THE APPLICATION OF THERMAL, CATALYTIC AND NON-THERMAL PLASMA OXIDATION PROCESSES TO ENHANCE NO-NO_2 OXIDATION IN THE ENGINE EXHAUST AND IMPROVE DPF REGENERATION AT LOWER TEMPERATURES

by

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ABSTRACT

The particulate matter (PM) emissions from diesel engine continue to cause public and environmental concern due to their adverse effects on human health and air quality. The application of a Diesel Particulate Filter (DPF) is believed to be one of the most effective methods to overcome this problem and provides an efficient system that traps more than 90% of PM. However, after long periods of operation, the soot accumulated within the filter requires a regeneration process to recover its performance. Thus, the high oxidation ability of NO_2 prompts an application in the low temperature DPF regeneration process.

The intention of this thesis is to investigate several possibilities of on-board NO-NO_2 oxidation methods for increasing the NO_2/NO_X ratio in the exhaust gas, in order to provide sufficient NO_2 concentrations facilitated in NO_2-soot oxidation process in the DPF.

Possible NO to NO_2 oxidation routes are considered including enhancing the in-cylinder NO_2 production or exhaust gas treatment processes upstream the DPF. The NO to NO_2 oxidation is undertaken a wide range of engine exhaust gas temperatures by a non-thermal plasma oxidation (NTP) at low temperatures, catalytic oxidation for moderated temperatures and thermal oxidation for high temperatures studied.

The in-cylinder NO oxidation was significantly improved by adding H_2 or reformed EGR (REGR) to the diesel combustion. Some H_2 that escaped the combustion was used in the hydrocarbon selective catalytic reduction (HC-SCR) in the engine exhaust gas to reduce NO_X emissions and to further promote the NO-NO_2 oxidation. As a result, the combination of this system (REGR + HC-SCR) allows the simultaneous removal of both NO_X and PM emissions.

The thermal and NTP exhaust treatment methods cannot adequately achieve a satisfactory NO oxidation. Under these methods it was found that propane (C_3H_8) addition

may potentially create useful radicals (HO_2, RO_2) within the system leading to the conversion of a larger portion of NO into NO_2 in the exhaust gas. This is expected to improve the continuous regeneration of the DPF at lower exhaust temperature (< 250˚C) conditions.

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Symbol	Units	
C	F	Capacitance
LHV	MJ/kg	Lower heating value
LCV	MJ/kg	Lower calorific value
N	rpm	Engine speed
Q(t)	J	Charge of capacitor
SIE	J/L	Specific input energy
SV	h^{-1}	Space velocity
Vc	V	Capacitor voltage
Vpk-pk	V	Applied voltage peak to peak
η	g/kWh	Energy efficiency for NO conversion
η *ev*	eV/NO	Energy require for convert one mole of NO
λ		Relative air-to-fuel ratio

LIST OF ABBREVIATIONS

AC	Alternating current
Ag/Al_2O_3	Silver/Alumina
$AgNO_3$	Silver nitrate
AOTs	Advance oxidation technologies
$BaCO_3$	Barium carbonate
BTDC	Before top dead centre
C	Carbon
C_2H_4	Ethylene
C_2H_6	Ethane
C_3H_8	Propane
CA	Crank angle
CAD	Crank angle degree
CCRT	Catalysed continuously regenerating technology
CD	Corona discharge
CDPF	Coated diesel particulate filter
CH_4	Methane
CI	Compression ignition
CO	Carbon monoxide
cpsi	Cells per square inch
CRT	Continuously regenerated diesel particulate filter
DBD	Dielectric barrier discharge
DC	Direct current
DCM	Diffusion charging method
$DeNO_X$	NO_X removal
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
EGR	Exhaust gas recirculation
eV	Electronvolts
FPS	Future power system
GC	Gas chromatography
HC	Hydrocarbon
HC-SCR	Hydrocarbon selective catalytic reduction
HNC	Hydrogen cyanide
HO_2	Hydroperoxyl radicals
IC	Internal combustion
i-C_4H_{10}	Isobutane
IMEP	Indicated mean effective pressure
$N(^2D)$	metastable excited-state nitrogen atoms
$N(^4S)$	ground-state nitrogen atoms
N_2O	Nitrous oxide
NAC	NO_X adsorber catalyst
n-C_4H_{10}	n-butane
n-C_5H_{12}	n-pentane
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	Nitrogen oxides
NTP	Non-thermal plasma
$O(^1D)$	Metastable excited-state oxygen atoms
$O(^3P)$	ground-state oxygen atoms
O_3	Ozone
PAH	Polycyclic aromatic hydrocarbon
Pd	Palladium
PD	Pulsed discharge
PM	Particulate matter
ppm	parts per million
Pt	Platinum
Pt/SiO_2	Platinum/Silica dioxide
R&D	Research and development
REGR	Reformed exhaust gas recirculation
Rh	Rhodium
RO_2	Peroxy radical
ROHR	Rate of heat release
SO_4^{2-}	Sulphate
SCR	Selective catalytic reduction
SD	Surface discharge
SIC	Silicon carbide
SIE	Specific input power
SNCR	Selective non-catalytic reduction
SO_2	Sulphur dioxide
SO_3	Sulphur trioxides
SOCs	Surface oxygen complexes
SOF	Soluble organic fraction
TCD	Thermal conductivity detector
TP	Thermal Plasma
ULSD	Ultra low sulphur diesel
VOC	Volatile organic compounds
VOF	Volatile organic fraction

CHAPTER 1

INTRODUCTION

Diesel engines are gaining in popularity around the world thanks to their high efficiency, torque characteristic, reliability and lower fuel consumption. This expansion has not only penetrