measured at different engine loads. CO, $CO_2$, $H_2O$, $O_2$ and $C_2H_4$ results are shown in Figure 6.2. As can be seen, after a rapid fall in CO concentration at 0.5 kW, there is a gradual decrease in CO concentration while engine load increases to 2.4 kW. On the other hand, $CO_2$ concentration shows the opposite trend and it increases with the engine load increase. $H_2O$, $O_2$ and $C_2H_4$ concentration patterns are somehow similar. As it is shown, after a drop in concentrations at 0.5 kW, the concentrations of $H_2O$, $O_2$ and $C_2H_4$ remain almost constant by changing the engine load. Figure 6.3 shows the results of the nitrogen oxides concentrations on diesel exhaust by changing the engine output power. It was confirmed that $NO_2$ and NO increased along with the increase of the engine output power while $N_2O$ did not change a lot. Also, nearly 80% of the emitted $NO_x$ ($NO+NO_2$) is for NO in this diesel engine at all engine loads.

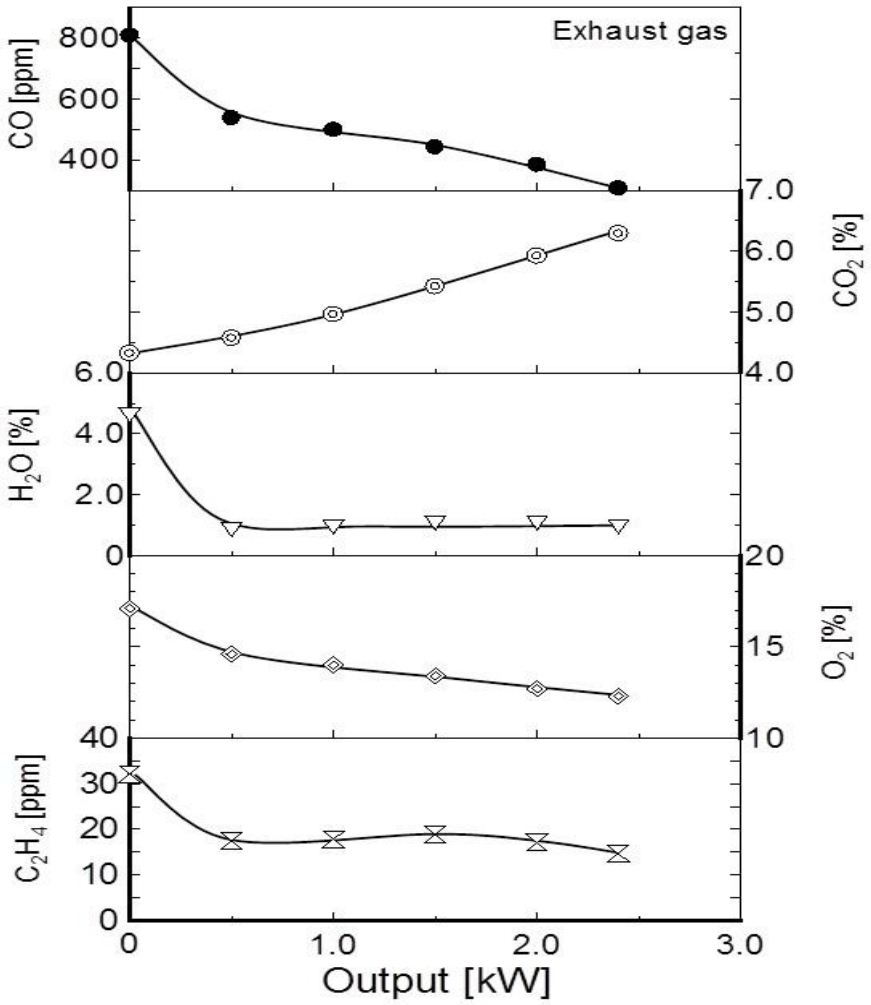


Figure 6.2: CO, $CO_2$, $H_2O$, O2, $C_2H_4$ concentrations in exhaust at different engine output powers

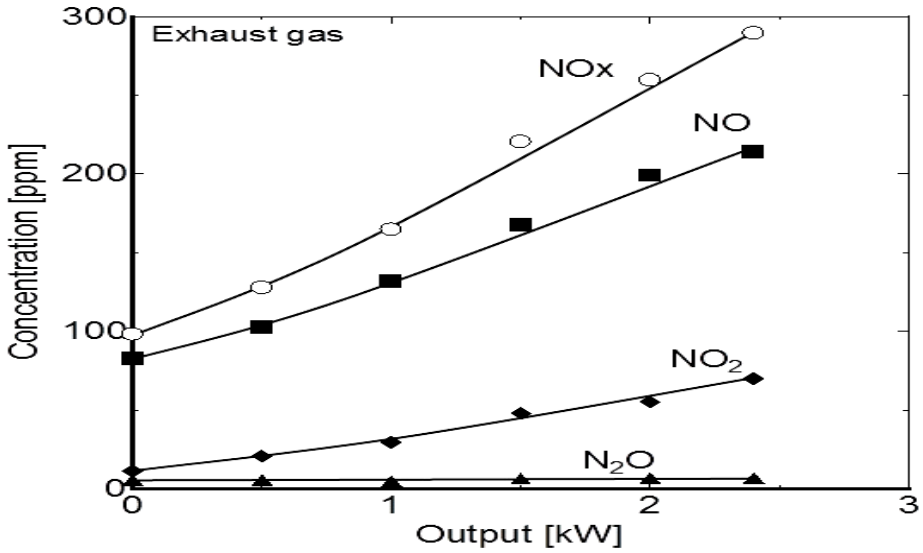


Figure 6.3: $NO_x$ concentration in diesel exhaust at different engine output powers

### 6.3.2 Discharge power characteristics

The AC voltage obtained from boosting the neon transformer (LECIP Inc., 100A-15UHCS) at 50Hz as a commercial power supply was applied between two electrodes of the DBD reactor to form the plasma inside the exhaust. The supply power source goes through two transformers before reaching the reactor. The primary transformer, also a volt slider, is used to adjust input applied voltage. The secondary transformer (Neon Transformer, ratio 1:150) converts the input voltage into high voltage in the range from 5 kV to 15 kV. A high voltage probe, Iwatsu HV-P30, with ratio 1000:1 is inserted into circuit to minimise load on the oscilloscope. A 0.2 μF capacitor was set up between the ground and peripheral electrode to define the stored charge in DBD reactor. Charge-voltage Lissajous technique is used to measure the discharge power inside the DBD reactor (Hui et al., 2013) .

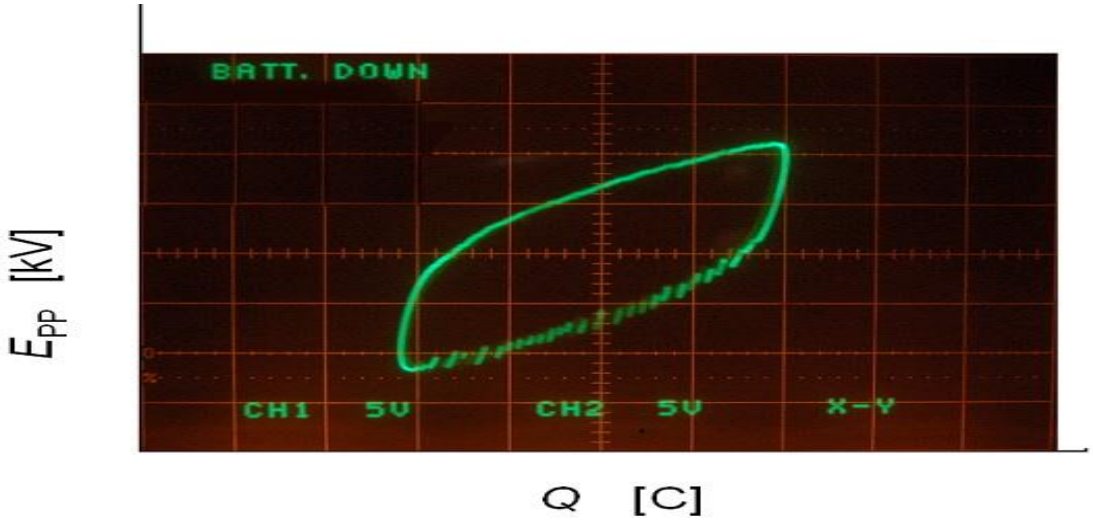


Figure 6.4: E-Q Lissajous diagram on oscilloscope

Figure 6.4 illustrates the charge amount Q [C] of the capacitor and the applied voltage between the electrodes Epp[V] obtained from a KENWOOD, C-S8010 oscilloscope. The area of the Q - Epp Lissajous figure represents the electrical discharge energy per cycle (W [J/cycle]) and the average discharge power (P[J/s=W]) can be calculated by multiplying the energy per cycle (W[J/cycle]) and the frequency (f[1/s]). The voltage was 7.5 kV for the first experiment and it is increased up to 13.5 kV. The Lissajous figures for all voltages have been obtained by taking photos from the oscilloscope screen. Then by the use of image processing, the discharge power has been calculated for all voltage levels. The result is plotted in Figure 6.5. When voltage is 7.5 kV, the discharge power is just 0.02 W which means at this condition, plasma cannot be maintained inside the exhaust. However when the voltage goes up, the discharge power increases, especially after 10.5 kV. As it can be seen, the discharge power jumps to about 1.4 W at 13.5 kV. At this point plasma can be

maintained and we can expect a lot of free radicals and ions and a lot of electron impact reactions inside the exhaust.

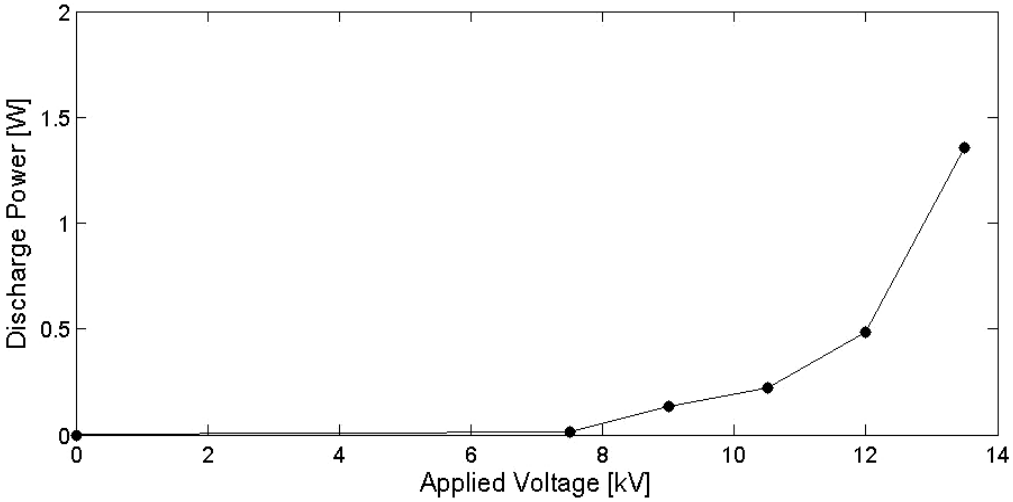


Figure 6.5: Average power discharge versus applied voltage for plasma DBD reactor

### 6.3.3 Particle size distribution under plasma discharge

The effect of plasma at different voltage levels is shown in Figure 6.6. As mentioned before, first the particle size distribution has been considered at the reactor inlet and outlet without any plasma and then the power supply was turned on. For the first case, the applied voltage was 7.5 kV and the particle size distribution is measured at reactor outlet (RO7.5kV). The voltage was increased up to 13.5 kV (named RO13.5 kV on Figure 6.6) by 1.5 kV voltage steps. As discussed on Figure 6.5 before, the discharge power and therefore plasma is weak at 7.5 kV and 9 kV. The former is in agreement with Figure 6.6 which shows that the particles at these two voltages are not ionised sufficiently to effect the particle size distribution. We thus conclude that at these two voltage levels the plasma is not powerful enough for removing particles and most of the PM removal is just due to the deposition.

When the voltage increases to 12 kV, there is a substantial decline in particle number in accumulation mode compared to PM numbers at the reactor inlet. For particles with diameters bigger than 30 nm, the DBD plasma reactor showed 77% removal efficiency of particle numbers. This is a promising phenomenon, which is obtained by a conventional DBD reactor and can be improved by reactor modifications in future plasma applications. However, when it goes to particles smaller than 30 nm, an increase on nucleation mode particles is observed. When the voltage gets to 13.5 kV, almost all of the particles larger than 30 nm have been removed. On the other hand, high numbers of particle concentrations in nucleation mode were found at this voltage level. PM size distribution peaks to $5.6 \times 10^6$ particles, which is 1.8 times greater than the maximum of particles number at reactor inlet. These nucleation mode particles can be formed due to the condensation of SOF derived

from the accumulation mode particles after oxidisation of their embedded elemental carbons and also due to the condensations from the gas phase. Volatile components in gas phase can be oxidized in plasma state. The vapour pressure of oxidized by-products is lower than the original volatiles. Therefore, they will condensate from gas phase to particle phase and SMPS will detect them in nucleation mode.

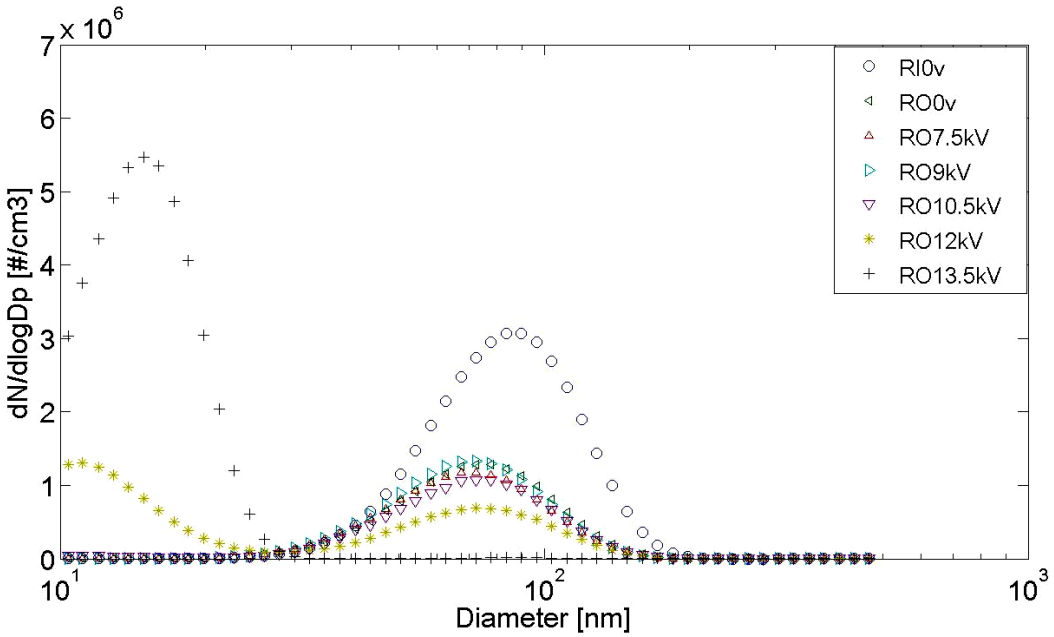


Figure 6.6: SMPS particle size distribution at different voltage levels

### 6.3.4 Effect of non-thermal plasma on diesel particle composition

The effect of non-thermal plasma on soot, SOF and sulfate is shown on Figure 6.7. The error bars in this figure represent one standard deviation. PM samples were collected on QR-100 Silica filters (Gas Collection Efficiency of 99.99% for 0.3 µm DOP) at the reactor outlet and then analysed by Horiba MEXA 1370PM. Regarding the filter's collection efficiency, most of the collected PMs on Silica filters can be assumed to be from the accumulation mode. When the voltage was zero, no plasma was formed inside the exhaust and SOF, soot and sulfate content of the emitted particles were 0.0026 mg/L, 0.0011 mg/L and 0.0007 mg/L, respectively. Therefore, particles emitted from the test engine appear to be as wet particles because the SOF content is considerably higher than the soot and sulfate contents. As expected, the sulfate fraction is very low at the reactor outlet measurements, due to the low sulfur content of employed diesel fuel, and remains almost unchanged under plasma treatment.

From Figure 6.7, a continuous decrease of soot concentration of PM by increasing applied voltage can be found. Soot concentration at the reactor outlet when there is no plasma is 0.0011 mgr/L, and it decreases to 0.0003 mgr/L when the voltage increases up to 13.5 kV. This is

equivalent to about 73% soot mass reduction at this voltage level when the plasma is formed strongly inside the exhaust. Since the soot basically can be considered as elemental carbon, this effect is expected due to the oxidative potential of plasma. Ozone and other active oxygen species (such as $O_2$+, $O_2$−, O, O+, O−, ionised ozone, etc.) produced by plasma are the most important candidates for oxidising the soot component of emitted particles (Okubo et al., 2008). This finding indicates a good potential of non-thermal plasma applications for carbonaceous particle removal.

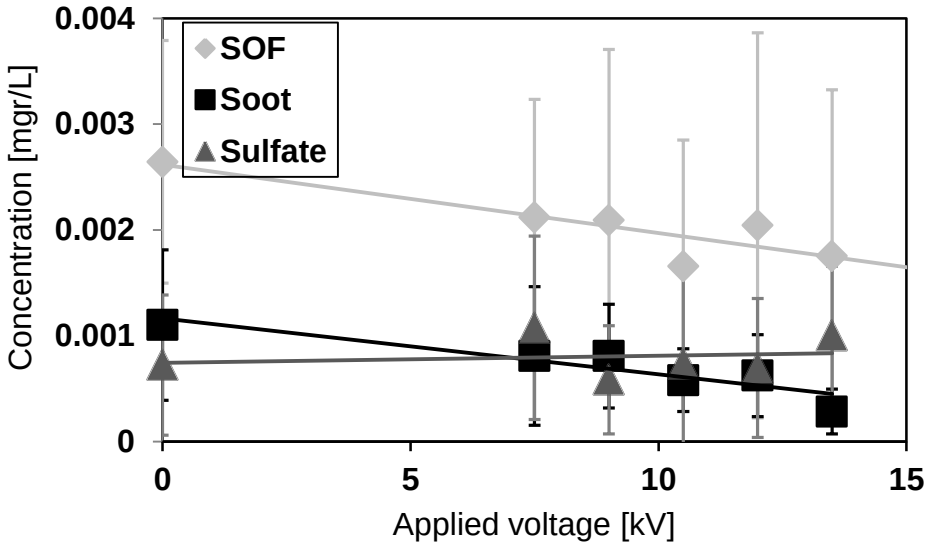


Figure 6.7: Effect of non-thermal plasma at different voltages on PM components

Despite some fluctuations in SOF data, the general trend of a decrease in SOF concentration can be found from Figure 6.7. A major fall about 37% in SOF concentration is observed at 10.5 kV; however, with the increase of voltage to 12 kV and 13.5 kV, the SOF ascends a bit. This outcome is in agreement with the results of Figure 6.6, which show a bimodal size distribution at 12 kV and 13.5 kV. While at these voltage levels the total particle number in nucleation mode increases, PM numbers on accumulation mode particles declines significantly. This increase in SOF content and decrease of PM numbers in accumulation mode can be explained as a rearrangement on PM structure. At these voltage levels, a considerable decrease in PM numbers and the soot component in accumulation mode are found, so we can assume that some SOF constituents of removed particles adhere on the surface of the remaining particles in accumulation mode and form some more wet particles. This assumption should be studied in more detail in the future.

### 6.3.5 Effect of energy density on PM removal efficiency

Energy consumption is an important challenge in plasma applications for PM removal. Energy density is usually employed for evaluating the discharge energy and defined as the ratio of discharge power to the exhaust flow rate. The magnitude of energy density affects the removal efficiency on plasma applications. The effect of energy density on removal efficiency of total particulate matter is

plotted on Figure 6.8. As we discussed previously, the PM numbers were increased on nucleation mode particles at 12 kV and 13.5 kV, so the PM removal has been considered for particles larger than 30 nm.

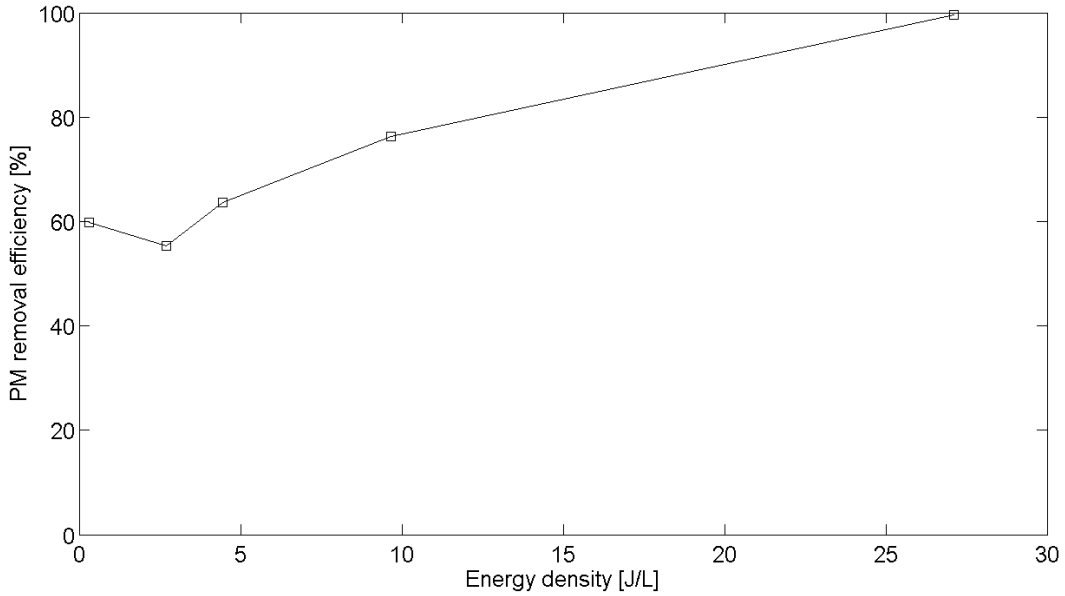


Figure 6.8: Effect of energy density on PM removal efficiency

As can be seen from Figure 6.8, there is a direct relationship between discharge power and removal efficiency. At first, the removal efficiency for the particles larger than 30 nm is about 59% and it rises to 76% at an energy density of 10 J/L. Nearly all particles larger than 30 nm can be removed when the discharge power is about 27 J/L.

### 6.3.6 Effect of non-thermal plasma on NOx concentration

The effect of non-thermal plasma on nitrogen oxides has been studied during the experiments as well. The samples are collected by a Tedlar bag and analysed by a Fourier transform infrared spectroscopy exhaust gas analyser (Horiba Co., Ltd, MEXA-4000FT) at the reactor outlet. Applied voltages have been changed from 7.5 kV to 13.5 kV, the same as in previous experiments, and NO, $NO_2$, $N_2O$ and total $NO_x$ ($NO+NO_2$) concentration have been considered. The results are summarised in Figure 6.9 and Figure 6.10. As can be seen, the change in concentration has been started after 9 kV. Therefore, plasma has not been powerful enough to make any significant variation in nitrogen oxide concentrations before this point. It was found that NO is oxidised to $NO_2$ due to the existence of different active oxygen species and ozone as it is reported on previous studies (Mohapatro and Rajanikanth, 2011b, Arai et al., 2004, Fitzsimmons et al., 1999). NO concentration decreased by about 72% and $NO_2$ concentration increased by about 77% by applying maximum voltage at 13.5 kV during the experiments. On the other hand, a small increase on $N_2O$ concentration has been found

during the experiments. The initial concentration of $N_2O$ was about 13 ppm when there is no plasma inside the exhaust and this concentration increased to about 18 ppm when applied voltage was 13.5 kV. This increase can be due to the reaction of $NO_2$ with produced N radicals during the plasma process by a reaction scheme of $NO_2 + N \rightarrow N_2O + O$ (Vinh et al., 2012c).

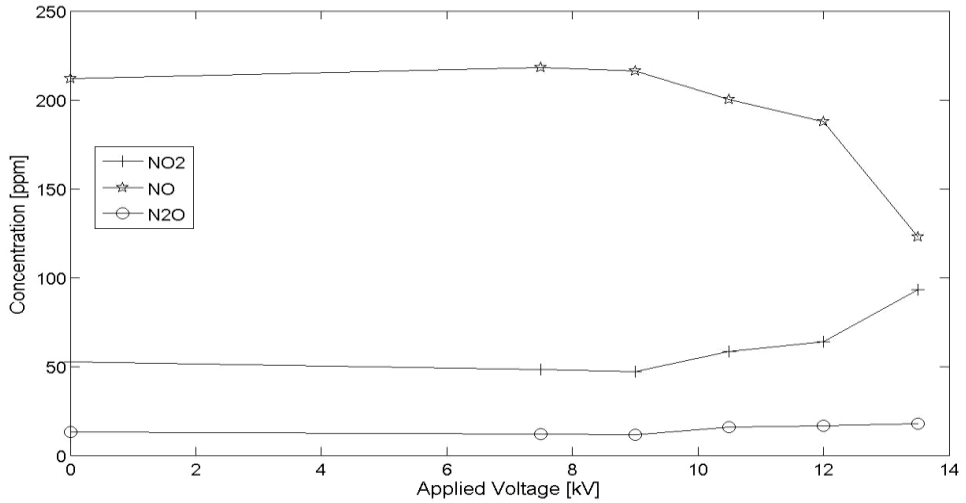


Figure 6.9: Effect of non-thermal plasma on different nitrogen oxides

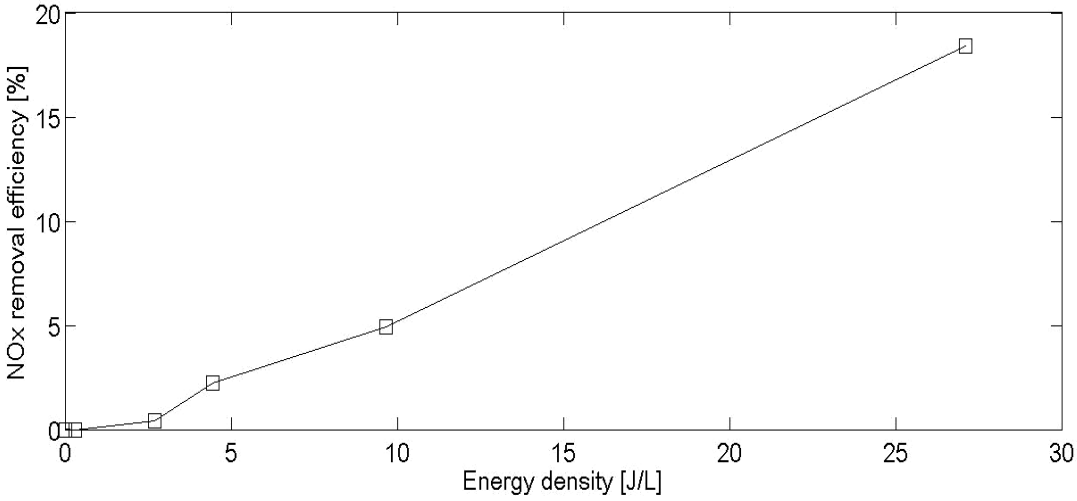


Figure 6.10: $NO_x$ removal efficiency at different energy densities

The effect of non-thermal plasma on $NO_x$ ($NO+NO_2$) emission reduction has been plotted in Figure 6.10. The maximum of energy density is limited by applied voltage at 13.5 kV, the same as in previous experiments. By increasing the energy density, a continuous increase of $NO_x$ removal efficiency has been observed. $NO_x$ removal efficiency is not very high while the energy density is changing up to 10 J/L. However, a significant increase on $NO_x$ removal efficiency has been observed when energy density has been increased to 27 J/L. For the given configuration, the maximum $NO_x$ removal efficiency of about 18% has been achieved when energy density was about 27 J/L. It should be noted that total $NO_x$ reduction cannot be concluded from considering the effect of plasma on NO,

$NO_2$ and $N_2O$ only. Other nitrogen oxides such as $NO_3$, $N_2O_5$ etc. can be formed during the process and they should be considered in future applications (Fitzsimmons et al., 1999).

## 6.4 CONCLUSION

In this study, the effects of NTP on PM structure and NOx emission of real diesel exhaust at different voltage levels (which corresponds to different discharge powers) have been investigated. Nitrogen monoxide (NO) was found to be oxidised to Nitrogen dioxide ($NO_{2)}$ during the experiments. This result was in good agreement with previous studies in this field. $NO_x$ removal efficiency increased by increasing the discharge power, with its maximum being about 18%. Moreover, the effects of NPT on PM components and PM size distribution have been studied simultaneously to get a better insight into PM removal mechanism. NTP was found very effective for PM removal, especially for soot reduction. A maximum reduction of 73% and 37% at energy density of 27 J/L has been found for soot and SOF mass concentration, respectively. The effect of NTP on PM size distribution has been studied by using SMPS data. Despite a considerable increase in nucleation mode particles at 13.5 kV, NTP showed a good potential for PM reduction in the range of 10 nm to 500 nm. Regarding the PM removal efficiency, energy consumption and PM size distribution on nucleation mode, running the DBD reactor at 12 kV can be considered as the optimum operating condition for the given configuration.

# Chapter 7: Performance evaluation of non-thermal plasma on particulate matter, ozone and $CO_2$ correlation for diesel exhaust emission reduction

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Publication: Due to be submitted to Journal of Hazardous Material

**Author Contribution**

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|---|---|
| Meisam Babaie | Conducted the experiments, performed the data analysis and drafted the manuscript |
| Signature | |
| Pooya Davari | Assisted with experiments and revised the manuscript |
| Pouyan Talebizadeh | Assisted with preparing the manuscript |
| Firuz Zare | Aided with the data analysis |
| Hassan Rahimzadeh | Supervised the project, Aided with the development of the paper |
| Zoran Ristovski | Supervised the project, aided with the development of the paper and data analysis |
| Richard Brown | Supervised the project, aided with the development of the paper, data analysis and extensively revised the manuscript |

**Principal Supervisor Confirmation**

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

| Name | Signature | Date |
|---|---|---|
| Associate Professor Richard Brown | R. J. Brown | 30/09/2014 |


**Abstract**

This study is seeking to investigate the effect of non-thermal (NTP) plasma technology in the abatement of particulate matter (PM) from the actual diesel exhaust. Ozone strongly promotes oxidation of PM, the main product of which is carbon dioxide ($CO_2$). The correlation between PM, $O_3$ and $CO_2$ is therefore a focus of this study. A dielectric barrier discharge (DBD) reactor has been designed with pulsed power technology to produce plasma inside the diesel exhaust. To characterise the system under varied conditions, a range of applied voltages, from 11 $kV_{pp}$ to 21 $kV_{pp}$ at repetition rates of 2.5, 5, 7.5 and 10 kHz, has been experimentally investigated and the results have been presented with relevant contour plots of discharge power, ozone, $CO_2$ and PM concentrations. This study shows that by increasing the applied voltage and frequency, higher discharge power and $CO_2$ dissociation can be achieved. The minimum PM concentration has been obtained at 19 $kV_{pp}$ and 10 kHz and the maximum ozone concentration has been found at 21 $kV_{pp}$ and 7.5 kHz. Furthermore, ozone, $CO_2$ and PM concentrations at different plasma states have been analysed for time dependence. Based on this analysis, an inverse relationship between ozone concentration and PM removal has been found and the role of ozone in PM removal in plasma treatment of diesel exhaust has been highlighted.



**Keywords:** Non-thermal plasma, Dielectric barrier discharge, Pulsed power, Particulate matter, Ozone, Carbon monoxide, Diesel engine

## 7.1 INTRODUCTION

The transport sector produces nearly one-fifth of total global carbon dioxide ($CO_2$). The road sector accounts for about three quarters of transport emissions and passenger cars and light trucks contribute to a considerable share of these emissions (Statistics, 2013). On the other hand, diesel engine applications in various heavy-duty and medium-duty vehicles are increasing, compared to gasoline engines. The emissions produced by diesel engines, however, are a ubiquitous air pollutant consisting of a complex mixture of gases, vapour and particles. The health effects of diesel emissions have been emphasised in the literature (Ristovski et al., 2012, Sydbom et al., 2001b, Talebizadeh et al., 2014) and lately diesel exhaust has been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC) (IARC, 2012).

Carbon monoxide (CO), hydrocarbon (HC), Nitrous Oxides ($NO_x$) and diesel particulate matter (DPM) have been globally regulated by diesel emission standards. DPM is usually composed of elemental carbons, which results in agglomerating and also absorbing other particles to form structures of complex physical and also chemical properties (Majewski, Revision 2013.08b). Along with DPM, $NO_x$, a generic term for the mono-nitrogen oxides, NO and $NO_2$ (Nitric Oxide and Nitrogen Dioxide), have also become the main concern of diesel emission control technologies. Up until now, several after treatment technologies, such as diesel oxidation catalyst (DOC) (Cooper and Roth, 1991b), diesel particulate filter (DPF) (Kuki et al., 2004, Ohno et al., 2002 -b), selective catalyst reduction (SCR) (Gieshoff et al., 2001, Radojevic, 1998) and fuel borne catalyst (FBC) (Farrauto and Voss, 1996) have been employed to reduce diesel exhaust emissions. However, there are some drawbacks in using conventional after treatment systems. For example, SCR catalysts need high temperatures (around 300°C) for activation and there is the possibility of ammonia leakage, catalyst poisoning and catalyst discharge under high temperature conditions (Tayyeb Javed et al., 2007, Skalska et al., 2010). Moreover, DPFs produce an additional pressure drop inside the diesel exhaust, due to the PM deposition. This deposition can cause filter choking and therefore filter regeneration is required at about 600°C. These effects cause more fuel consumption, which is not appropriate for low emission production and fuel economy. Furthermore, DPFs are inefficient in trapping small nanoparticles under 100 nm (Yezerets et al., 2003).

Considering the increasing environmental concerns and stringent emission standards, there is an imperative to develop new strategies for emission reduction. Non-thermal plasma (NTP) technology has shown notable potential for emission control in various applications (Jidenko and Borra, 2012, Vandenbroucke et al., 2011a, An et al., 2014, Obradović et al., 2011, Mizuno, 2007). Plasma is the fourth state of matter that can be considered as an ionised gas. In the plasma state, sufficient energy is provided to free electrons from atoms or molecules and to allow species, ions and

electrons, to coexist. Based on the relative temperature of the gas, plasmas can be classified into thermal and non-thermal plasma (NTP) (Fridman, 2008, Talebizadeh et al., 2014). In non-thermal plasma, the kinetic energy (temperature) of charged particles and kinetic energy (temperature) of background gas are similar (Fridman et al., 2005). In the NTP application for exhaust emissions reduction, the input electrical energy is transferred to the electrons, which generates free radicals through collisions of electrons and promotes the desired chemical changes in the exhaust. While the applied electric energy in NTP reactors will be consumed for the purpose of breaking the bonds in the parent molecules, there is no sensible heating of the gas, and discharged energy is not lost either in heating up the gas or to the surroundings (Mukkavilli et al., 1988).

A variety of research studies, concerning different aspects of NTP application for NOx removal, have been documented in the literature (Vinh et al., 2012c, Mohapatro and Rajanikanth, 2010, Yamamoto et al., 2003a, Arai et al., 2004, Jolibois et al., 2012b, Talebizadeh et al., 2014, Babaie et al., 2012). NTP $NO_x$ reduction generally can be divided in two groups: $NO_x$ removal reactions that result in $NO_x$ reduction to $N_2$ and NO to $NO_2$ conversion reactions, which is more dominant (Penetrante, 1994, Rajanikanth et al., 2004). Moreover, NTP has been used in packed bed reactors and in combination with catalysts to achieve higher efficiency. Rajanikanth and Rout (Rajanikanth and Rout, 2001) investigated the effect of three kinds of dielectric pellets (Alumina, Alumina coated with palladium and Barium titanate) for $NO_x$ removal. They used gas cylinders of NO in $N_2$, CO and $O_2$ to simulate the vehicle exhaust. The results obtained showed that the presence of the packed dielectric bed increases the discharge power and NO removal efficiencies. They found NO removal of 84%, 72% and 100% for Almunia, Almunia coated with palladium and Barium titanate pellets, respectively. Ravi et al. (Ravi et al., 2003b) studied the conventional dielectric barrier discharge (DBD) plasma reactor combined with an SCR catalyst ($V_2O_5$-$WO_3$/$TiO_2$) for a simulated gas. It was found that the rate of NO oxidation to $NO_2$ decreases with temperature and NO removal efficiency at a temperature of 100°C was shown to be 88% for an energy input of 30 J/L.

In comparison with the large amount of research conducted on the influence of plasma on $NO_x$ removal, much less has been dedicated to the effect of plasma on PM removal. Okubo et.al employed indirect or remote NTP for DPF regeneration (Li and Liu, 2000, Chang, 2001, Kanazawa et al., 1998, Urashima et al., 1998, Okubo et al., 2004). In their method, the NTP-treated air was injected into the exhaust, which causes the NO oxidation to $NO_2$. This induced $NO_2$ and produced activated oxygen species by plasma oxidise deposited carbon soot on the DPF surface. Song et.al considered the PM, hydrocarbons (HC) and $NO_x$ removal by DBD plasma reactor, simultaneously (Song et al., 2009). They studied the effect of peak voltage, frequency and engine load on diesel emission

removal. Their frequency was varied from 10 to 20 kHz and across most voltages, the maximum discharge power and consequently maximum removal efficiency, was at the frequency of 15 kHz. Based on their experiments, the maximum PM, HC and $NO_x$ removal approached 80%, 70% and 65%, respectively.

As discussed above, NTP has been found to be very effective for PM, and HC reduction. Few studies on PM removal of diesel engines have been conducted in the literature and removal mechanisms have not been studied extensively (Ye et al., 2005, Babaie et al., 2013b, Talebizadeh et al., 2014). Furthermore, most of the research in this area has considered simulated diesel exhaust instead of actual exhaust. Therefore, the results can be different from the actual diesel operating conditions, since the diesel exhaust is a complex mixture of thousands of gases and plasma chemistry and related electron impact reactions may vary considerably.

The purpose of this paper is to investigate the effect of NTP on reduction of PM and $CO_2$ emitted by a diesel engine at different discharged voltages and frequencies. In addition, the mechanism of PM removal has been discussed in detail and the effect of ozone as the key parameter for PM removal has been highlighted.

## 7.2 EXPERIMENTAL APPARATUS AND METHOD

### 7.2.1 Experimental setup

The experiments have been conducted using a modern turbo-charged 6 cylinder Cummins diesel engine. The engine has a capacity of 5.9 L, a bore of 102 mm, a stroke length of 120 mm, compression ratio of 17:3:1, and maximum power of 162 kW at 2500 rpm. All experiments have been conducted at a speed of 1500 rpm and at the load of 160 Nm to achieve the most uniform diesel exhaust performance. For all experiments, diesel exhaust from the exhaust pipe was passed through the dilution tunnel before flowing into the DBD reactor. The role of the dilution tunnel is to reduce the temperature and concentration of exhaust before flowing into the measurement instruments. By manipulating the flow direction at the reactor inlet using a three way valve, the emission concentration has been measured before and after plasma treatment. The schematic diagram of the experimental set-up is shown in Figure 7.1.

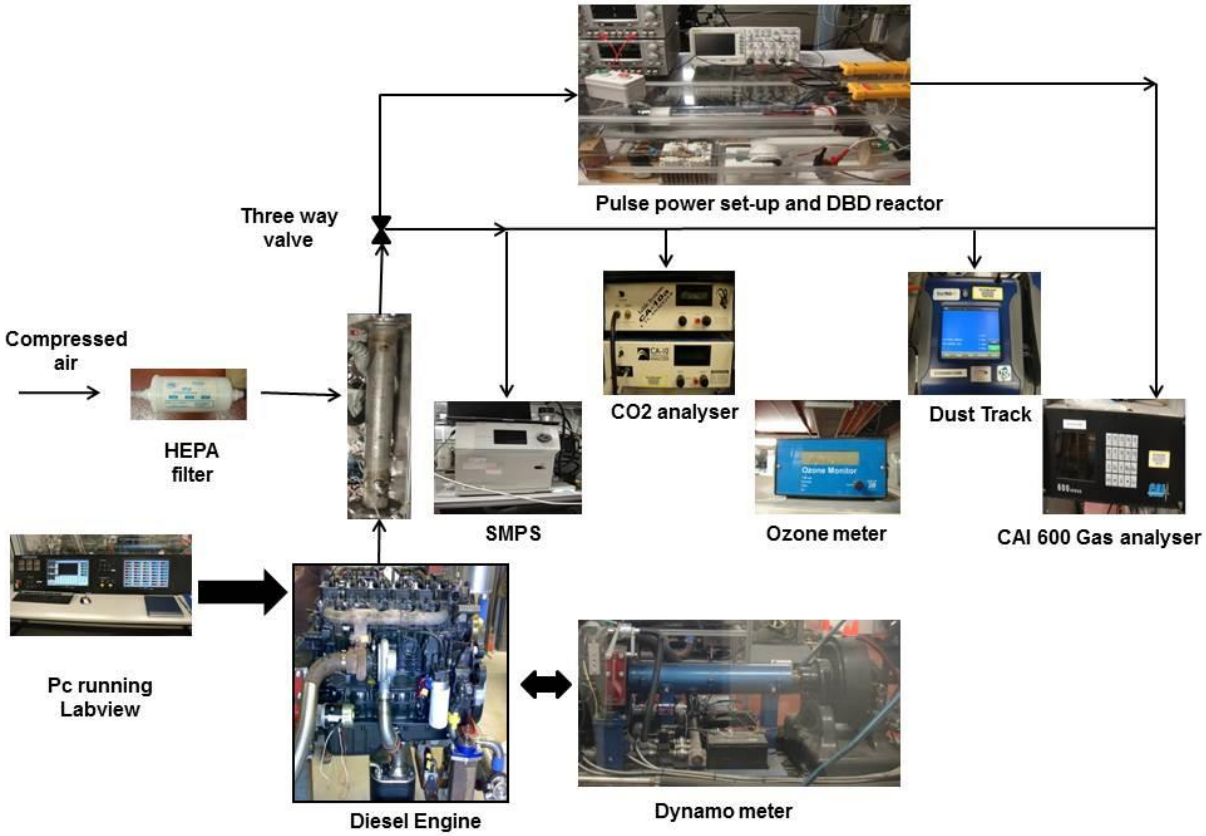



Figure 7.1: Schematic diagram of the experimental setup.

### 7.2.2 Dielectric barrier discharge reactor

In all experiments, a conventional DBD reactor was used, as shown in Figure 7.2. The overall dimensions of the DBD were also shown in this figure as well. It consists of two concentric quartz tubes with dimensions of 400 mm long and wall thickness of 1.5 mm. The outer diameters of the tubes are 20 and 25 mm, respectively. The diesel engine exhaust generated by the diesel engine was passed through the gap between these two quartz tubes. With its predesigned geometry, the discharge gap was 1 mm. The reactor is equipped with external and internal electrodes which can be energised through a pulsed power supply. The internal electrode is a copper cylinder and the external electrode is made of copper coil that wraps the exterior part of the outer quartz tube. The electrodes were located in the middle of the DBD reactor, the length of which was 100 mm. The quartz tubes were installed by using two Teflon caps at both ends of the DBD reactor. The diesel exhaust enters the reactor at the angle of 45° and then flows throughout the gap; it leaves the reactor with the same angle as well.

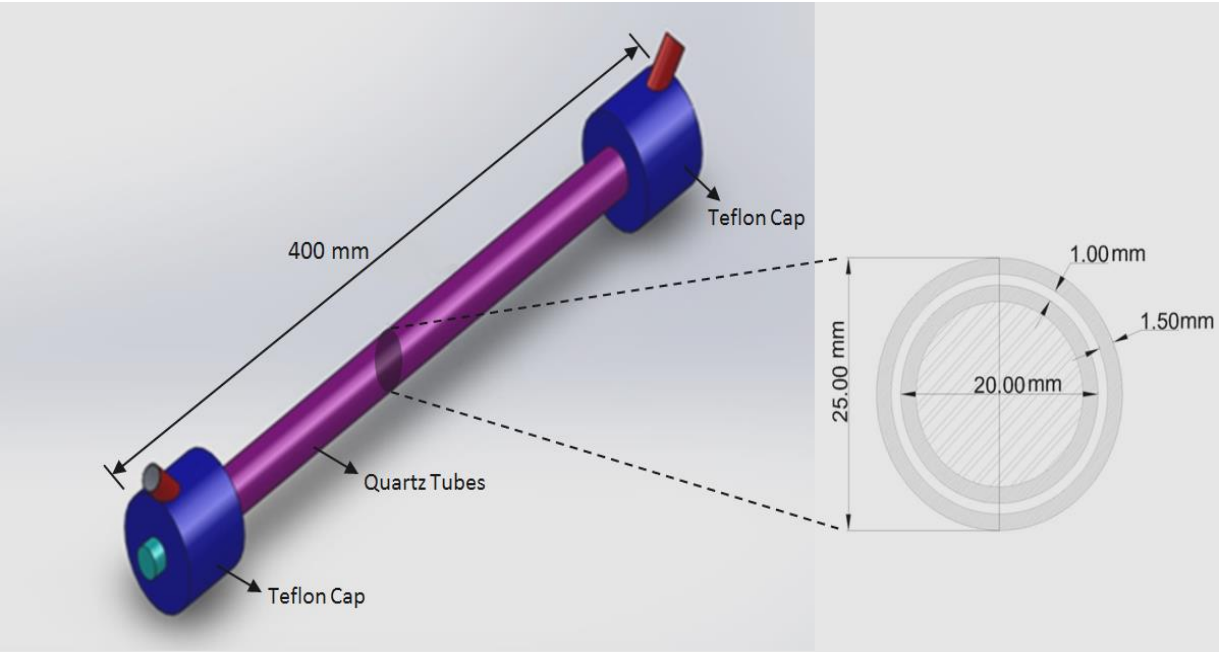



Figure 7.2: Dielectric barrier discharge reactor

### 7.2.3 Electrical and pulsed power system

Rapid release of stored energy as electrical pulses into a load, thereby resulting in the delivery of large amount of instantaneous voltage over short period of time, is known as pulsed power. Pulsed power technology has been previously considered by different researchers in different applications (Akiyama et al., 2007, Tehrani et al., 2014). Furthermore, pulsed power technology for NTP generation in pollution control application has gained a lot of advantages (Babaie et al., 2013a, Shimomura et al., 2011, Matsumoto et al., 2009, Namihira et al., 2001b, Hackam and Akiyama, 2001, Talebizadeh et al., 2014) and using power electronics topologies in pulsed power applications is recognised as being quite beneficial, particularly in terms of having efficient, cost effective and high power density (Babaie et al., 2013a, Shimomura et al., 2011, Matsumoto et al., 2009, Namihira et al., 2001b, Hackam and Akiyama, 2001, Davari et al., 2012b).

For all experiments in this research, a bipolar pulsed power supply is employed to sustain NTP and prevent it from arcing. The employed topology is based on a push-pull inverter (Babaie et al., 2013b, Davari et al., 2012c, Davari et al., 2013). Due to the capacitive behaviour of the DBD load, it is possible to put the push-pull inverter in resonant mode and generate semi-sinusoidal waveforms at the output. Figure 7.3A depicts a typical measured voltage waveform ($V_0$) with a peak-to-peak value of 21 $kV_{PP}$ at repetition rate ($f_r$) of 2.5 kHz. The detail of the pulsed power supply hardware setup was fully explained in (Davari et al., 2013).

In order to extract and analyse important electrical properties such as power consumption of the DBD reactor, the V-Q Lissajous method as a standard process for diagnostics of DBD systems has been used (Pipa et al., 2012, Hong, 2013, Davari et al., 2013). To measure Q, an auxiliary capacitor is placed in series with the DBD. Thus, by measuring the voltage across the auxiliary capacitor and multiplying its value by capacitance, it is possible to calculate Q. It should be noted that value of the auxiliary capacitor should be large enough so as not to affect the DBD capacitance. The area of V-Q curve (Figure 7.3B) at different operating points is a measure of the energy consumption per pulse of the DBD reactor. By multiplying the calculated areas with the employed repetition rate, the power consumption of the DBD reactor can be determined. The relevant equations are as follows:

$$W = \oint Q(t)dv \tag{7.1}$$

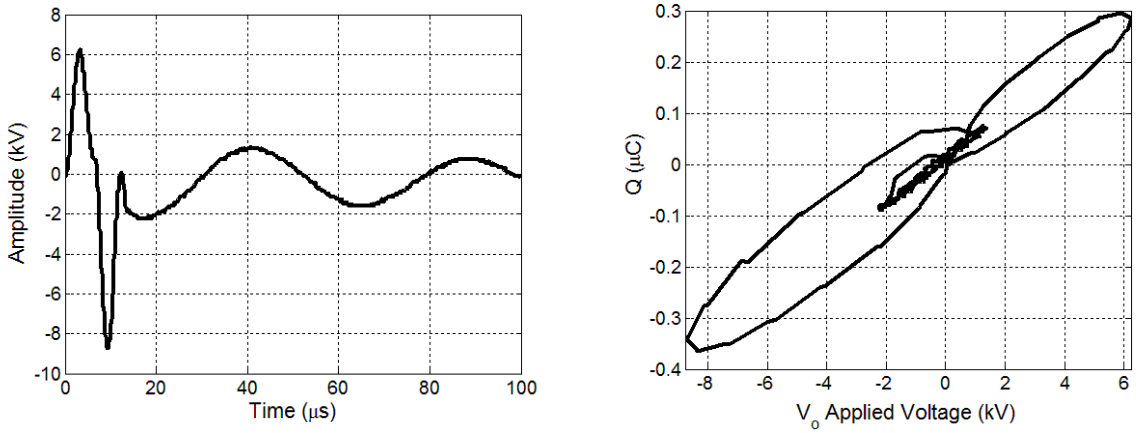
$$C(t) = \frac{d\,Q(t)}{d\,V(t)} \tag{7.2}$$

Substituting the capacitance equation into energy equation:

$$W = \oint \frac{Q(t)}{C} dQ = \frac{1}{2} CV^2 \tag{7.3}$$

DBD power consumption is calculated as:

$$P_{average} = W \times f = f \times \oint \frac{Q(t)}{C} dQ = \frac{1}{2} CV^2 f \tag{7.4}$$




(A) (B)

Figure 7.3: Typical measurement at 21 kVpp and 2.5 kHz (A) applied voltage waveform, (B) V-Q plot with the area of 17.15 Watts

## 7.3 RESULTS AND DISCUSSION

When plasma is introduced inside the exhaust emissions, oxidation processes will be started and NOx, unburned hydrocarbons, and particulate matter can be oxidised (Babaie et al., 2013b). In addition, due to the effectiveness of NTP on the removal of a variety of species inside the exhaust, the concentration variation of a special component may affect the other species differently during the experiments. In this paper, different contour plots have been presented to evaluate the effect of NTP on discharge power, ozone production, $CO_2$ and PM concentrations. All these parameters have been plotted against voltage and frequency using a minimum-to-maximum mesh grid, with interpolation for every single unit of frequency and voltage using MATLAB version 2013a. In the following sections, the contour plots of discharge power, ozone, $CO_2$ and PM at different voltages and frequencies are discussed separately, and then the interrelation between them under different plasma operating conditions has been studied.

### 7.3.1 Discharge power evaluation

Discharge power is one of the main challenges of NTP applications, so the analysis of the DBD reactor electrical characteristics has been considered at a range of voltage level and operating frequency. Output voltage ($V_0$) and repetition rate ($f_r$) were designated as controlling parameters to determine the transferred power. The high voltage pulses were applied to the reactor at six different voltage levels including 11, 13, 15, 17, 19 and 21 $kV_{PP}$ and four different repetition rates of 2.5, 5, 7.5 and 10 kHz. The 24 operating points are selected, based on a combination of varied operating frequencies and voltages, to evaluate the behaviour of the DBD reactor at varied power levels.

Figure 7.4 shows a contour plot of the discharge power at different frequencies and voltages calculated from Eq.7.4. The values of discharge power for the area in yellow are very low. Due to the insufficient level of the applied voltage, the effect of plasma has not been observed in this area. Hence, varying the applied voltage and repetition rate does not affect the discharge power (Song et al., 2009).

The slope of the discharge power contour plots is about 45° and it increases with the applied voltage levels, correspondingly. This means that the discharge power has been influenced by the applied voltage more than the repetition rate, especially by approaching the higher voltage levels. This finding can be confirmed from Eq. 7.4 since the discharge power is related to the applied voltage squared.

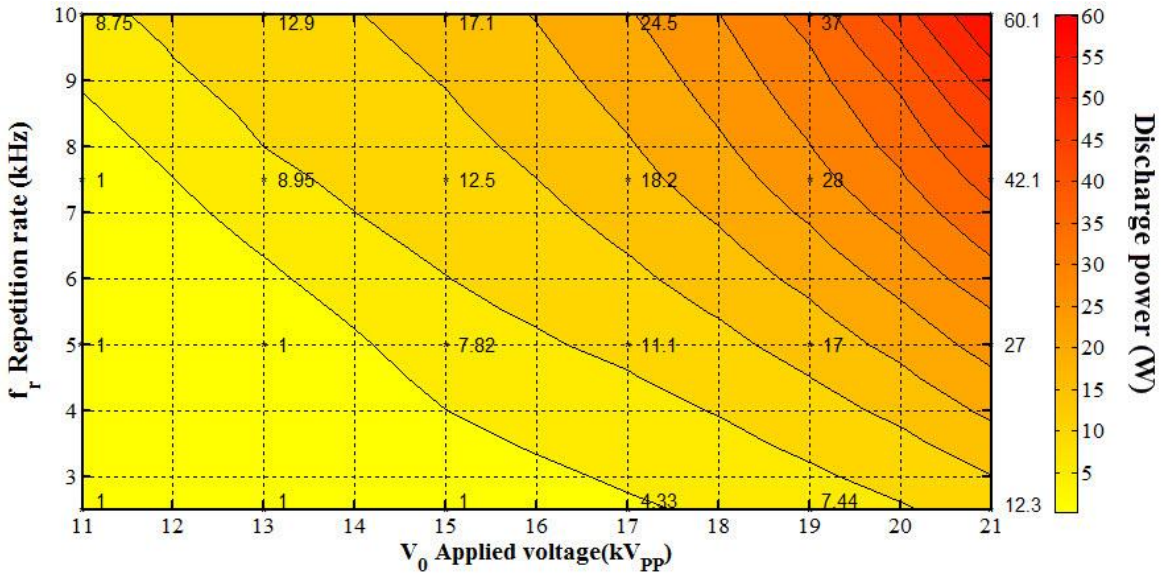



Figure 7.4: Discharge power at different applied voltages and frequencies

### 7.3.2 Effect of NTP on $CO_2$ concentration

The dissociation of $CO_2$ molecules after applying plasma is due to the electron impact reactions, which can reduce the $CO_2$ concentration. Moreover, different active oxygen species can be involved in $CO_2$ concentration reduction. The common removal mechanism of $CO_2$ can be summarised by the following equations (Fridman, 2008, Spencer, 2012, Indarto et al., 2008):

$$CO_2 + O \rightarrow CO + O_2 \quad 7.5$$

$$CO_2 + O_2 \rightarrow CO + O_3 \quad 7.6$$

$$e + CO_2 \rightarrow CO + O + e \quad 7.7$$

$$e + CO_2^* \rightarrow CO + O \quad 7.8$$

$$2CO_2 + 2N_2^* \rightarrow 2CO + O_2 + 2N_2 \quad 7.9$$

where $CO_2^*$ and $N_2^*$ are the excited forms of $CO_2$ molecule and $N_2$ molecule, respectively and the produced CO from varied reactions is in different levels of energy (Fridman, 2008, Spencer, 2012, Indarto et al., 2008)

Figure 7.5 shows a contour plot of normalised $CO_2$ concentration as a function of applied voltage and frequency. As pulse frequency and applied voltage increase, the concentration of $CO_2$ is reduced. This reduction is due to the higher electric field and higher discharge power, which can be obtained by an increase of the applied voltage and frequency. At higher discharge power, electrons

will gain more energy to start the electrons' impact reactions and the electrical field can be powerful enough to excite the carbon dioxide molecules. Therefore, the probability of producing free electrons and ions is higher and the above mentioned reduction equations are more likely to occur, thus decomposing more $CO_2$.

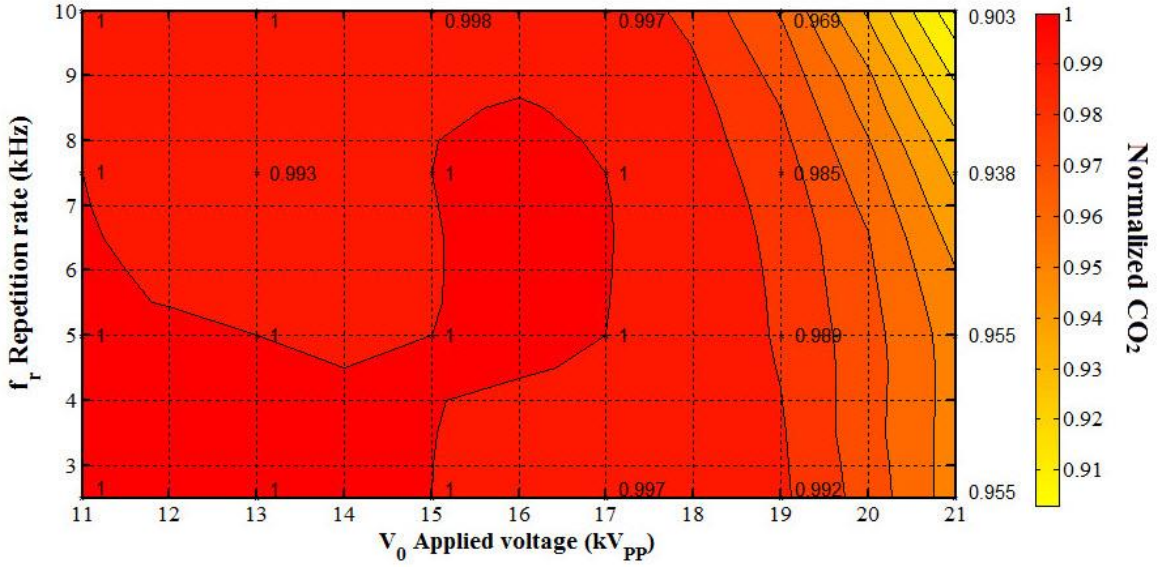



Figure 7.5: Effect of pulse frequency and applied voltage on normalised $CO_2$

As the obtained results show (Figure 7.5), $CO_2$ contours are close to vertical, especially at high voltages and low frequencies. This implies that at high voltage levels, the variation of repetition rate ($f_r$) does not affect the concentration of $CO_2$ significantly and the applied voltage has a greater impact on $CO_2$ decomposition of diesel exhaust.

Moreover, Figure 7.5 shows that a given amount of $CO_2$ removal efficiency can be achieved by more than one operating point. Therefore the possibility of achieving a high $CO_2$ decomposition at lower energy consumption levels can be optimised. For example, for an applied voltage level of 21 kVpp at a repetition rate of 2.5 kHz (Case 1) and the voltage level of 17 kVpp at 10 kHz (Case 2), the concentration of $CO_2$ is found to be almost the same. However, from Figure 7.4, the discharge power for Case 1 and Case 2 are 24.5 W and 12.3 W, respectively. Therefore, the discharge power for Case 2 is almost half of Case 1 with the same amount of removal efficiency. This shows the possibility of operating the system at lower power consumption levels while maintaining its removal efficiency.

### 7.3.3 Effect of NTP on PM concentration

Carbonaceous PM or soot in plasma treated gas can be incinerated by $NO_2$, $O_3$ and activated oxygen components according to the following reactions (Kim et al., 2002, Okubo et al., 2010b, Okubo et al., 2008):

$$C + 2NO_2 \rightarrow CO_2 + 2NO \quad 7.10$$

$$C + NO_2 \rightarrow CO + NO \quad 7.7$$

$$2C + NO_2 \rightarrow 2CO + 2N_2 \quad 7.8$$

$$2C + 2NO_2 \rightarrow 2CO_2 + N_2 \quad 7.9$$

$$2C + 2O_3 \rightarrow 2CO_2 + O_2 \quad 7.10$$

$$C + O_3 \rightarrow CO + O_2 \quad 7.11$$

The first two reactions occur at oxygen rich conditions and the last two in oxygen lean conditions. Note that $NO_2$ exists in the exhaust and it will be increased under plasma conditions. $NO_2$ can be formed from the oxidation of NO in oxygen rich conditions and is also due to NO reaction with $O_3$ and other radicals of O and OH under plasma conditions. On the other hand, $NO_2$ and $O_3$ will be consumed for PM incineration reactions as presented by Eq.7.11.

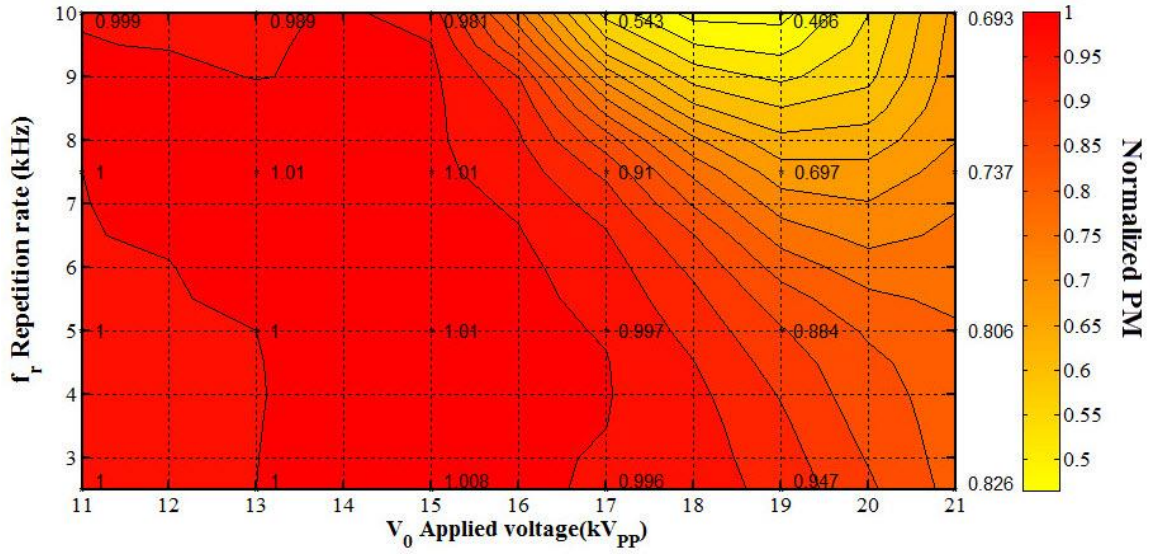



Figure 7.6: Effect of pulse frequency and applied voltage on normalised PM mass concentration

Figure 7.6 is the contour plot of normalised PM mass concentration as a function of applied voltages and repetition rates. Generally it is found that by increasing the voltage level and repetition rate, PM concentration is decreased. As shown, the optimum value for PM concentration occurs at a voltage level of 19 kVpp and repetition rate of 10 kHz. At higher frequencies, such as 7.5 and 10 kHz, the minimum value of PM concentration has been found at 19 kVpp, which is just less than the maximum applied voltage. The reason for the PM removal decrease at high repetition rates, after

approaching the optimum value of applied voltage, will be explained in more detail in section 7.3.5. Briefly, at lower repetition rates (2.5 and 5 kHz) the normalised PM has been decreased continuously by increasing the applied voltage. Therefore, the optimum value of PM removal may occur at even higher voltage levels for the two aforementioned repetition rates. It can also be observed that at high voltages, normalised PM is always decreased by increasing the pulse repetition rate.

### 7.3.4 Effect of NTP on ozone concentration

Ozone is produced by many devices, such as electronic air cleaners, laser printers and copiers, which rely on atmospheric discharges (Chen and Davidson, 2002). Ozone participates in many reactions in plasma treated gas and it can be considered as one of the main factors in NTP exhaust treatment. The main reaction for ozone production in the plasma state is the reaction of the O radical with oxygen, based on the following reaction (Arai et al., 2004, Chang et al., 1991b):

$$O_2 + O + M \rightarrow O_3 + M \qquad 7.12$$

where M is a third-body collision partner.

In addition, as was shown in previous sections, ozone will be consumed through Eq.7.10 and Eq.7.11. Furthermore, the ozone will be consumed by the following reactions for plasma exhaust treatment (Arai et al., 2004, Obradović et al., 2011, Vinh et al., 2012a):

$$N + O_3 \rightarrow NO + O_2 \qquad 7.13$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad 7.14$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad 7.15$$

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \qquad 7.16$$

Therefore, ozone will be produced over some conditions and consumed in other conditions during plasma treatment. Figure 7.7 displays the contour plot of ozone concentration as a function of applied voltage and repetition rate. As displayed in this figure, by increasing the applied voltage, ozone concentration increases after formation of plasma inside the exhaust. If the applied voltage increases, a higher electric field will be generated and then more O radicals will be formed inside the exhaust. The concentration of ozone is also increasing, by increasing the pulse repetition rate during the experiments (Lukes et al., 2005, Penetrante et al., 1997). This trend can be observed at all voltages and repetition rates except for 21 kVpp and 10 kHz. At this state, due to the high amount of discharge power (60.1 W) and also high concentration of nitrogen atoms inside the exhaust emission,

the destruction of ozone could occur (Eq.7.10) (Lukes et al., 2005). Moreover, oxygen saturation inside the reactor at this high discharge power level can be reached, which results in reduction of ozone concentration.

Another interesting finding is that for the low applied voltages, ozone concentration is almost constant and it is not changed by increase of the repetition rate. It shows the weakness of plasma at those operating conditions and also a higher dependency of plasma to the voltage level rather than to the repetition rate. Furthermore, since the plasma is weak at this voltage range, low rate of O radical can be produced and therefore the ozone production and reduction rate is almost the same.

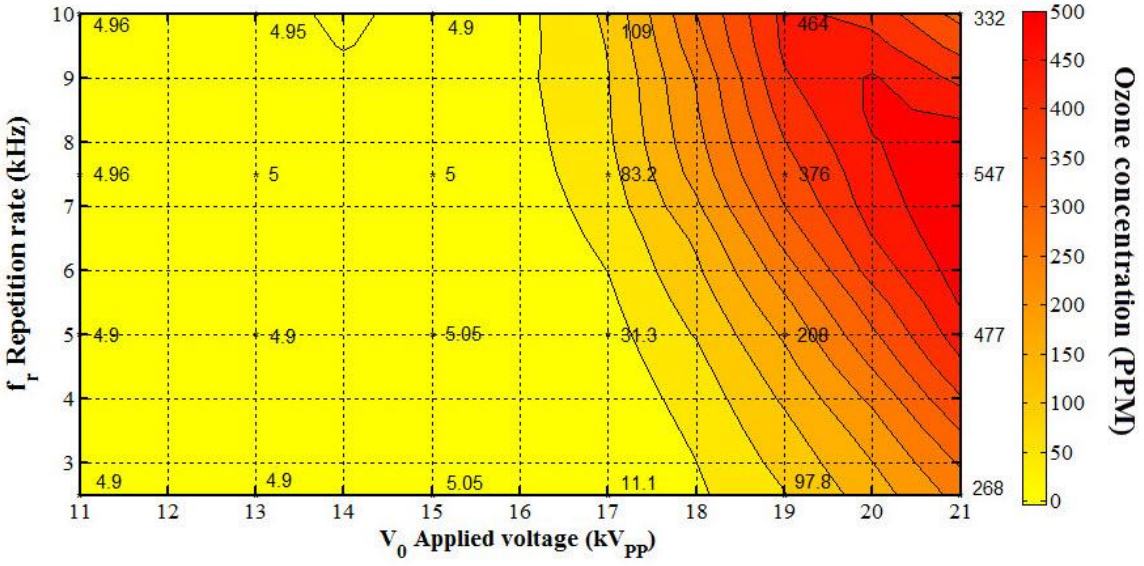
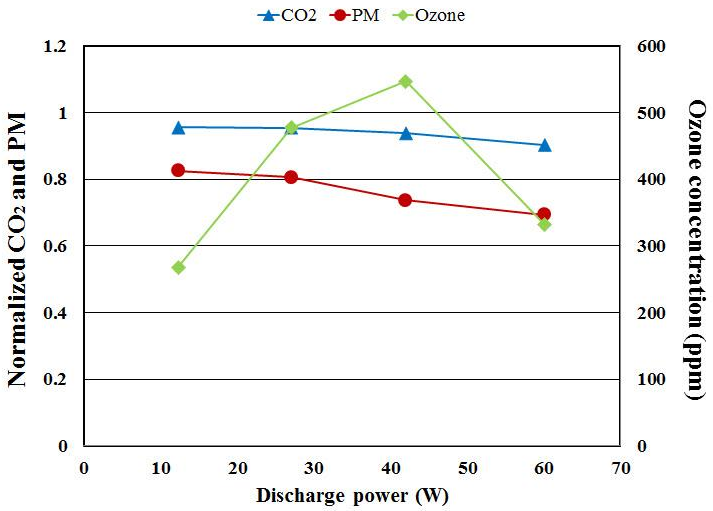


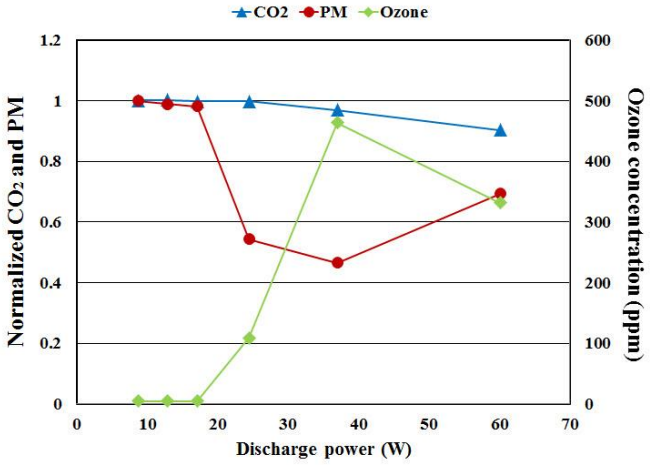

Figure 7.7: Effect of pulse frequency and applied voltage on ozone concentration

### 7.3.5 Interrelationship of ozone, $CO_2$ and PM concentration

As already discussed, the highest performance of NTP can be achieved at higher voltage levels and repetition rates. Figure 7.8A and Figure 7.8B show the variation of ozone, $CO_2$ and PM as a function of discharge power at 21 $kV_{PP}$ for different repetition rates, and at 10 kHz for different voltage levels, respectively. In both figures, $CO_2$ decreases slightly with the increase of applied voltage and repetition rate. Moreover, by increasing the repetition rate at 21 $kV_{PP}$ the concentration of ozone increases except at 10 kHz (Figure 7.8A), and with increasing the applied voltage, ozone concentration increases except at 21 $kV_{PP}$ (Figure 7.8B). As displayed in Figure 7.8A, PM concentration decreases continuously for all the studied repetition rates. However, at 10 kHz the PM concentration increases slightly at 21 $kV_{PP}$ after a continuous decrease (see Figure 7.8B).




(A)




(B)

Figure 7.8: The variation of ozone, $CO_2$ and PM as a function of discharge power A) at 21 $kV_{PP}$ for different pulse frequencies B) at 10 kHz frequency for different applied voltages

To provide a better understanding of plasma behaviour, time dependent diagrams of $CO_2$, PM and ozone concentration have been plotted at different voltage levels and repetition rates. As depicted in Figure 7.9-Figure 7.11, at each operating condition the diesel exhaust was passed through the plasma reactor for a period of 180 seconds and all results have been plotted. The advantage of analysing the measured results is to understand the correlation between ozone, $CO_2$ and PM under plasma conditions.

As shown in Figure 7.9, regardless of applied repetition rate, normalised $CO_2$ concentration generally decreases with an increase of voltage level. However, at low repetition rates and voltage levels, plasma has not made any sensible changes in $CO_2$ concentration. As clearly shown, when the voltage level reaches 19 kVpp, plasma starts to dissociate $CO_2$ molecules for all frequencies.

However, the effectiveness improves by increasing the repetition rate. $CO_2$ does not show significant variation during the test period (180 s) except at 21 $kV_{PP}$ where the maximum $CO_2$ removal can be obtained. At 21 $kV_{PP}$, a continuous decrease of $CO_2$ concentration during the experiment can be observed for all repetition rates due to the high amount of discharge power. Therefore, it can be concluded that the threshold discharge power for $CO_2$ dissociation in diesel exhaust is higher than the plasma formation threshold.

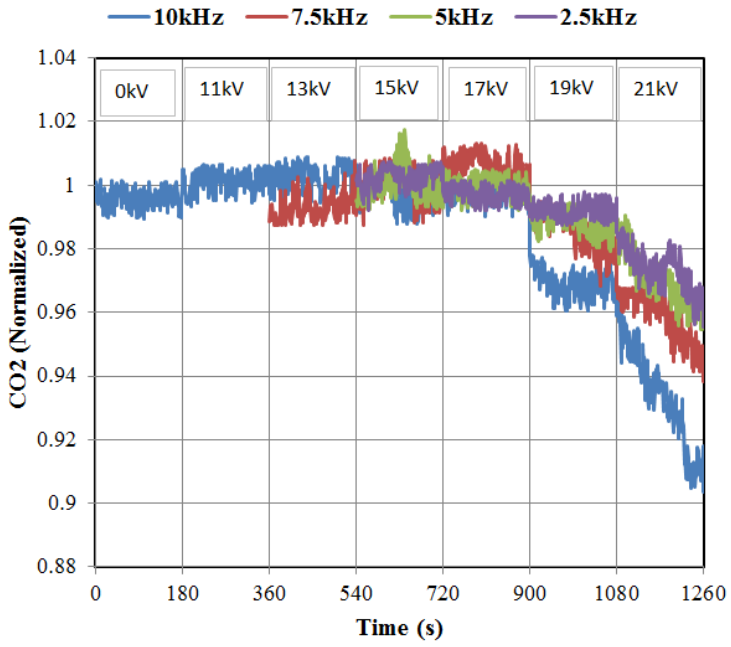



Figure 7.9: Normalised $CO_2$ as a function of time at different applied voltages and different frequencies

To study PM concentration variation at varied operating conditions, the obtained measurements have been illustrated in Figure 7.10. PM concentration decreases slightly before a voltage of 17 $kV_{PP}$ especially as the repetition rate increases. From this point on (17 $kV_{PP}$), PM concentration starts to decrease significantly while for each repetition rate, this reduction starts at a different voltage level. Generally, for all ranges of voltage level, the obtained PM removal at 7.5 kHz and 10 kHz is higher compared to two other repetition rates. It is interesting that the maximum drop is at 17 $kV_{PP}$ with repetition rate of 10 kHz, while the minimum PM concentration occurs at the same repetition rate with 19 $kV_{PP}$. Furthermore, for the voltage levels of 19 $kV_{PP}$ and 21 $kV_{PP}$ at the frequency of 10 kHz, and also for the voltage of 21 $kV_{PP}$ at frequency of 7.5 kHz, PM concentration is increasing over the time period of the experiment. This important finding is explained in conjunction with the ozone data from Figure 7.11.

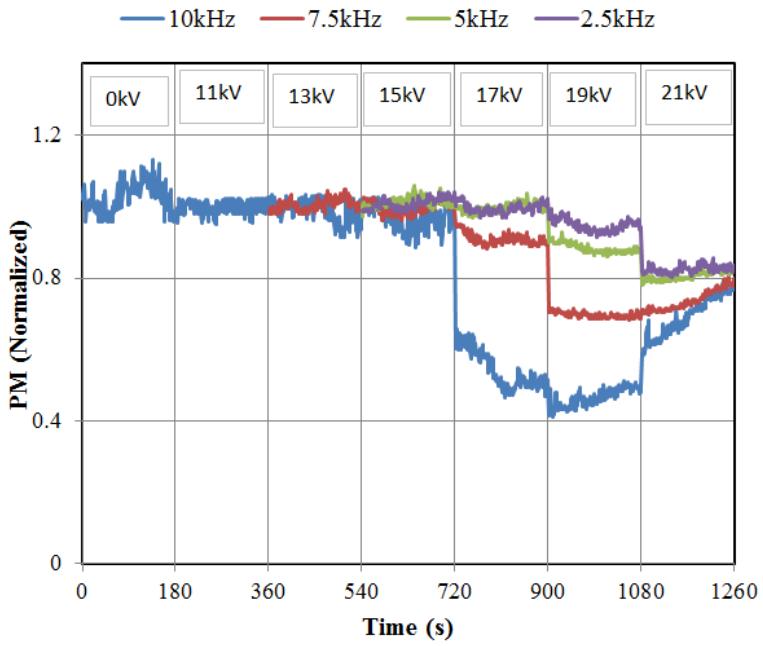



Figure 7.10: Normalised PM as a function of time at different applied voltages and different frequencies

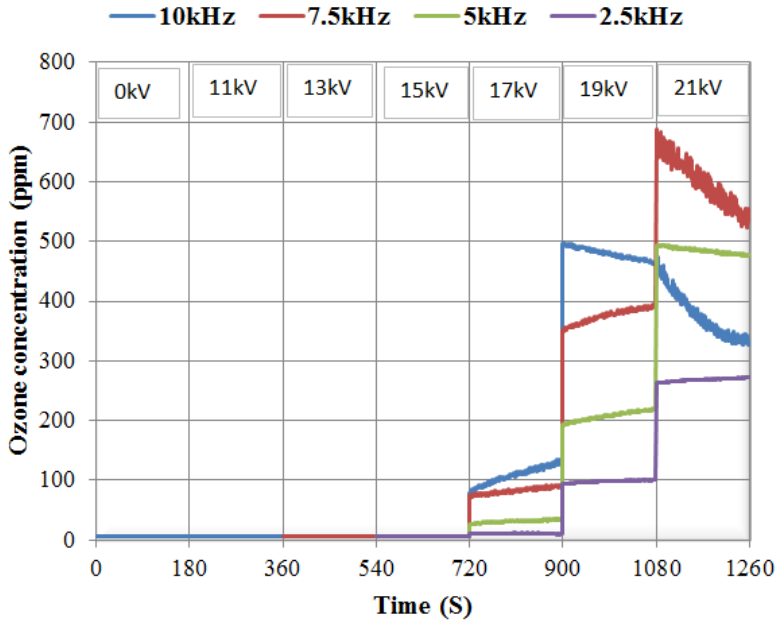



Figure 7.11: Ozone concentration as a function of time at different applied voltages and different frequencies

Figure 7.11illustrates the concentration of ozone over the time period of experiments. Ozone concentration is very low below the voltage level of 17 $kV_{PP}$ regardless of the applied repetition rates, which implies no ozone production by NTP at these levels. When the applied voltage approaches 17 $kV_{PP,}$ ozone concentration increases significantly for all repetition rates. The ozone concentration at 17 $kV_{PP}$ is almost constant over the period of study for 2.5 and 5 kHz. However, it increases slightly at 7.5 kHz and more significantly at 10 kHz. For 19 $kV_{PP}$, ozone concentration

increases at 2.5, 5 and 7.5 kHz with different gradients over the period of study. On the other hand, in the same period of time, ozone concentration has been decreased continuously at 19 $kV_{PP}$ and 10 kHz. This trend is in contrast with the PM concentration trend obtained from Figure 7.10 at the same operating points. Thus, decreasing the ozone concentration, a lesser amount of PM can be removed by the DBD plasma reactor at this state. The same trade-off can be observed between ozone and PM at 21 kVpp for repetition rates of 7.5 and 10 kHz as well. As can be seen in Figure 7.9 $CO_2$ concentration at 21 $kV_{PP}$ and 10 kHz will be constant and even increase to some extent at the end of the time period of the experiment. This can be due to the reduction of ozone and also PM oxidation at this state. Therefore, ozone is found to be a key parameter for PM removal from diesel exhaust, which should be considered in all plasma emission treatment applications.

Furthermore, a slow transient response has been observed in Figure 7.11 at 10 kHz, when voltage increases from 19 kV to 21 kV. The reason can be the increase in energy loss for 21 kV at high frequencies. Fluctuation in level of applied voltage is possible at this voltage because the electronic part heating has been observed during the experiment. The reactor could be reached to maximum possible ozone production level at 19 kV. It means it is not possible to observe further increase in ozone level while the ozone level cannot remain the same due to the energy lessees and it is decreasing during the experiment. This issue should be considered in future research.

## 7.4 CONCLUSION

In this paper, the NTP technique has been employed for emission reduction of actual diesel exhaust. NTP has been introduced inside the diesel exhaust by using a DBD reactor. Measurements have been conducted before and after introducing plasma inside the reactor to illustrate the effect of NTP on diesel emissions. The effect of NTP on PM, $CO_2$ and ozone has been considered experimentally and the interrelationship between them has been clarified. Discharge power has been calculated at each operating point by means of the V-Q Lissajous method. Discharge power has been found to increase continuously by increase of the applied voltage and frequency, and the maximum value of 60.1 W has been obtained for discharge power at 10 $kV_{PP}$ and 10 kHz. NTP was found to be effective for PM removal and $CO_2$ reduction while a considerable amount of ozone has been produced during the experiments.

The minimum value for PM concentration has been achieved at the applied voltage of 19 kVpp and a repetition rate of 10 kHz. Discharge power, emission reduction and ozone production have been influenced by variation of applied voltage more than the repetition rate. The correlation study of emissions showed the key role of ozone in PM reduction. $CO_2$ concentration was decreased continuously by increasing the voltage level at all repetition rates over the time period of study,

except at the end of the test with voltage level of 21 kVpp at 10 kHz, due to the reduction in ozone concentration. Furthermore, an opposite trend has been observed in the concentration of ozone and PM. For all operating conditions when ozone is increasing at the beginning of experiments, PM concentration has been decreased continuously. However, at 19 kVpp/10 kHz, 21 kVpp/10 kHz and 21 kVpp/7.5 kHz, reduction of ozone production by plasma over the time resulted in PM concentration being increased due to the PM oxidation reduction. The effect of NTP in emission reduction applications is more pronounced in time dependant analysis and it is strongly recommended for use in future research instead of using the simple averaging method.

# Chapter 8: Influence of non-thermal plasma after treatment technology on regulated and unregulated emissions from a diesel engine

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Publication: Under review by Fuel Journal

**Author Contribution**

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| P. Talebizadeh | Assisted with preparing the manuscript and Data analysis |
| M. A. Islam | Assisted with PROMETHEE-GAIA data analysis |
| Y. Zama | Supervised the experiments |
| M. Arai | Supervised the project, aided with the development of the paper and data analysis |
| T. Furuhata | Supervised the experiments |
| H. Rahimzadeh | Supervised the project, Aided with the development of the paper |
| Z. Ristovski | Supervised the project, Aided with the development of the paper and data analysis |
| R. J. Brown | Supervised the project, aided with the development of the paper, data analysis and extensively revised the manuscript |

**Principal Supervisor Confirmation**

I have sighted email or other correspondence from all co-authors confirming their certifying authorship.

| Name | Signature | Date |
|---|---|---|
| Associate Professor Richard Brown | R. J. Brown | 30/09/2014 |


**Abstract**

Regulated and unregulated emissions from diesel engines have remained as one of the enduring environmental concerns of past decades. Recently, non-thermal plasma (NTP) has been considered as a method of pollution reduction in different applications. In this work, a dielectric barrier discharge (DBD) reactor has been employed to study the effect of plasma on diesel exhaust emissions. A variety of regulated and unregulated emissions has been examined under different plasma operating conditions. During the experiments, applied voltage was changed from 7.5 kV to 13.5 kV with the step of 1.5 kV in order to provide different discharge powers into the exhaust. By using the NTP technique, $NO_x$ and total hydrocarbon (THC) concentration decreased by about 18.4% and 18.8%, respectively. However, an increase in total aldehydes has been observed when the applied voltage approached 13.5 kV. PROMETHEE-GAIA analysis is used to facilitate the interpretation of our data. This analysis has revealed that some emissions, such as CO, NO, $NO_2$, $N_2O$ and THC have been affected more by changing the applied voltage. It has also been found that THC decrease by plasma is more relevant to the $C_2H_4$ concentration reduction.



**Keywords*:*** Non-thermal plasma, Regulated and unregulated emissions, Diesel engine, Dielectric barrier discharge

## 8.1 INTRODUCTION

Diesel fuels basically consist of a range of hydrocarbons, while the carbon amount is roughly about 2,778 gr of carbon per gallon of fuel (Facts, 2005). Therefore, only carbon dioxide ($CO_2$), water ($H_2O$) and excess air are expected to remain after a complete combustion. However, as a result of incomplete combustion and/or reactions of fuel additives, lubricant oil and non-hydrocarbon constitutes, diesel exhaust is a complex mixture of hundreds of chemical components and pollutants such as carbon monoxide (CO), nitrogen oxide ($NO_x$), hydrocarbons (HC), particulate matter (PM), etc.

Diesel emissions can be considered in two main categories, regulated and unregulated emissions. There are some limits for regulated engine emission concentrations of diesel exhaust, which are defined by emission standards. Primarily, under most of the diesel exhaust emission standards, only $NO_x$ ($NO+NO_2$), CO, PM and HC have been regulated. However, a lot of unregulated pollutant components such as sulfur oxides, aldehydes, polycyclic aromatic hydrocarbons, usually with low concentration, exist in diesel exhaust after the combustion process (Kašpar et al., 2003). In spite of their low concentrations, in some cases they are highly toxic. For example, benzene in diesel exhaust (which is directly related to the aromatic content of the fuel) is a serious source of potential health concern (Kaiser et al., 1991).

Recently, some of the unregulated diesel emissions such as carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) are considered by greenhouse gas (GHG) regulations (Baumert et al., 2005, LaHood, 2010). $CO_2$ is the main GHG emissions of internal combustion engines, which is originated from carbon oxidation of the fuel and so directly depends on engine fuel combustion. $N_2O$ is in the category of nitrogen oxides, while it is not included in $NO_x$ emission standards. Regarding the diesel exhaust pollutant, greenhouse gas regulations in most circumstances are separate from emission standards and they can be considered as respective classes of control technologies (Majewski, Revision 2012.08). Moreover, other emission pollutants will likely be added to forthcoming emission standards, due to increasing health and environmental concerns around the world (Kim and Lee, 2006, Yao et al., 2006a, Hasan et al., 2011). Therefore, it is important to consider unregulated emissions together with regulated pollutants in detailed emission research applications.

The health effects of diesel emissions have been emphasised in literature (Ristovski et al., 2012, Sydbom et al., 2001b) and lately diesel exhaust has been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC, 2012). However, the side effects are not limited to regulated emissions only. Different diesel emitted hydrocarbons and other chemical components, such as aldehydes, 1,3-butadiene and polycyclic organic materials, are

reported to be carcinogens with various levels of toxicity (Loh et al., 2007). The carcinogenic and mutagenic features of unsaturated hydrocarbons have been testified by many studies (Melnick et al., 1994, Huff et al., 1985). Thus, it is crucial to address these concerns, either by in-cylinder control technologies (Agarwal et al., 2013, Maiboom and Tauzia, 2011) or by after treatment systems (Maiboom and Tauzia, 2011, He et al., 2010, Biswas et al., 2009).

Non-thermal plasma (NTP) has been considered as a promising technology for exhaust emission treatment in various research studies (Wang et al., 2010, Vinh et al., 2012b, Jolibois et al., 2012b, Babaie et al., 2013b). Matter exists in four states: solid, liquid, gas and plasma. Plasma can be formed either by heating, which is called thermal plasma, or by using high electrical energy which is non-thermal plasma (NTP). NTP has attracted a lot of attention in different applications such as food processing, medical treatment, ozone generation etc. (Kogelschatz, 2003, Moreau et al., 2008). In plasma state, the electrons can get enough energy to leave their orbits and move out of the molecular force influence. Therefore, in plasma state, there are a lot of free electrons, ions, excited molecules and radicals. Since free radicals and ions are highly reactive, they can recombine with other atoms and/or molecules to produce new components (EPA, 2005). For example, nitric oxide (NO) as one of the exhaust components is a molecule containing one oxygen and one nitrogen atom in its normal state. In plasma state, it can be reduced to $N_2$ by N radicals or oxidised into $NO_2$ by other free radicals and ions such as O, OH and $O_3$ (Basfar et al., 2008). The capability of NTP on $NO_x$ reduction has been discussed in literature and different aspects of this technique for $NO_x$ removal have been evaluated in a variety of publications (Basfar et al., 2008, Leipold et al., 2006, Lin et al., 2004, Mohapatro and Rajanikanth, 2011b, Vinh et al., 2012c). NTP showed a good potential for PM removal too; however, the number of publications about PM and other emissions are limited compared to the diversity of research about $NO_x$ (Song et al., 2009, Babaie et al., 2013b, Okubo et al., 2007).

Hence, the objective of this research is to clarify the effect of NTP technology on regulated, and especially on unregulated, emissions discharged from diesel engines. More than 20 different gas species have been evaluated under six different NTP operating conditions. Among regulated emissions, the potential of the NTP technique on reduction of $NO_x$ (including NO, $NO_2$ and $N_2O$), CO and hydrocarbons (including C1-C7) have been tested. In addition, NTP influence on other unregulated components such as 1, 3-butadiene and benzene emissions, together with the other hydrocarbons, has been discussed. Some of the tested compounds have rarely been considered in the literature, especially for NTP exhaust treatment applications.

## 8.2 EXPERIMENTAL

### 8.2.1 Engine specification

The experimental engine was a 0.4-litre, four-stroke, two-cylinder, indirect injection diesel engine with a swirl chamber type (Kubota, Z-402E). The engine specification is presented on Table 8-1in detail. During the experiments, engine load was kept constant at 2 kW and all the tests have been directed under steady state conditions. To get the steady state condition, a warm-up period of 30 minutes has been considered after starting the engine. A sample of diesel exhaust at constant flow rate of 3Lit/min has been passed through a Dielectric Barrier Discharge (DBD) reactor to introduce plasma inside the exhaust for all experiments. The diesel exhaust has been cooled down to room temperature before passing through the DBD reactor. A schematic diagram of the experimental setup is shown in Figure 8.1.

Table 8-1: Summary of engine specifications

| | |
|---|---|
| Engine name | Kubota Z402-E |
| Engine type | 4-stroke E-TVCS Diesel engine |
| Displacement (cc) | 400×two cylinder |
| Bore×stroke | 64×62.2 |
| Cooling type | Water cooled |
| Rated output (kVA) | 7.28 |
| Rated Speed ($min^{-1}$) | 3600 |
| Fuel | JIS No.2 diesel fuel or equivalent |

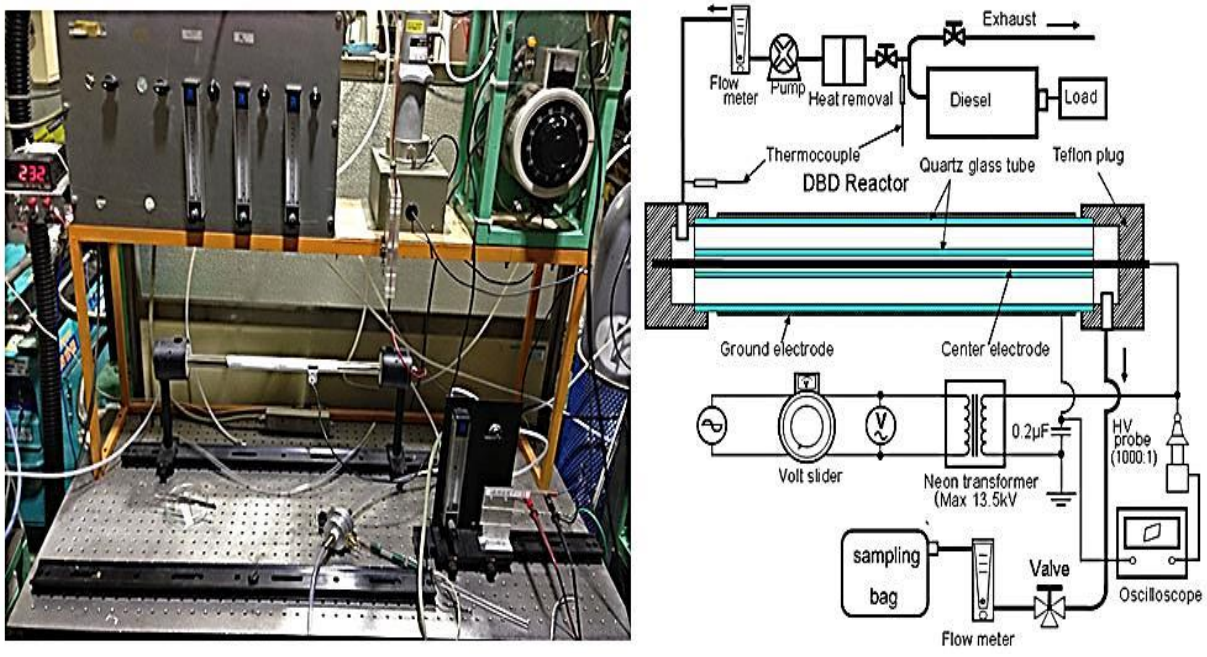



Figure 8.1: Schematic diagram of experimental set up

### 8.2.2 Dielectric barrier discharge (DBD) reactor

For these experiments, a Dielectric Barrier Discharge (DBD) is used to produce plasma inside the exhaust emission. The DBD is very common in plasma emission treatment applications due to the formation of stable and homogeneous plasmas, effectiveness, low operational cost and its compact size (Kogelschatz, 2003). The DBD reactor used for these experiments is made up of two concentric quartz tubes, which are stoppered by heat resistant Teflon caps on both ends. Diesel exhaust passes through the gap between these two quartz tubes. Based on the given configuration, the discharge gap has been 3 mm. The high voltage electrode is a stainless steel rod with diameter of 6 mm, which is passed through the inner glass tube. Aluminum foil was wrapped over the surface of the outer glass tube as the ground electrode. AC voltage provided by a commercial power supply at 50 Hz has been applied between the electrodes to form plasma inside the exhaust. Applied voltage has been changed from 7.5 kV up to 13.5 kV with the step of 1.5 kV at constant frequency of 50 Hz during the experiments. As has been shown in Figure 8.1., a 0.2 μF capacitor was installed between the ground and high voltage electrode to find the stored charge in the DBD reactor and the charge-voltage. The Lissajous technique was used to calculate the discharge power inside the DBD reactor (Nie et al., 2013, Hui et al., 2013) . After obtaining the discharge power, energy density as the ratio of discharge power to the exhaust flow rate can be calculated. The variation of energy density on different voltage levels has been plotted in Figure 8.2.

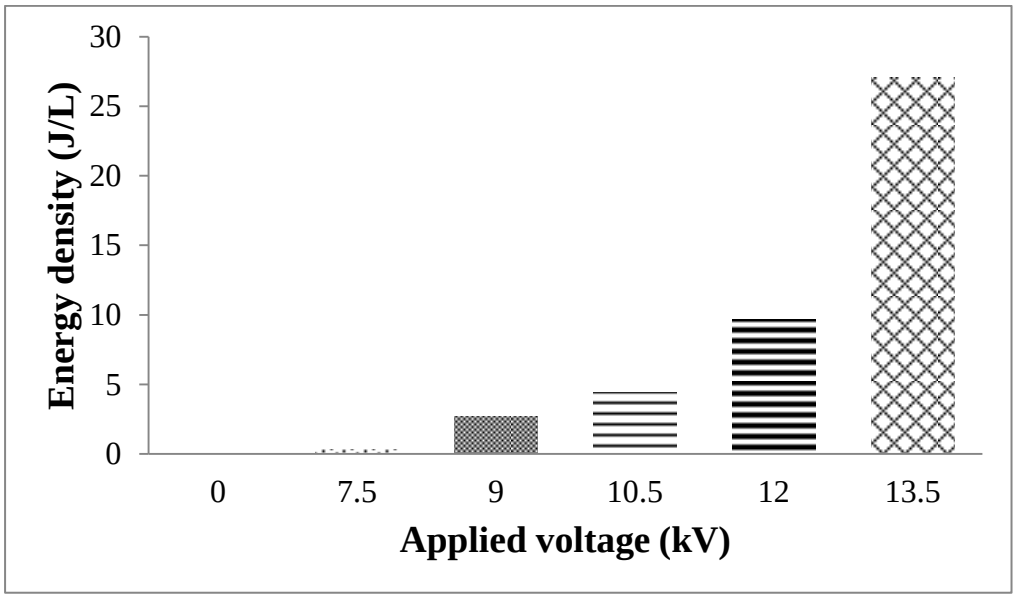



Figure 8.2: Energy density versus applied voltage for plasma DBD reactor

### 8.2.3 Emission measurement apparatus

Exhaust gas samples have been collected by a Tedlar bag after passing through the DBD reactor. Then, collected samples were analysed by an FTIR exhaust gas analyser (Horiba Co., Ltd.,

MEXA-4000FT), which operates based on infrared radiations. The concentrations of about 22 different species including different hydrocarbons, carbon monoxide, carbon dioxide, nitrogen oxides (including NO, $NO_2$ and $N_2O$), sulfur dioxide, formaldehyde etc. have been measured by this instrument for different operation conditions.

## 8.3 RESULTS AND DISCUSSION

All tested gases in this research have been listed in Table 8-2. Moreover, these exhaust emissions have been categorised with respect to the IARC[1] classification regarding the carcinogenic potential to humans. Among the studied gases in this paper, 1,3-butadiene, Benzene and Formaldehyde are classified as carcinogenic to humans (Group 1) while Acetaldehyde is considered as possibly carcinogenic to humans (Group 2B) and ethylene and toluene are classified into Group 3 by IARC.

Table 8-2: List of studied gases

| engine-out compound | Chemical formula | Group | IARC classification |
|---|---|---|---|
| Methane | $CH_4$ | | |
| Ethylene | $C_2H_4$ | | 3 |
| Ethane | $C_2H_6$ | | |
| Propene | $C_3H_6$ | hydrocarbon | |
| 1,3-butadiene | 1,3-$C_4H_6$ | | 1 |
| Benzene | $C_6H_6$ | | 1 |
| Isobutylene | iso-$C_4H_8$ | | |
| Toluene | $C_7H_8$ | | 3 |
| Formaldehyde | HCHO | | 1 |
| Acetaldehyde | $CH_3CHO$ | | 2B |
| Ammonia | $NH_3$ | | |
| Acetone | $CH_3COCH_3$ | | |
| Formic acid | HCOOH | carboxylic acid | |
| Methanol | $CH_3OH$ | alcohol | |
| Nitric oxide | NO | | |
| Nitrogen dioxide | $NO_2$ | | |
| Nitrogen oxides | $NO_x$ | | |
| Nitrous oxide | $N_2O$ | | |
| Carbon monoxide | CO | | |
| Carbon dioxide | $CO_2$ | | |
| Water | $H_2O$ | | |
| MTBE | $(CH_3)_3COCH_3$ | | |
| Sulfur dioxide | $SO_2$ | | 3 |

1: carcinogenic to humans; 2B: possibly carcinogenic to humans; 3: Not classifiable as to its carcinogenicity to humans.

[1] International Agency for Research on Cancer

### 8.3.1 Effect of NTP on nitrogen oxides

Several types of nitrogen oxides exist in the environment: $N_2O$, NO, $NO_2$, $N_2O_3$, $N_2O_4$, $NO_3$, and $N_2O_5$; however, the most common species in emission standards, which are also measured by the FTIR analyser, are NO, $NO_2$, and $N_2O$. In this study, the abbreviation of $NO_x$ is related to a summation of nitric oxide, nitrogen dioxide and nitrous oxide concentrations. Figure 8.3 represents the effect of NTP on $NO_x$ ($NO+NO_2+N_2O$) concentrations for various applied voltages. As can be seen, by increasing the applied voltage, the concentration of total $NO_x$ decreases, due to the occurrence of a series of reactions in plasma state.

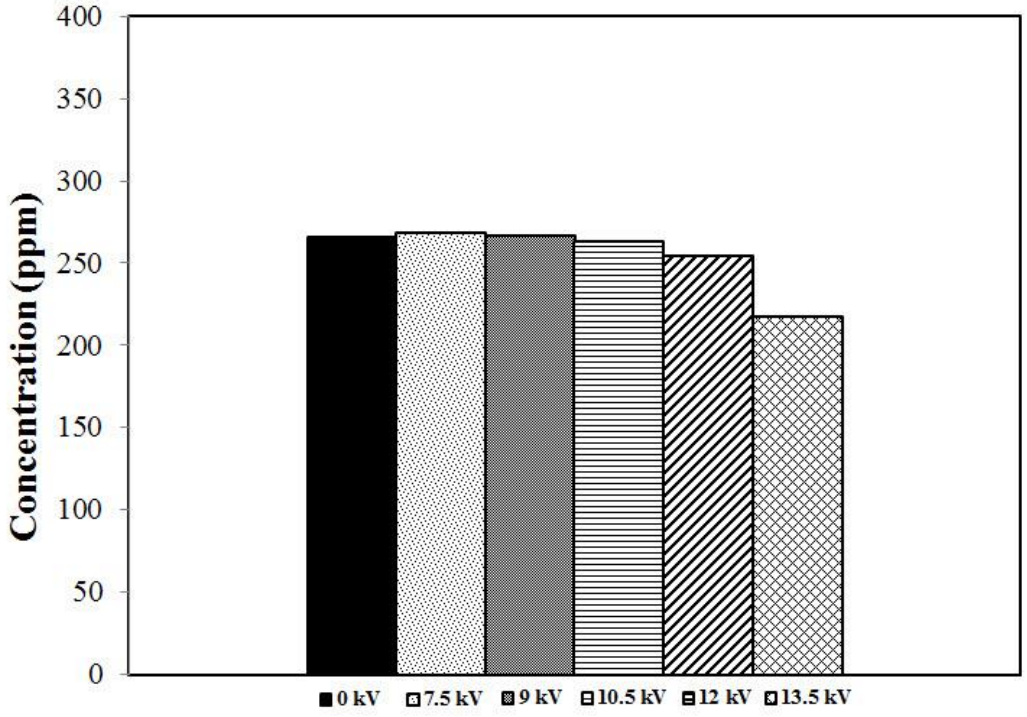



Figure 8.3: Effect of NTP on Nitrogen oxides concentration for different applied voltages

Regarding the $NO_x$ removal by plasma, two main groups of reactions can be considered: NO reduction to $N_2$ and NO oxidation to $NO_2$ (Rajanikanth et al., 2004). In the following, the main responsible reactions for NO and $NO_2$ concentration variations are presented (Penetrante and Schultheis, 1994, Atkinson et al., 1989, Kossyi et al., 1992a, Atkinson et al., 1997, Sathiamoorthy et al., 1999, Zhao et al., 2004):

$$NO + N \rightarrow N_2 + O \quad 8.1$$

$$N_2(A) + NO \rightarrow N_2 + N + O \quad 8.2$$

$$NO_2 + N \rightarrow N_2 + O_2 \quad 8.3$$

$$NO + O \rightarrow NO_2 \quad 8.4$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad 8.5$$

$$NO_2 + N \rightarrow N_2O + O \quad 8.6$$

where $N_2(A)$ represents $N_2$ metastable state.

NO can be removed through Eqs. 8.1 and 8.2 and it can be oxidised to $NO_2$ through 8.4 and 8.5. Regarding the above equations, the concentration of $NO_2$ is increased by Eq.8.4 and 8.5 and it can be decreased by Eq 8.3 and8.6. At the range of discharge power in this paper, an increase in the concentration of $NO_2$ by Eq. 8.4 and 8.5 is stronger than $NO_2$ removal by Eq. 8.3 and 8.6 (Rajanikanth and Ravi, 2002). Furthermore, due to the presence of a high concentration of NO in the exhaust emission (around 210 ppm initially), the drop in $NO_x$ concentration is more related to the decrease of NO concentration by Eq. 8.1 and 8.2.

In addition to the reactions related to NO and $NO_2$, due to the existence of hydrocarbons and soot, more reactions will happen in a plasma state, which helps the reduction of both NOx and hydrocarbons. The possible reactions are discussed as follows (Rajanikanth and Sinha, 2008, EPA, 2005, Majewski, 2004):

$$C_3H_6OHOO + NO \rightarrow C_3H_6OHO + NO_2 \quad 8.7$$

$$NO_2 + \text{soot} \rightarrow CO + CO_2 + N_2 + H_2O + NO \quad 8.8$$

Moreover, due to the presence of water, some other reactions are also involved, which are as follows (Jolibois et al., 2012a):

$$NO + OH \rightarrow HNO_2 \quad 8.9$$

$$NO_2 + OH \rightarrow HNO_3 \quad 8.10$$

$$NO + H_2O \rightarrow NO_2 + OH \quad 8.11$$

Therefore, in addition to the previous equations, the concentration of NO can be decreased by Eq.8.7, 8.9 and 8.11.

### 8.3.2 Effect of NTP on hydrocarbons

In Figure 8.4A to F, the effects of NTP on C1-C7 hydrocarbon species are presented. As shown in Figure 8.4A and B, the methane concentration in exhaust emission is very low and NTP does not affect it too much, however, the Ethylene concentration is reduced by increasing the applied voltage during the experiments. The reduction on Ethylene concentration can be explained in conjunction with nitric oxide and oxygen related reactions. Ethylene can be decomposed by O atoms, which are generated by plasma by the following equation (Saito et al., 2006):

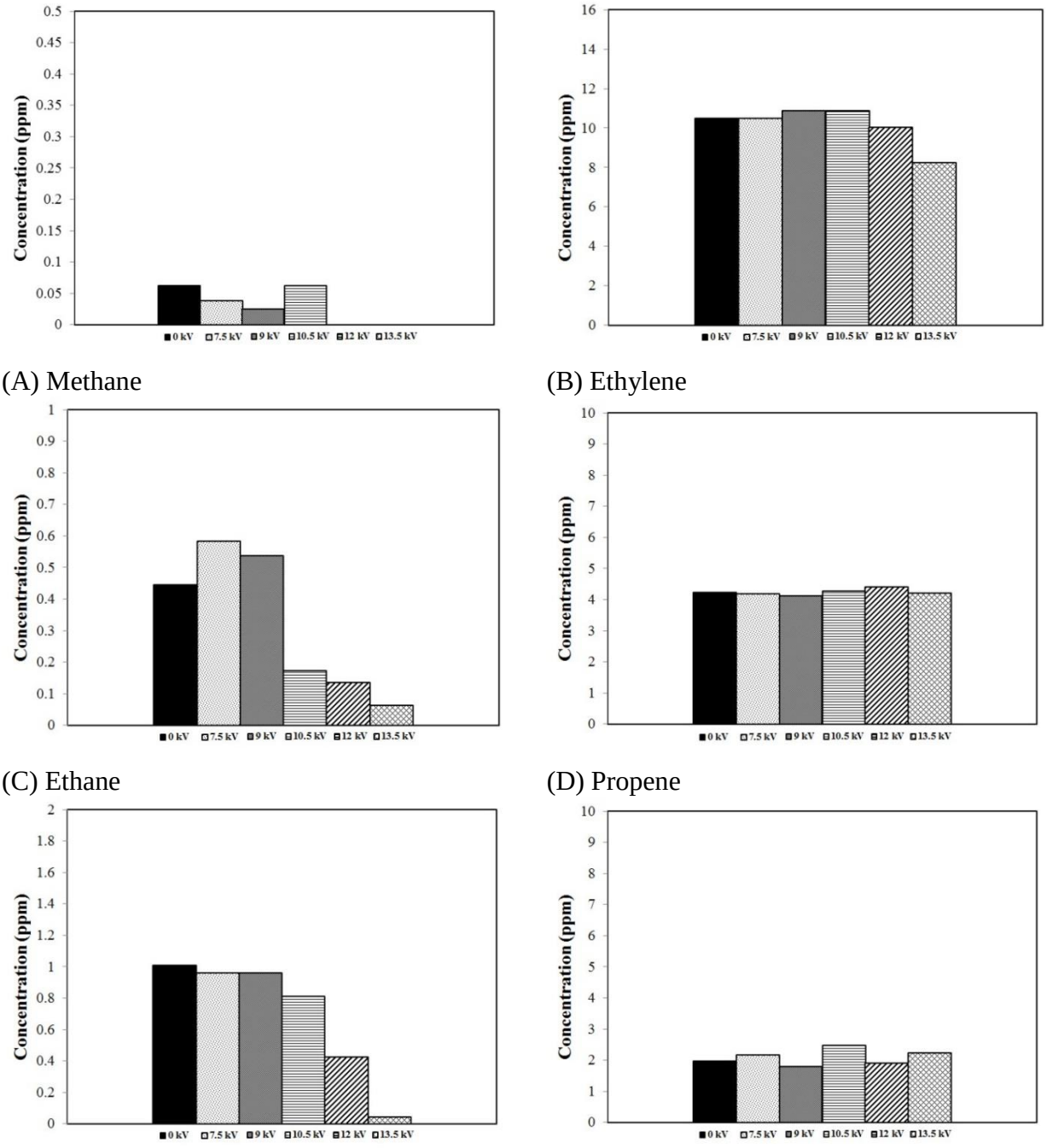
$$C_2H_4 + O \rightarrow CH_3 + CHO \quad 8.12$$

Then, the produced methyl helps the reduction of NO through the following reactions (Saito et al., 2006):

$$CH_3 + O_2 \rightarrow CH_3O_2 \quad 8.13$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad 8.14$$

which results in Ethylene reduction.




(A) Methane (B) Ethylene

(C) Ethane (D) Propene

(E) 1,3-butadiene (F) Toluene

Figure 8.4: The effect of NTP on hydrocarbons for different applied voltages

The concentration of ethane and 1,3-butadiene is found to be reduced by increasing the applied voltage into the exhaust, as shown in Figure 8.4C and E. Nevertheless, from Figure 8.4D and F, the propene and toluene concentrations have not been affected too much by applying the NTP technique. It should be noted that during the experiments, the isobutylene and benzene concentrations were considered as well; however, the concentration was zero based on the FTIR measurement. Therefore, NTP shows a good potential for hydrocarbon reductions, especially for ethane, ethylene and 1,3-butadiene.

To illustrate the effect of the NTP on total hydrocarbons (THC), the measured concentrations of the above hydrocarbons (C1-C7) have been added together and the results are plotted in Figure 8.5. As displayed in this figure, by increasing the applied voltage the total concentration of hydrocarbons decreases continuously and about a 19% decrease in THC concentration can be obtained at 13.5 kV.

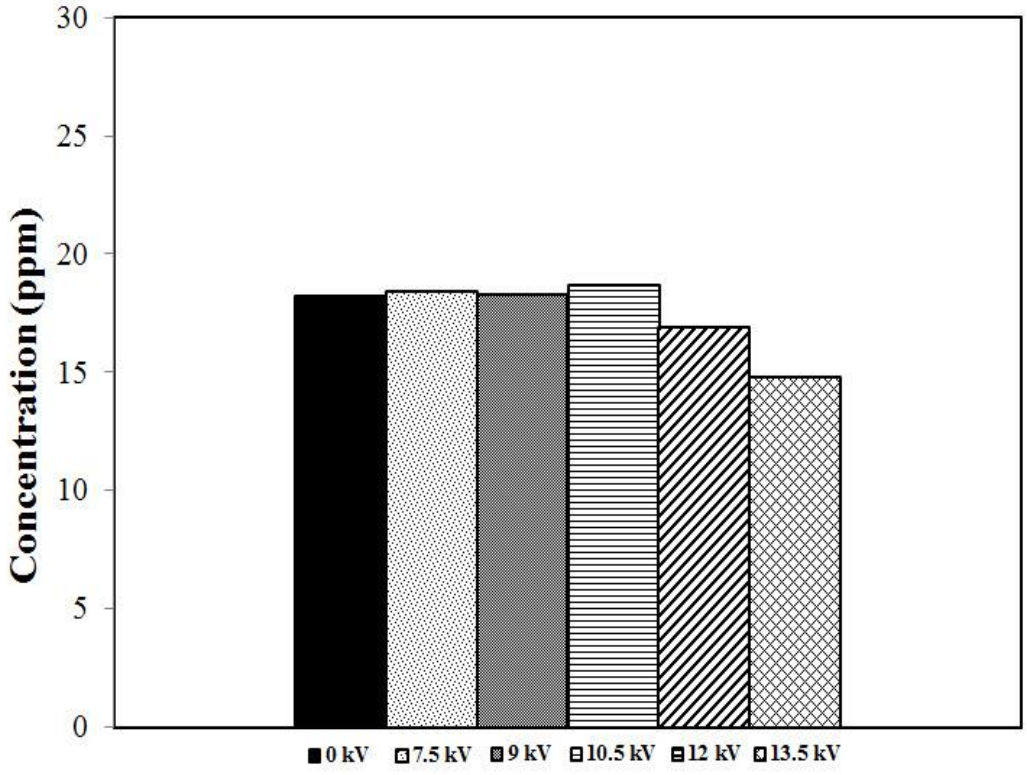



Figure 8.5: The effect of NTP on THC for different applied voltages

### 8.3.3 Effect of NTP on aldehydes

Figure 8.6 shows the variation of the total aldehydes as a function of applied voltage. Two of the most important aldehydes, i.e. formaldehyde and acetaldehyde, have been measured by FTIR during the experiments and the total Aldehyde concentration is considered to be equal to the summation of Formaldehyde and Acetaldehyde concentrations. As displayed in the figure, the total

concentration of Aldehydes is increased by increasing the applied voltage. It can be explained as the following: the O, OH and $O_3$ produced by the plasma react with hydrocarbons and generate alkyl (R), alkoxy (RO), and acyl (RCO) radicals. Then, the alkoxy radicals, such as $CH_3O$, react with oxygen and produce aldehydes such as formaldehyde (Srinivasan and Rajanikanth, 2007b). This effect has been confirmed in Figure 8.7.

Figure 8.7 displays the variation of formaldehyde concentration as a function of applied voltages and Figure 8.8 shows the concentration of acetaldehyde for different applied voltage. As shown in Figure 8.7, by increasing the applied voltage to 12 kV, formaldehyde starts to be produced in the exhaust and then by increasing voltage up to 13.5 kV and getting more powerful plasma, the concentration increases more and gets to 0.7 ppm. However, it is interesting that for the Acetaldehyde, the concentration is continuously increased by increasing the applied voltage to 12 kV, and then a small reduction can be observed at 13.5 kV from Figure 8.8.

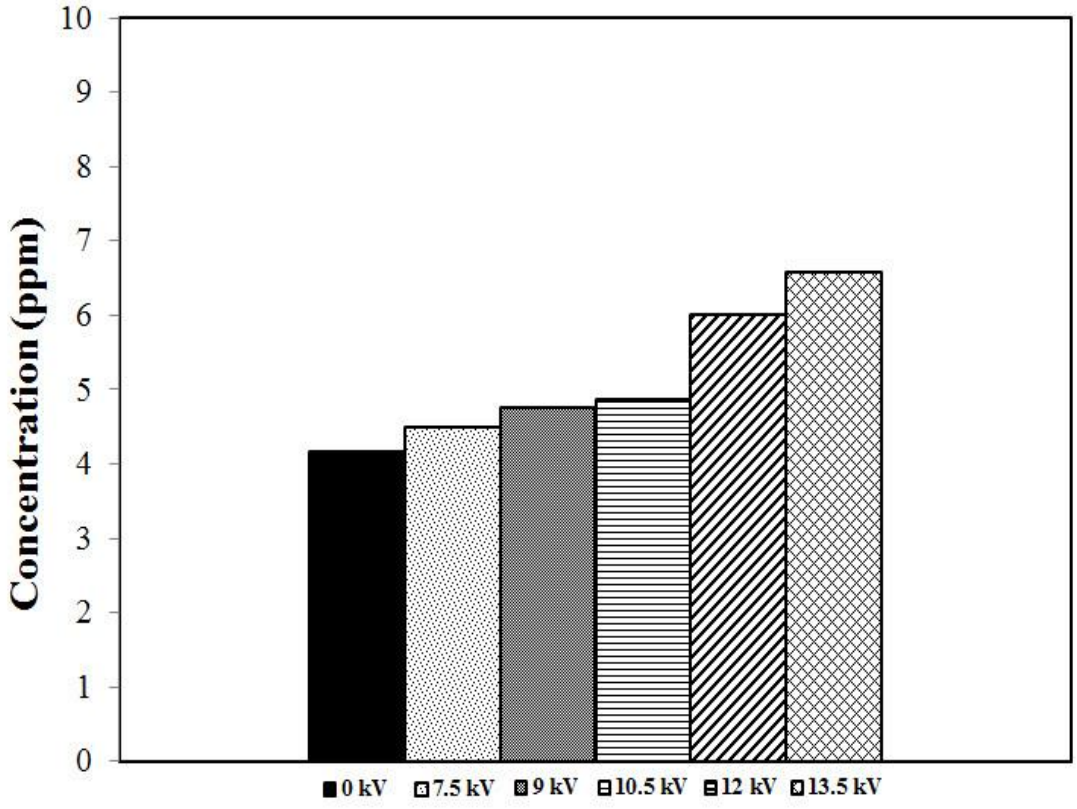



Figure 8.6: The effect of NTP on the total Aldehyde concentration for various applied voltages

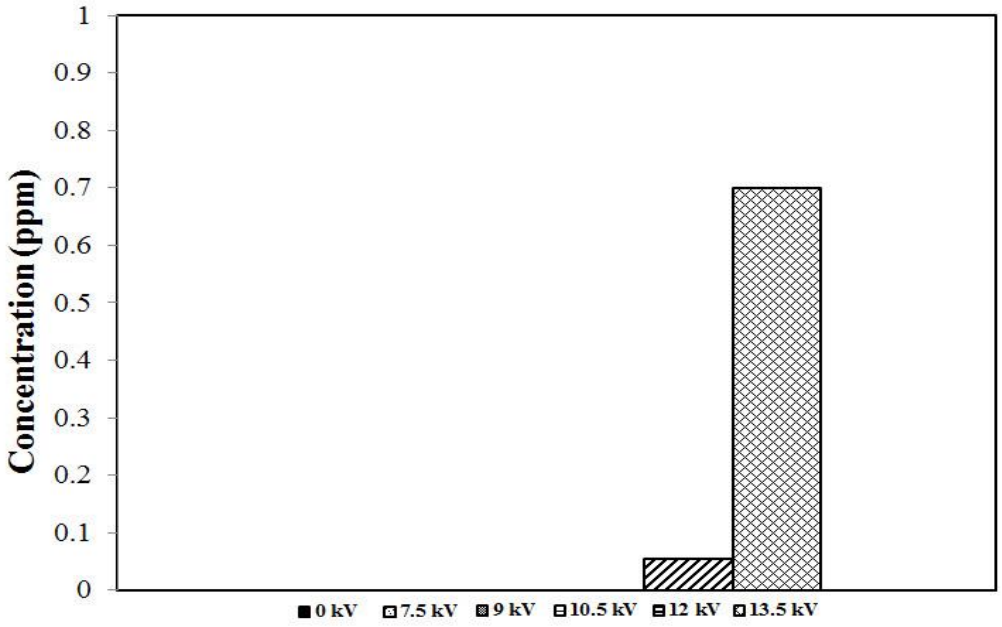



Figure 8.7: The effect of NTP on Formaldehyde concentration for various applied voltages

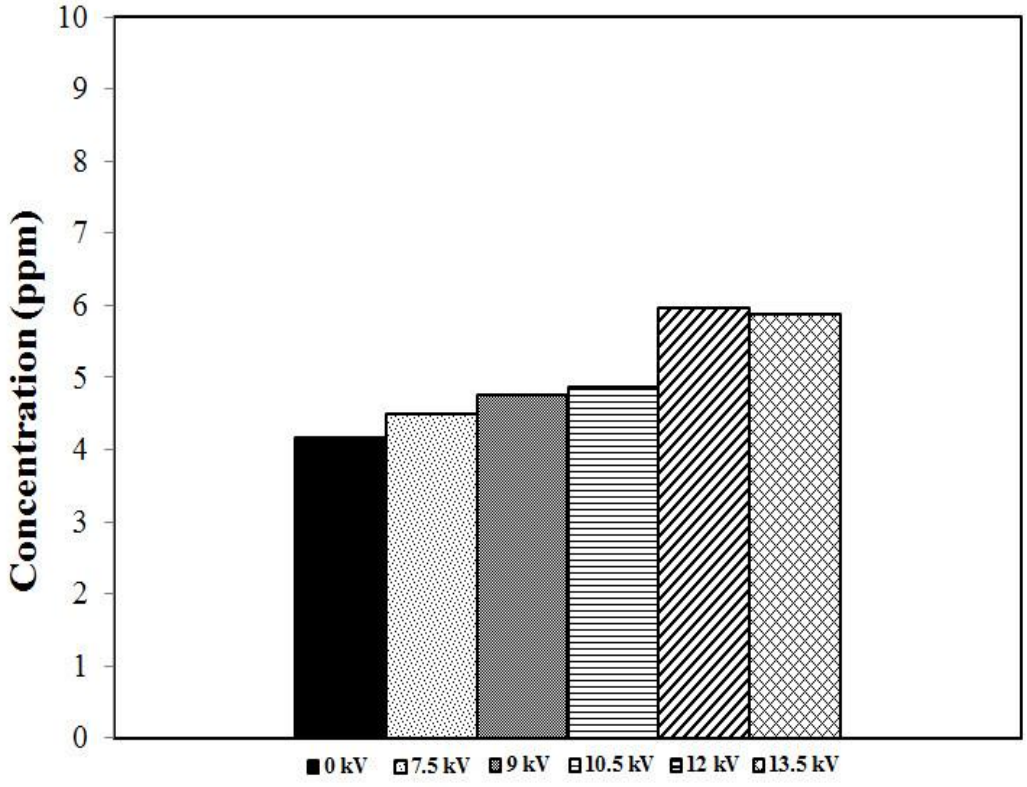



Figure 8.8: The effect of NTP on Acetaldehyde concentration for various applied voltages

### 8.3.4 Effect of NTP on CO, $CO_2$, $H_2O$ and $NH_3$

Figure 8.9 and Figure 8.10 show the CO and $CO_2$ concentration for different applied voltages, respectively. As displayed, the concentration of CO is increased by applying higher voltages while the $CO_2$ concentration does not changing considerably. It means that at the given energy density range (less than 30 J/L), with respect to the amount of oxygen content of the exhaust, hydrocarbons and soot were removed and converted to CO more than $CO_2$ (Thomas et al., 2000b) during our experiments. The removal mechanism can be explained by considering the oxidation of hydrocarbons to CO in the main gas (Yamamoto et al., 2003b, Thomas et al., 2000b). For example, the produced $CH_3O$ from Eq. 8.14 can increase the CO concentration by the following equations (Saito et al., 2006):

$$CH_3O + O_2 \rightarrow CH_2O + H_2O \quad 8.15$$

$$CH_2O + O \rightarrow CHO + OH \quad 8.16$$

$$CHO + O_2 \rightarrow CO + HO_2 \quad 8.17$$

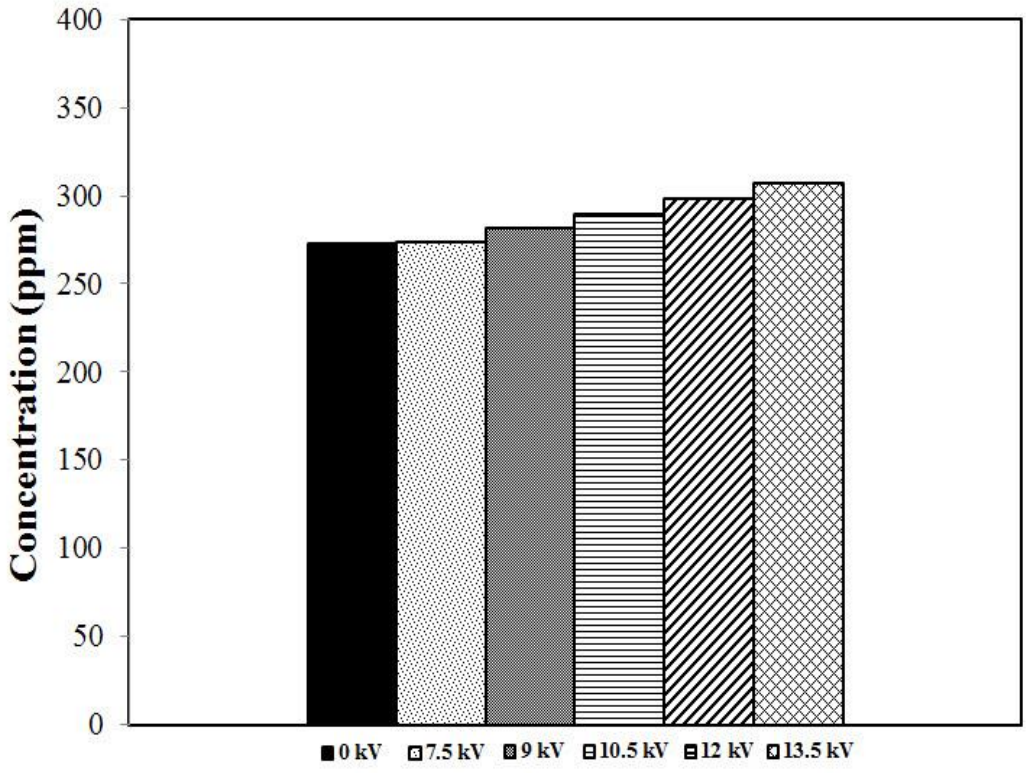



Figure 8.9: The effect of NTP on CO concentration for different applied voltages

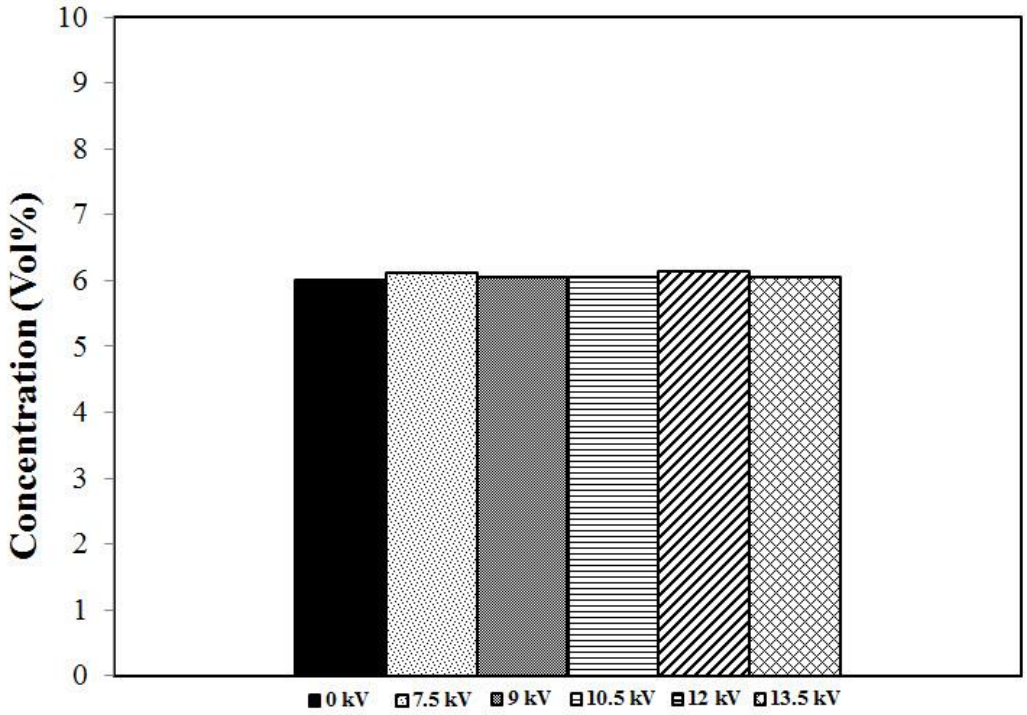



Figure 8.10: The effect of NTP on $CO_2$ concentration for different applied voltages

Figure 8.11 displays the effect of NTP on the existing water in the diesel exhaust. As is expected, the plasma does not affect the $H_2O$ concentration and it has almost the same values at different voltages.

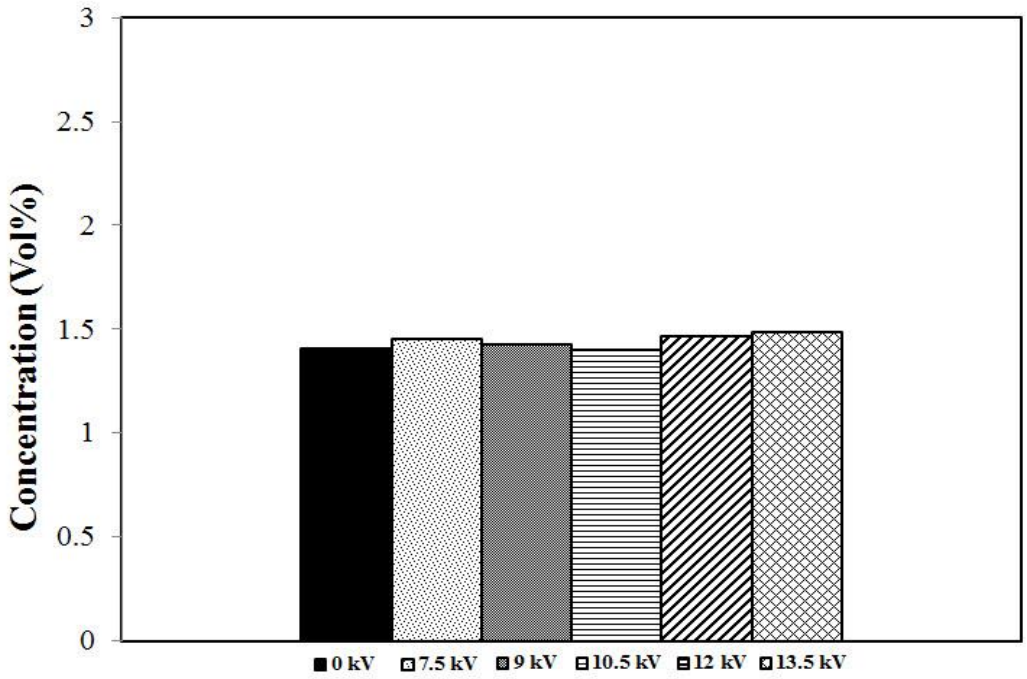



Figure 8.11: The effect of NTP on $H_2O$ concentration for different applied voltages

The variation of Ammonia concentration as a function of applied voltage has been plotted on Figure 8.12. The Ammonia concentration decreases by increasing the applied voltage because $NH_3$ acts as a reducing agent in some reactions, such as the reduction of $NO_2$ to $N_2$. Therefore, as shown in the figure, the concentration of Ammonia is decreased by introducing plasma (Kim, 2004a).

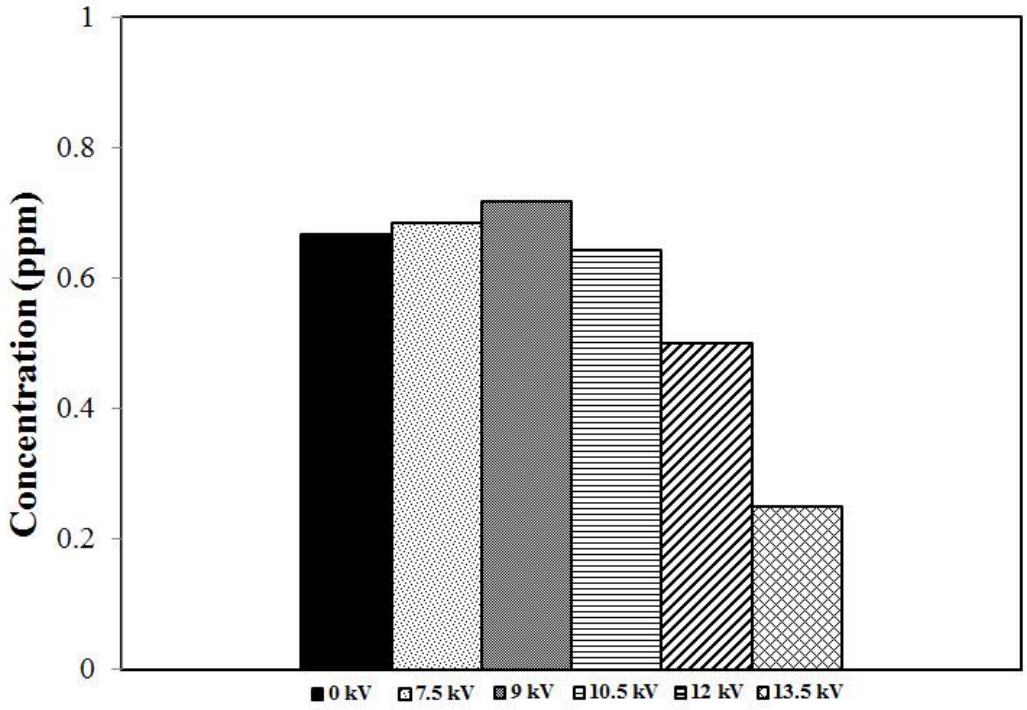



Figure 8.12: The effect of NTP on $NH_3$ concentration for different applied voltages

### 8.3.5 Effect of NTP on acetone, formic acid and methanol

In this study, the effect of NTP on Acetone, Formic acid and Methanol has also been considered. In general, the concentrations of these gases were very small in the exhaust emission for these experiments. The Acetone concentration was zero based on the FTIR measurement and it did not vary by changing the applied voltage. However, Formic acid and Methanol concentration changed during the experiments and Figure 8.13 and Figure 8.14 present the variation of their concentrations as a function of applied voltage, respectively. The results show that the existing low concentration Methanol in the exhaust is removed by introducing the plasma inside the gas. However, the Formic acid concentration does not change so much and only a small increase can be observed.

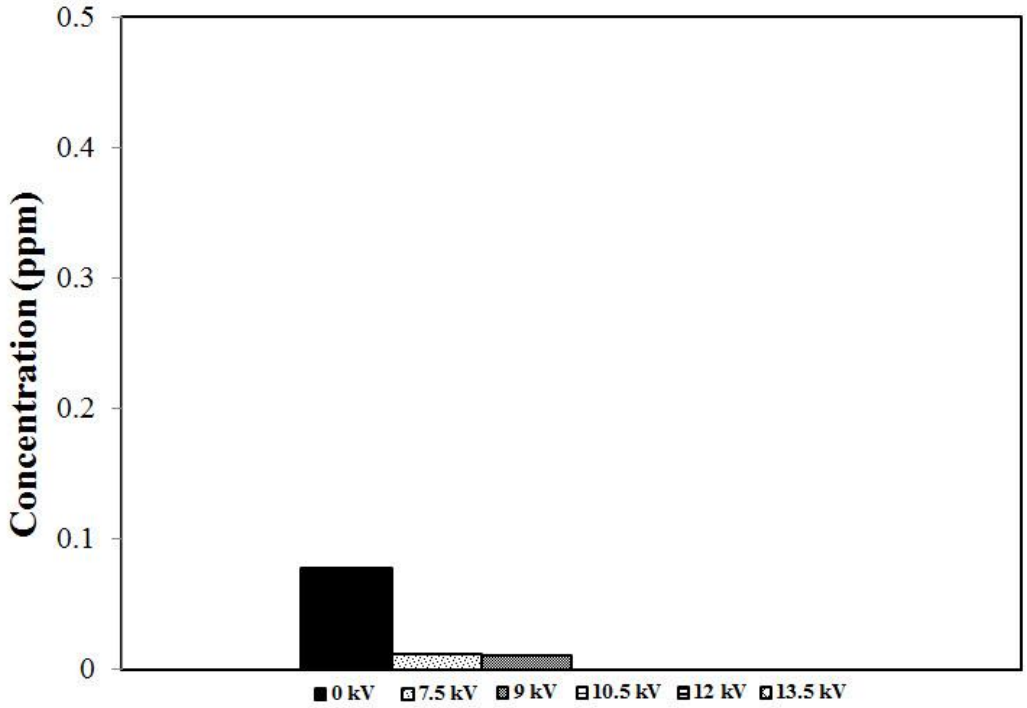



Figure 8.13: The effect of NTP on Methanol concentration for different applied voltages

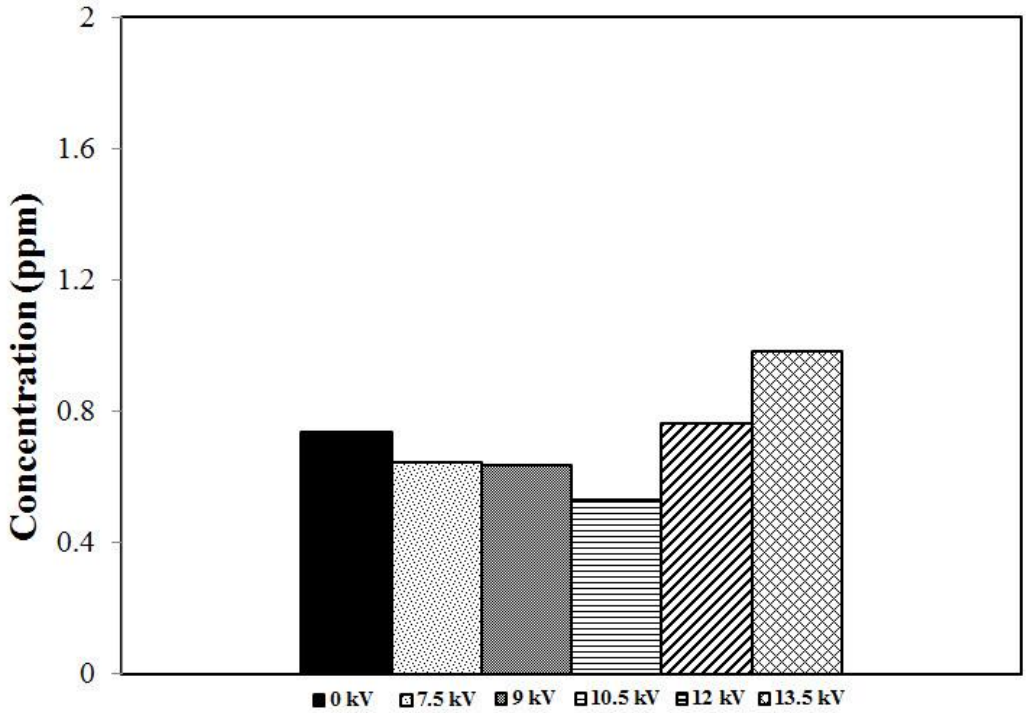



Figure 8.14: The effect of NTP on Formic acid concentration for different applied voltages

Two other gases i.e. the Sulfur dioxide and MTBE (Methyl tert-butyl ether) are also measured in this paper. However, the concentration was zero, based on the FTIR measurement.

In a final analysis to provide an overall view for the effect of NTP on different emissions, all tested gases have been plotted on Figure 8.15, Figure 8.16 and Figure 8.17 at two different operating conditions: 0 kV (when plasma is not on) and at 13.5 kV (when discharge power is at maximum level) . As we can see, plasma can decrease concentration of some emissions such as NOx, THC (including methane, ethylene, ethane, propene, 1, 3-butadiene and not toluene), ammonia and methanol. On the other hand, the concentration of other emissions such as CO, formic acid, acetaldehyde and formaldehyde was found to be increased after applying NTP to the exhaust. However, the concentrations of these components are not so high, so the percentage rise should not be misunderstood. It should be noted that the concentration of HCHO is changed from 0 ppm at 0 kV to 0.7 ppm at 13.5 kV during the experiments.

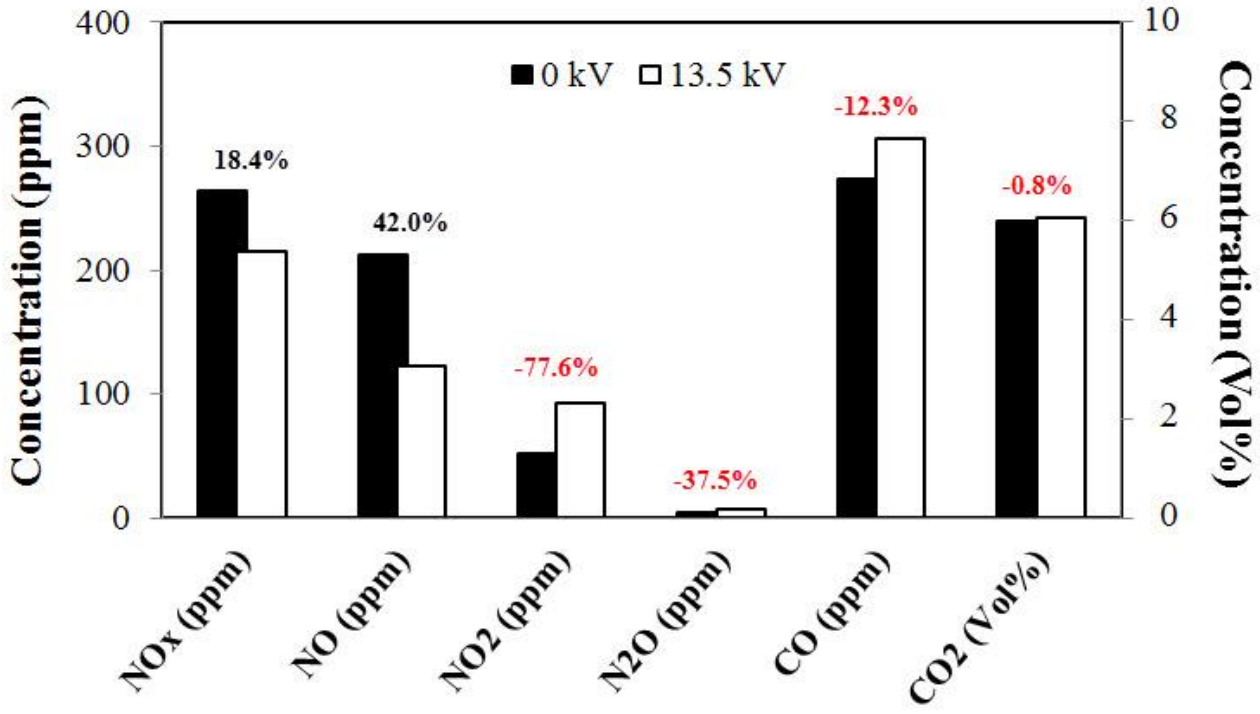



Figure 8.15: The effect of NTP on NO, $NO_2$, $N_2O$, NOx, CO and $CO_2$ before and after applying a high voltage of 13.5 kV

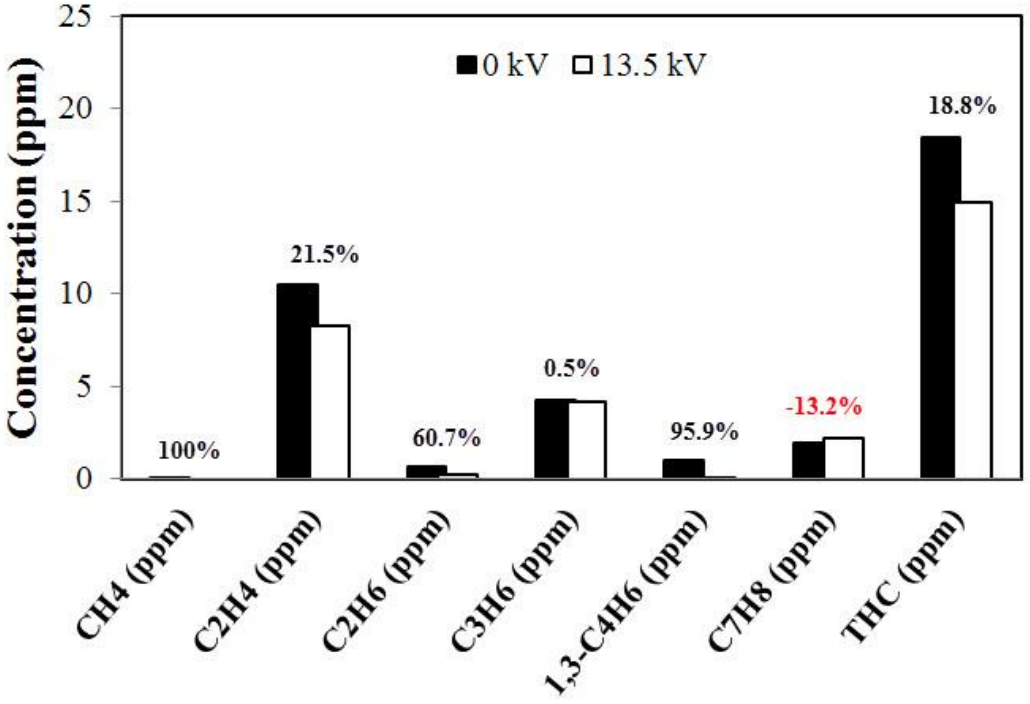



Figure 8.16: The effect of NTP on different hydrocarbons before and after applying a high voltage of 13.5 kV

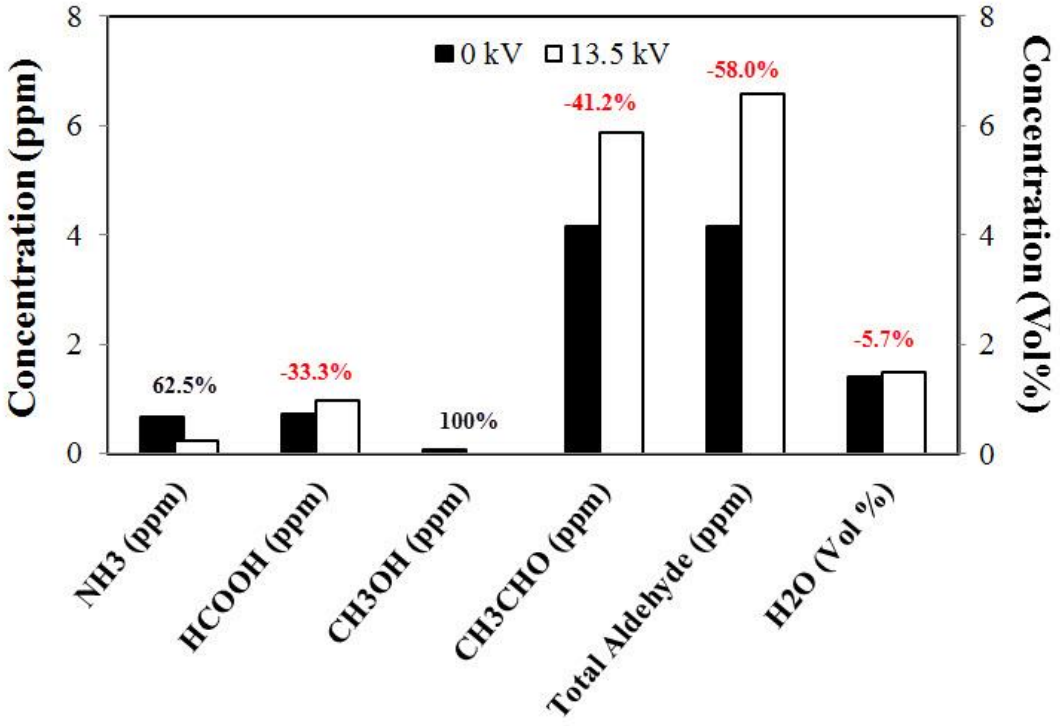



Figure 8.17: The effect of NTP on $NH_3$, HCOOH, $CH_3OH$, $CH_3CHO$, total Aldehyde and $H_2O$ before and after applying a high voltage of 13.5 kV

### 8.3.6 Multivariate data analysis (MDA)

In order to study the effects of applied voltages on the emissions of the diesel fuels, a data matrix with 20 criteria (different diesel engine emissions from Table 8-1excluding $C_6H_6$, iso-$C_4H_8$, $H_3COCH_3$, $(CH_3)_3COCH_3$ and $SO_2$) and six variables (applied voltages) was submitted to Visual PROMETHEE software to perform PROMETHEE-GAIA ranking analysis.

This procedure is a mathematical method, which has been used in different environmental problems (Lim et al., 2005, Al-Shiekh Khalil et al., 2005, Ayoko et al., 2004). It has the capability of providing the interrelationships among a given data matrix in a brief but precise manner to aid in conceptualising the data set (Kelly et al., 2005). The goal of this process is to provide a summary of the necessary information for ranking and interpretation patterns in the entire data set matrix (Lim et al., 2007).

In PROMETHEE-GAIA analysis, first, criteria are ranked by PROMETHEE based on preference functions and weighting conditions of the variables. The preference functions of objects were selected as the V-shape in Visual PROMETHEE software, which is more suitable for quantitative values in environmental applications (Gunawardena et al., 2012). Moreover, preference functions of objects are modelled as minimum since lower emissions (which show the engine is producing fewer pollutants) are favoured and all components receive an equal weighting in software. On the other hand, GAIA as a visual complement to PROMETHEE provides a principal component analysis-like biplot, which can be used for object–variable, variable–variable and object–object relationships (Gunawardena et al., 2014). In PROMETHEE-GAIA analysis, a data pre-treatment method will be developed by PROMETHEE before GAIA analysis and the PROMETHEE outcome will be used by GAIA to develop the GAIA biplot (Espinasse et al., 1997). The results of PROMETHEE-GAIA analysis have been shown in Figure 8.18.

From this figure, U values are found to be positive for variables such as 13.5 kV and 12 kV and they are negative at 0 V, 7.5 kV and 9 kV, and applied voltage of 10 kV can be considered as a kind of threshold. As was seen before, the plasma was not so efficient as to make a lot of changes at 7.5 kV and 9 kV and the similar behaviour of these two voltages with the state of no plasma (0 V) has also been confirmed from this figure. Furthermore, the length of each criteria vector represents its influence by the variables (Islam et al., 2013). Very short criteria vectors ($CO_2$, $C_7H_8$, $C_3H_6$, $CH_4$, $NH_3$, 1, 3-$C_3H_6$, $CH_3OH$, $H_2O$, etc.) indicate that changing the applied voltages showed little to no effect on these pollutants. Therefore, it can be concluded that the NTP technique does not affect these species so much. On the other hand, NTP was found to be affecting $NO_X$ (including NO, $NO_2$ and $N_2O$), THC (especially because of $C_2H_4$), CO and, to some extent, aldehydes. Generally, the

criteria that are close to each other with the angle of ±45° are correlated, while the anti-correlated ones are in reverse directions with the angle of 135−225°, and approximately, criteria in orthogonal directions have no or less relationship (Islam et al., 2013, Espinasse et al., 1997). For example, we can find a reverse relationship between $NO_x$ and NO with $NO_2$ from the figure, due to the oxidation of NO to $NO_2$ by non-thermal plasma, as is expected. One interesting finding is an anti-correlation between CO with NO and $NO_x$. We can conclude the occurrence of some reactions inside the plasma, which can reduce NO concentration while increasing CO concentration simultaneously. These reactions can be relevant to the hydrocarbons. Existence of hydrocarbons in diesel exhaust can promote the NO to $NO_2$ conversion, while they produce a considerable amount of CO during NO conversion (Shin and Yoon, 2003). Also, we can see THC is correlated to $C_2H_4$. It means that among different hydrocarbons, the reduction of THC by plasma is more relevant to the $C_2H_4$ concentration reduction.

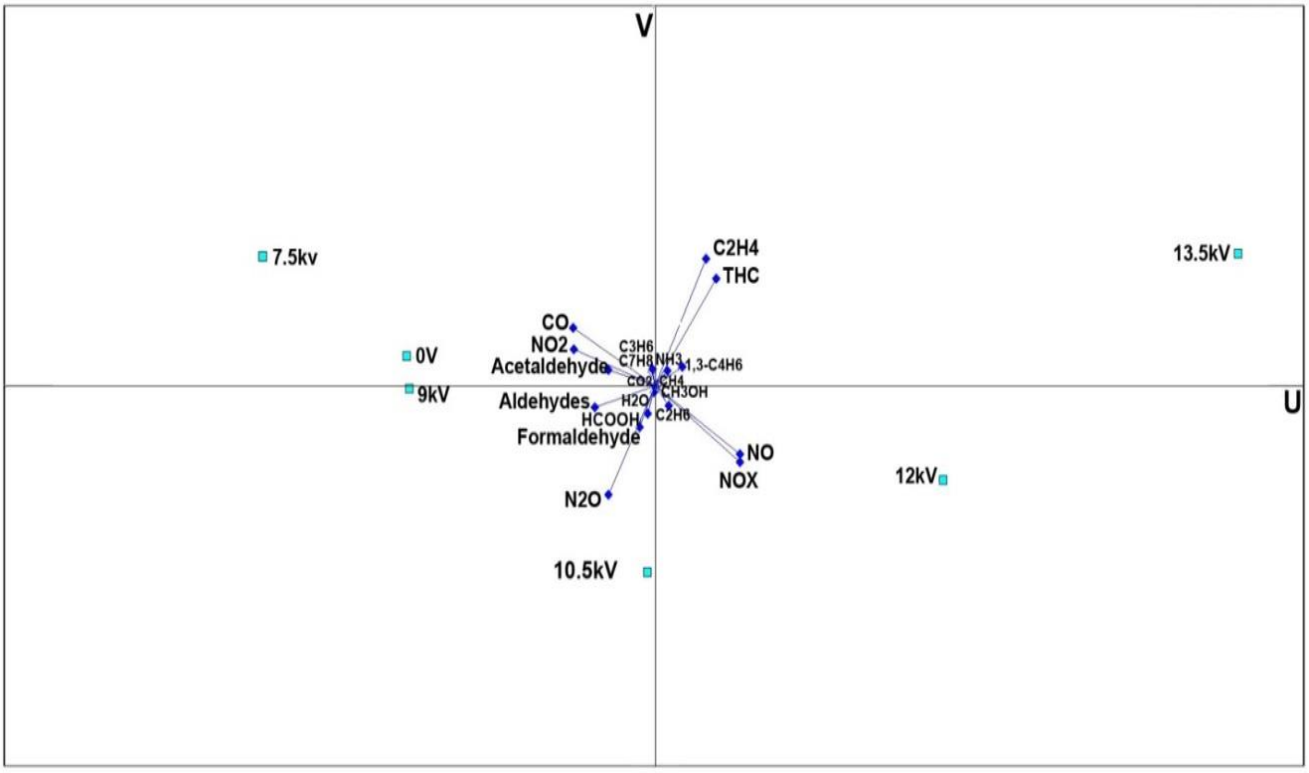



Figure 8.18: The GAIA plot of the effect of different applied voltages on different gaseous emissions

## 8.4 CONCLUSION

Investigation of more than twenty different species of exhaust emissions at six different applied voltages has revealed that the NTP technique can strongly affect regulated and unregulated diesel engine emissions. In particular, NTP showed a good potential for $NO_x$ and hydrocarbon reduction. On the other hand, the total concentration of Aldehydes has been increased by increasing the applied

voltage. Moreover, a continuous increase in CO concentration has been found during the experiments while the $CO_2$ concentration did not change considerably. It revealed that, during our experiments, hydrocarbons and soot are removed and converted to CO more than $CO_2$.

Furthermore, principal component analysis (PCA) is considered to facilitate the interpretation of our data. From this analysis, $CO_2$, $C_7H_8$, $C_3H_6$, $CH_4$, $NH_3$, 1, 3-$C_3H_6$, $CH_3OH$, $H_2O$, etc. with very short criteria, are found not to be affected so much by varying the applied voltages. In contrast, NTP affected $NO_X$ (including NO, $NO_2$ and $N_2O$), THC (especially because of $C_2H_4$), CO and to some extent aldehydes with longer criteria vectors. The reverse relationship between $NO_x$ and NO with $NO_2$ concentration under plasma condition is confirmed from PCA analysis as well. Further to this, an anti-correlation between CO with NO and $NO_x$ has been observed. This can be relevant to the existence of hydrocarbons in diesel exhaust, which can promote the NO to $NO_2$ conversion while producing a considerable amount of CO.

The results of this study could be related to formation of nucleation mode particles which has been observed in previous chapters at high voltage levels. As it has been observed in this study, the concentration of some components such as acetaldehyde and formaldehyde increased at high voltage levels. Therefore, further research is required to find out any relationship between the presented gaseous emissions and other species such as polycyclic aromatic hydrocarbon with the formation of particles in nucleation mode.

# Chapter 9: Conclusion and future research

## 9.1 CONCLUSIONS ARISING FROM THIS STUDY

This research was a multidisciplinary research topic developed on a foundation of mechanical and environmental engineering. The focus was on plasma treatment of diesel exhaust and especially PM removal. The approach was from an engineering perspective, however many chemical issues have arisen in relation to the use of plasma, such as the role of ozone, chemical and electron impact reaction mechanism, role of gas pressure in plasma formation and subsequent reactions that can be studied from a chemistry point-of-view in any future research. This experimental study has developed the knowledge in mechanical and environmental engineering towards controlling diesel emission by using non-thermal plasma technology, which has made a considerable contribution in the understanding of NTP effects on diesel particulate matter.

NTP has been examined under a wide range of discharge powers by varying the applied voltage and frequency. The impact of NTP on PM composition and PM removal mechanisms from the actual diesel exhaust have been investigated in detail. In this thesis, both PM mass reduction and PM size distribution has been investigated during PM removal by plasma. Finally, due to the significant effect of NTP technology on gaseous emissions, this technique has been evaluated for a variety of regulated and unregulated gaseous emissions. Overall, the obtained results highlighted the potential of NTP technology for PM removal; however, several areas, such as the formation of extra ultrafine particles at high energy levels, were identified to require further improvement for introducing this technology in real applications. The results presented in this thesis shed a light on different aspects of NTP applicability as a potential after treatment system for PM removal, which can have significant benefits for human health, air quality and global warming in future.

After discussing the methodological aspect of this research in the first chapter of the thesis, a comprehensive literature review was developed in Chapter 2 and Chapter 3. The main focus of literature in this area is found to be on $NO_X$ removal and the first manuscript (Chapter 2) reviewed the current literature concerning $NO_X$ removal from the diesel exhaust. This chapter provided a summary of findings on how plasma can operate for $NO_X$ removal from simulated gases and actual diesel exhaust. The main argument presented in this section suggests that there is a strong correlation between mechanical, chemical and electrical parameters involved in plasma production and exhaust treatment, which will ultimately result in the improvement of diesel engine emission treatment. Combining NTP with a catalyst or adsorber can improve the NTP capabilities for $NO_X$ removal.

Furthermore, based on the existing publications, energy consumption has been considered as the main challenge for using this technology in real applications. Further research is required to improve the electrical aspects and also the reactor design to overcome this issue. In the literature, pulsed power technology has shown more efficiency for generating plasma, and was considered for developing the electrical set-up for PM removal. DBD reactor configuration and other related technical aspects of developing the experimental set-up and research process were found during this literature review.

The current literature related to the application of NTP technology for PM removal was explored in Chapter 3. There is a lack of research about PM reduction by using NTP technology compared to the numerous papers for NOx removal, and the focus of this limited research was on PM mass reduction only. The PM removal mechanism by using NTP has not been trialled effectively yet. Most of the research in this area has been conducted from an electrical point of view and was mostly based on simulated gas. The limitation of current literature in addressing different aspects of PM removal by plasma, considering PM size distribution in conjunction with PM mass reduction, detailed study of the PM removal mechanism and examining NTP technology for real exhaust operating conditions was the basic motivation of this research study, which has been recognised through this literature review. As mentioned before, energy consumption is the major concern for practical mobile application. The NTP power consumption about 3% of the engine output power has been introduced as the practical limit for a 3-L-class diesel engine in literature.

The third manuscript (Chapter 4) investigated the results of preliminary experiments on DPM by using a DBD reactor. Three voltages including 15, 17 and 19.44 $kV_{PP}$ at repetition rates of 10 kHz have been tested. Wall attachments of particulates were found to be an important parameter and which has been considered in all experiments. NTP technology affected PM mass concentration and also PM size distribution. NTP was very effective for PM mass reduction and a maximum PM removal efficiency of 43.9% was obtained at 19.44 kVpp. However, at this voltage level, the number of ultrafine particles increased significantly. Therefore, the performance of plasma at such high voltage levels is not desirable due to the production of ultrafine particles, which are known to deposit the deepest in lungs and even transfer into the blood stream. Considering the PM mass reduction and PM size distribution simultaneously, an optimum voltage level of 17 kVpp at 10 kHz with PM removal efficiency of 38.6% was found for the given configuration and operating condition.

To investigate the formation of extra particles, which has been observed in previous chapter at high voltage levels, a series of experiments with the same experimental set-up and operating conditions of the previous study (Chapter 4) was developed. The fourth paper (Chapter 5) considered the mechanism of ultrafine PM formation at high voltage levels. A HEPA filter was added at the

reactor inlet to remove all particles before entering the DBD reactor. PM size distribution and PM mass has been monitored during the experiments. The HEPA filter removed almost all the particles prior to introducing plasma into the exhaust. When plasma was introduced at 15 $kV_{PP}$ and 17 $kV_{PP}$ no extra particles were produced. But when the applied voltage approached 20 $kV_{PP}$ a significant number of ultrafine particles was observed. Therefore, it was shown that the condensation of gaseous emissions to particles (gas to particle) is possible by introducing plasma into the exhaust at high voltage levels.

The fifth manuscript (Chapter 6) explored the effect of NTP technology on DPM structure and $NO_X$ reduction. NTP was found to be effective for PM removal in previous chapters and the formation of ultrafine particles at high voltage levels was discussed. As was explained in the literature review, DPM is essentially composed of a solid fraction (soot), soluble organic fraction (SOF) and sulfate particulates. To investigate the effect of NTP on DPM in more detail, each component of diesel particulate matter (soot, SOF and sulfate) was considered separately under plasma treatment. The DBD reactor was employed for producing plasma inside the diesel exhaust. A range of discharge powers by varying the applied voltage ranging from 7.5 kV to 13.5 kV at a frequency of 50 Hz have been evaluated during the experiments. The effect of NTP on PM size distribution and other components of DPM including soot, SOF and sulfate were studied. NTP was found to be very effective for PM removal, especially for soot reduction. The maximum reduction of 73% and 37% at energy density of 27 J/L has been found for soot and SOF mass concentration, respectively. The sulfate fraction was very low due to the low sulfur content of employed diesel fuel and remained almost unchanged under plasma treatment. The effect of NTP on PM size distribution has also been quantified. Despite a considerable increase in nucleation mode particles at 13.5 kV, NTP showed a good potential for PM reduction in the range of 10 nm to 500 nm. A direct relationship between discharge power and PM removal efficiency for the total number of particles larger than 30 nm was observed. At first, the removal efficiency was about 59% and it increased to about 76% at an energy density of 10 J/L. Nearly all particles larger than 30 nm were removed when the discharge power was about 27 J/L. The result of PM size distribution is in agreement with the result of chapter 4 and 5. While a smaller engine with different DBD geometry has been used in this chapter, the trend of PM size distribution was similar. For example, formation of nucleation mode particles has been obtained at high voltage levels in both experiments. However, some qualitative difference such as occurrence of bimodal size distribution in chapter 9 can be observed. Furthermore, the maximum $NO_x$ removal efficiency of about 18% was achieved when energy density was about 27 J/L. Nitrogen monoxide (NO) was found to be oxidised to nitrogen dioxide ($NO_2$) and a small increase in nitrous oxide ($N_2O$) concentration has been found during the experiments.

Then, the study has been brought into the wider range of NTP operating conditions to characterise the effectiveness of the NTP technique for PM removal under various modes of operations and to find the possible optimum operating points. Therefore, in the sixth manuscript (Chapter 7) NTP technology was characterized for PM removal under a wide range of applied voltages and repetition rates, and also investigated the correlation of ozone, $CO_2$ and PM during plasma treatment of exhaust emissions. A wide range of applied voltages from 11 $kV_{PP}$ to 21 $kV_{PP}$ at repetition rates of 2.5, 5, 7.5 and 10 kHz, have been experimentally investigated and the results have been presented with relevant contour plots of discharge power, ozone, $CO_2$ and PM concentrations. The slope of discharge power contour lines was about 45° and increased with the applied voltage levels, correspondingly. This means that the discharge power was influenced by the applied voltage more than the repetition rate, especially when approaching the higher voltage levels. Furthermore, a small $CO_2$ dissociation was observed in $CO_2$ contour plots with plasma treatment. $CO_2$ contours were almost vertical, especially at high voltages and low frequencies. This means that applied voltage showed a greater impact on $CO_2$ decomposition of diesel exhaust. From PM contour plots, it was found that by increasing the voltage level and repetition rate, the PM concentration was decreased. The minimum value for PM concentration was found at a voltage level of 19 kVpp and repetition rate of 10 kHz. The role of ozone is one of the main factors in NTP exhaust treatment and was evaluated using a contour plot of ozone concentration as a function of applied voltage and repetition rate. Generally, by increasing the applied voltage and pulse repetition rate the concentration of ozone was increased except for 21 kVpp and 10 kHz. At this state, oxygen saturation inside the reactor can occur, which results in a reduction of ozone concentration. The correlation study of $CO_2$, ozone and PM was conducted by considering time dependant analysis. The key role of ozone in PM reduction was found from this analysis. During the period of study, a continuous decrease in $CO_2$ concentration was observed by increasing the voltage level at all repetition rates, except at the end of the test with a voltage level of 21 kVpp at 10 kHz. At this state, $CO_2$ concentration remained almost the same, which could be due to the reduction in ozone concentration and PM oxidation. Regarding PM and ozone concentration, an opposite trend was observed for the time period of the study. For all operating conditions, when ozone has been increased PM concentration has decreased. However, at 19 kVpp and 10 kHz, 21 kVpp and 10 kHz, and 21 kVpp and 7.5 kHz, PM concentration increased over the time due to the reduction of ozone production, which means reduction in PM oxidation.

The last manuscript (Chapter 8) explored the influence of NTP technology on a wide number of regulated and unregulated gaseous emissions. As noted, PM removal experiments in this thesis have been conducted in actual diesel exhaust and the final purpose of using NTP technology is to be used as a diesel after treatment system in real operating conditions. Therefore, it is important to

evaluate the effect of this technology on gaseous emissions during PM removal as well. The effect of NTP on about 22 different species including different hydrocarbons (C1-C7), carbon monoxide, carbon dioxide, nitrogen oxides (including NO, $NO_2$ and $N_2O$), sulfur dioxide, formaldehyde and other gases have been investigated. In this study, concentration of total $NO_x$ ($NO+NO_2+N_2O$) $NO_x$ decreased due to the occurrence of a series of reactions in the plasma state. NTP affected the hydrocarbons (C1-C7) differently, however; by increasing the applied voltage the total concentration of hydrocarbons decreases continuously and about a 19% decrease in THC concentration can be obtained at 13.5 kV. On the other hand, the total concentration of aldehydes (formaldehyde and acetaldehyde) was found to be increased by increasing the applied voltage. The concentration of CO increased when applying higher voltages, while the $CO_2$ concentration did not change considerably. It showed more oxidation of soot and hydrocarbons to CO compared to $CO_2$. Moreover, it can be concluded that the low energy density level during experiments (less than 30 J/L) was not enough to achieve dissociation of stable molecules such as $CO_2$. Multivariate data analysis (MDA) has also been employed to provide a summary of interpretation patterns in the entire data. A data matrix that includes criteria (different diesel engine emissions) and variables (applied voltages) was submitted to Visual PROMETHEE software to perform PROMETHEE-GAIA ranking analysis. From this analysis the interrelationships among the data matrix components were achieved. It was revealed that the concentration of $CO_2$, $C_7H_8$, $C_3H_6$, $CH_4$, $NH_3$, 1, 3-$C_3H_6$, $CH_3OH$, $H_2O$, etc. with very short criteria vectors has not been affected by changing the applied voltages very much during the experiments. On the other hand, NTP was found to be affecting $NO_X$ (including NO, $NO_2$ and $N_2O$), THC (especially because of $C_2H_4$), CO and, to some extent, aldehydes with longer criteria vectors. Furthermore, from this analysis, a reverse relationship between $NO_x$ and NO with $NO_2$ and between CO with NO and $NO_x$ was found. The former is due to the oxidation of NO to $NO_2$ by non-thermal plasma and the latter is related to the reactions of hydrocarbons and soot.

## 9.2 RECOMMENDATIONS FOR FUTURE RESEARCH

Diesel engines will quite likely be the dominant power source in both mobile and stationary applications in the future. Considering the health and environmental side effects of diesel engines and the development of emissions legislation, there is therefore a strong requirement for further research to explore new after treatment systems in diesel engine applications. Non-thermal plasma, as a promising technology for diesel engine emission reduction, has been evaluated for diesel particulate matter removal in this research.

Further research is required to understand the chemistry involved in PM removal. The chemistry of plasma treatment of exhaust is very complicated. Many chain electron impact reactions

are involved. The chemical composition of exhaust is also very complicated and variable. The chemical reactions for PM and other diesel emissions during NTP treatment should be studied in detail. Chemical reactions relevant to $NO_X$, ozone and electron impact reactions as the main pathways for PM removal need to be explained. Combining NTP technique with conventional catalysts and DPF, and studying the effect of different pellets and the catalysts and chemistry involved for plasma PM removal, should be considered from a chemical point of view. High voltage can increase the tendency of particle deposition inside the reactor same as what is happening in electrostatic precipitators. This effect can be studied in future research as well.

From the electrical point of view, a variety of variables such as applied voltage, frequency, discharge power, specific energy density, pulse rise time, pulse shape, polarity, pulse width and other electrical parameters are involved. The most important challenge in applicability of NTP as an after treatment system is energy consumption and it should be improved by monitoring these parameters in conjunction with emission removal effects. Furthermore, instead of using an uncontrolled discharge energy in a one-step discharge, the system can be designed as a multi-stage energy discharge because diesel exhaust is composed of thousands of components, and different pollutants may be removed or even produced in different discharge energy levels by plasma. Using a novel discharge method such as a gliding arc, which showed good potential in other applications, is recommended.

There is a clear gap in this area from the modelling and simulation point of view. Developing numerical models with respect to experimental results can be very helpful. There are a lot of possibilities for developing numerical simulation to study plasma formation and reactor performance. A coupled model of pollution removal and plasma formation for solving the Boltzmann equation can be developed. The results obtained from mass spectrometry experiments can also be considered to develop a model to correlate plasma formation parameters to diesel engine emission reduction. Moreover, the CFD simulation of flow for reactors can be considered for improving the parameters such as particle deposition and residence time distribution. Using this modelling approach, it is possible to study the flow pattern and pressure drop inside the reactor. Also, the increase of particle deposition inside the reactor can be considered. Residence time distribution (RTD) is another parameter that should be modelled in combination with flow modelling. Increasing RTD and keeping exhaust flow for a longer time inside the reactor provides more time for the occurrence of relevant chemical reactions for exhaust treatment in the plasma state.

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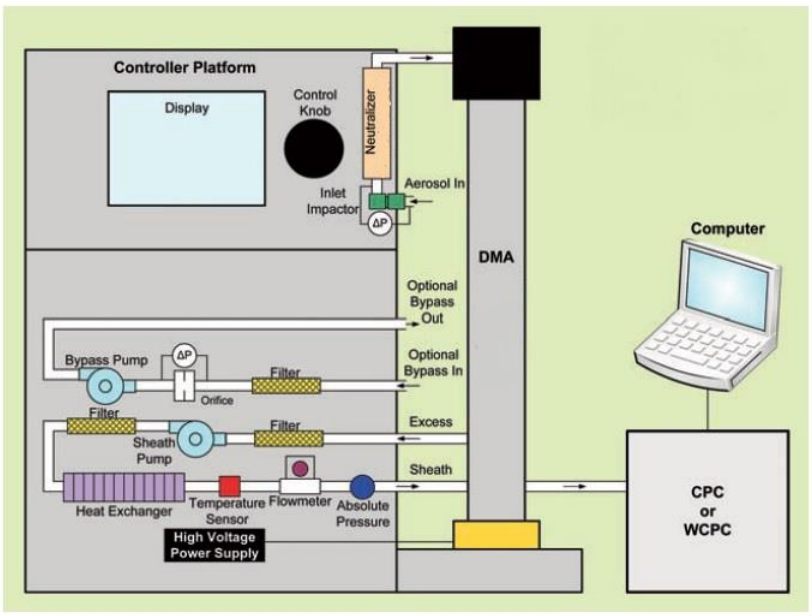
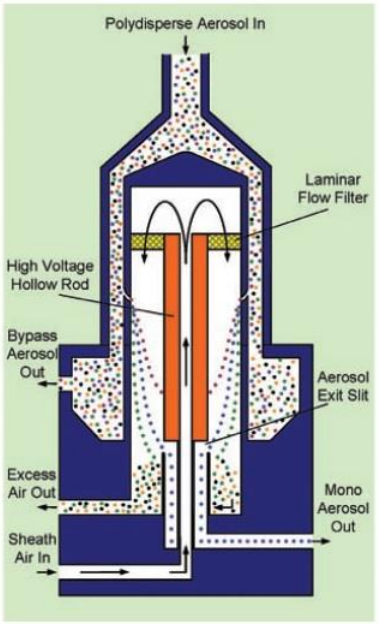
# Appendices

### Appendix A: Particulate matter (PM) size distribution measurements

An SMPS has been used for particle size distribution measurements. This instrument uses an electrical mobility separation technique for measuring the size distribution. Three main components of an SMPS are a Bipolar Am-241charge neutralizer, a built-in DMA (deferential mobility analyser) for particle size separation and a built-in CPC (condensation particle counter) for concentration measurement. In SMPS 3034, the particle size range is 10 to 487 nanometres and the total particle concentration range is $10^2$ to $10^7$ particles per cubic centimetre. Inlet (aerosol sample) flow rate is 1 L/min and sheath flow is 4 L/min. Each scan from 10 to 487 nanometres takes about 3 minutes by this instrument and data has been presented after taking an average in this thesis. The repeatability of the results has been checked by repeating the test with same operating condition in different days.

**Figure A-1:** SMPS operating principal.

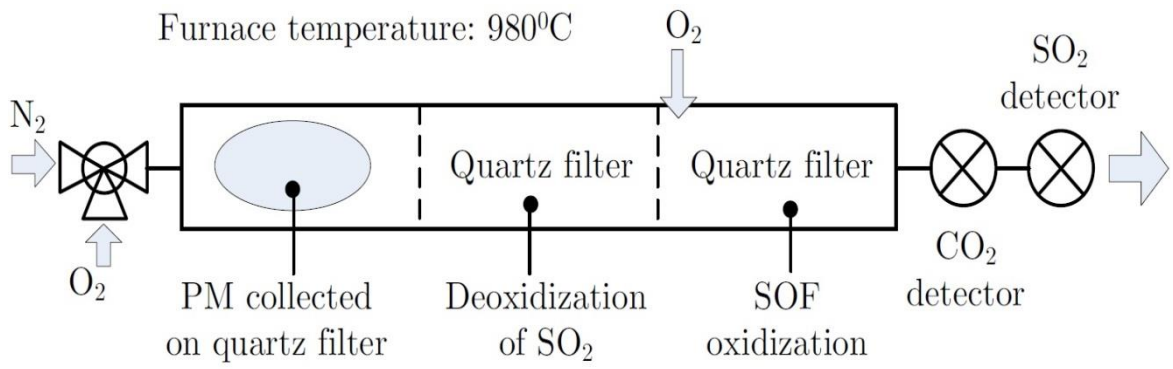


## Appendix B: The operating principle of MEXA-1370PM

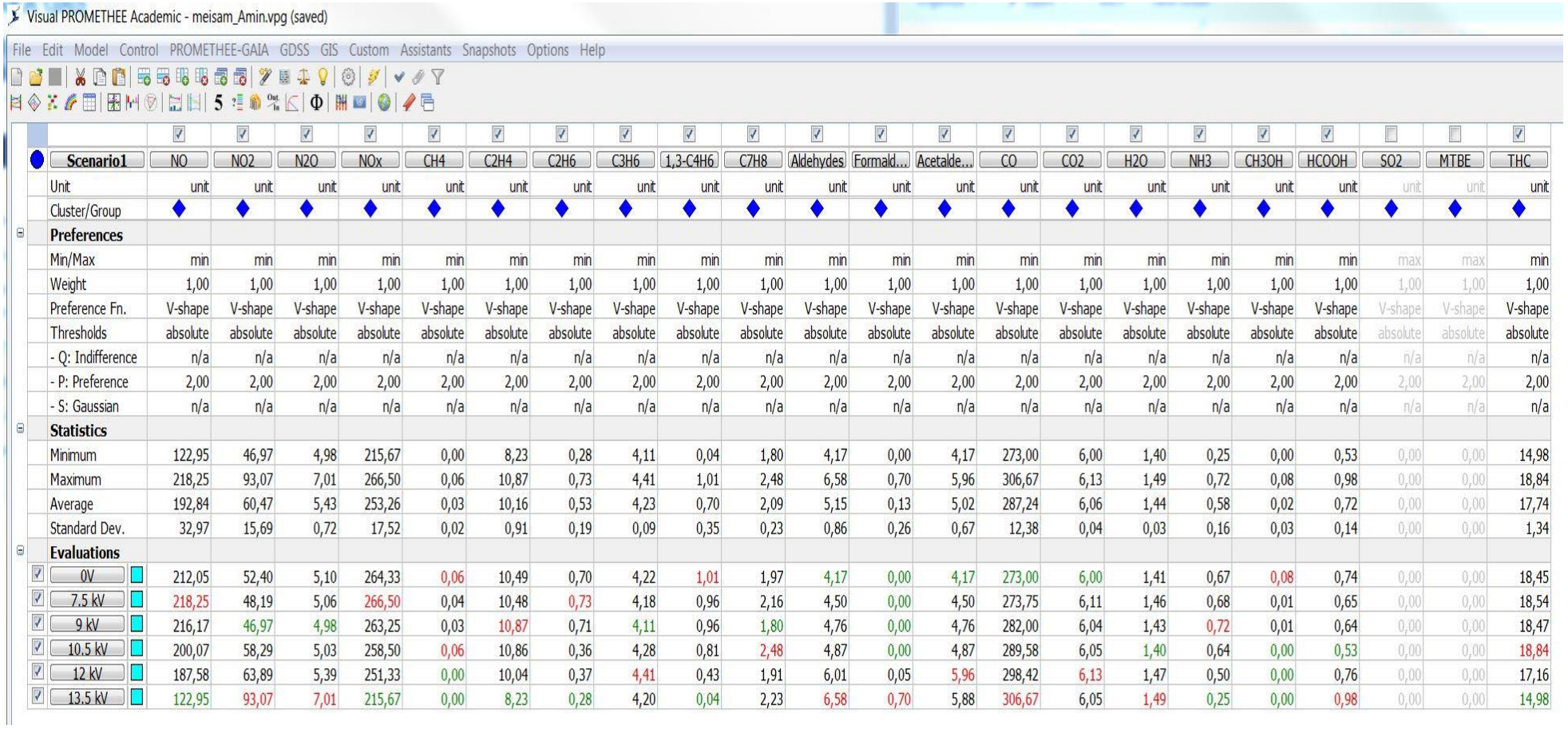
Particulate matter should be collected on Silica filters and placed in the furnace of the analyser. Filters are heated to 980 C in a $N_2$ gas flow inside a MEXA-1370PM. Soluble organic fraction (SOF) and sulfate components of trapped particles are vaporized by heating in $N_2$ gas. Vaporized sulfate is oxidized to $SO_2$ and it is measured by a $SO_2$ non-dispersive infra-red (NDIR) detector. Then, the vaporized organic fraction is oxidized by constant flow of $O_2$ and measured as $CO_2$ by NDIR detector. Finally, after the evaporation of SOF and sulphate components of collected samples, $O_2$ will be introduced into the analyser. The remaining soot fraction on the filter is then oxidized to $CO_2$ and the NDIR analyser measures the soot concentration as $CO_2$. The operating principal and the flow paths for the MEXA-1370PM is depicted on Figure B-1.

**Figure B-1:** Mexa-1370PM operating principal.



## Appendix C: PROMETHEE-GAIA model details

**Figure C1:** Data matrix submitted to Visual PROMETHEE software including criteria (different emissions such as NO, $NO_2$, etc.) and variables (different voltage levels)




| Scenario1 | NO | NO2 | N2O | NOx | CH4 | C2H4 | C2H6 | C3H6 | 1,3-C4H6 | C7H8 | Aldehydes | Formald... | Acetalde... | CO | CO2 | H2O | NH3 | CH3OH | HCOOH | SO2 | MTBE | THC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit | unit |
| Cluster/Group | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ | ♦ |
| **Preferences** | | | | | | | | | | | | | | | | | | | | | | |
| Min/Max | min | min | min | min | min | min | min | min | min | min | min | min | min | min | min | min | min | min | min | max | max | min |
| Weight | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 |
| Preference Fn. | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape | V-shape |
| Thresholds | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute | absolute |
| - Q: Indifference | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
| - P: Preference | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 | 2,00 |
| - S: Gaussian | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
| **Statistics** | | | | | | | | | | | | | | | | | | | | | | |
| Minimum | 122,95 | 46,97 | 4,98 | 215,67 | 0,00 | 8,23 | 0,28 | 4,11 | 0,04 | 1,80 | 4,17 | 0,00 | 4,17 | 273,00 | 6,00 | 1,40 | 0,25 | 0,00 | 0,53 | 0,00 | 0,00 | 14,98 |
| Maximum | 218,25 | 93,07 | 7,01 | 266,50 | 0,06 | 10,87 | 0,73 | 4,41 | 1,01 | 2,48 | 6,58 | 0,70 | 5,96 | 306,67 | 6,13 | 1,49 | 0,72 | 0,08 | 0,98 | 0,00 | 0,00 | 18,84 |
| Average | 192,84 | 60,47 | 5,43 | 253,26 | 0,03 | 10,16 | 0,53 | 4,23 | 0,70 | 2,09 | 5,15 | 0,13 | 5,02 | 287,24 | 6,06 | 1,44 | 0,58 | 0,02 | 0,72 | 0,00 | 0,00 | 17,74 |
| Standard Dev. | 32,97 | 15,69 | 0,72 | 17,52 | 0,02 | 0,91 | 0,19 | 0,09 | 0,35 | 0,23 | 0,86 | 0,26 | 0,67 | 12,38 | 0,04 | 0,03 | 0,16 | 0,03 | 0,14 | 0,00 | 0,00 | 1,34 |
| **Evaluations** | | | | | | | | | | | | | | | | | | | | | | |
| 0V | 212,05 | 52,40 | 5,10 | 264,33 | 0,06 | 10,49 | 0,70 | 4,22 | 1,01 | 1,97 | 4,17 | 0,00 | 4,17 | 273,00 | 6,00 | 1,41 | 0,67 | 0,08 | 0,74 | 0,00 | 0,00 | 18,45 |
| 7.5 kV | 218,25 | 48,19 | 5,06 | 266,50 | 0,04 | 10,48 | 0,73 | 4,18 | 0,96 | 2,16 | 4,50 | 0,00 | 4,50 | 273,75 | 6,11 | 1,46 | 0,68 | 0,01 | 0,65 | 0,00 | 0,00 | 18,54 |
| 9 kV | 216,17 | 46,97 | 4,98 | 263,25 | 0,03 | 10,87 | 0,71 | 4,11 | 0,96 | 1,80 | 4,76 | 0,00 | 4,76 | 282,00 | 6,04 | 1,43 | 0,72 | 0,01 | 0,64 | 0,00 | 0,00 | 18,47 |
| 10.5 kV | 200,07 | 58,29 | 5,03 | 258,50 | 0,06 | 10,86 | 0,36 | 4,28 | 0,81 | 2,48 | 4,87 | 0,00 | 4,87 | 289,58 | 6,05 | 1,40 | 0,64 | 0,00 | 0,53 | 0,00 | 0,00 | 18,84 |
| 12 kV | 187,58 | 63,89 | 5,39 | 251,33 | 0,00 | 10,04 | 0,37 | 4,41 | 0,43 | 1,91 | 6,01 | 0,05 | 5,96 | 298,42 | 6,13 | 1,47 | 0,50 | 0,00 | 0,76 | 0,00 | 0,00 | 17,16 |
| 13.5 kV | 122,95 | 93,07 | 7,01 | 215,67 | 0,00 | 8,23 | 0,28 | 4,20 | 0,04 | 2,23 | 6,58 | 0,70 | 5,88 | 306,67 | 6,05 | 1,49 | 0,25 | 0,00 | 0,98 | 0,00 | 0,00 | 14,98 |

# Appendix D: Fuel quality certificate

Intertek

Neumann Petroleum
Attn: Scott Loveday

Our Ref: 860-12-0142
Lab No: L10742
16/3/2012

## ANALYTICAL REPORT

| | | |
|---|---|---|
| Vessel | : | ATLANTIC LILLY |
| Terminal | : | Neumann Petroleum |
| Sample Description | : | DIESEL<br>Composite sample (U,M,L) drawn from shore tank 7945 after discharge. |
| Sample Dated | : | 16/3/2012 |
| Sample Drawn by | : | Intertek Testing Services (A) P/L in accordance with ASTM E300 |

The above samples were analysed as detailed below and the following results obtained.

| TEST | SPEC | Shore Tank 7945 |
|---|---|---|
| **Appearance Visual** | Clear & Bright | Clear & Bright |
| **Density g/cm$^3$ @ 15 ° C ASTM 4052** | Report | 0.8369 |
| **Flash Point ° C ASTM D93** | 61.0°C min | 64.0 |
| **Conductivity ASTM D 2624 @ 25°C** | 50 min | 548 |

Vince Mudaliar
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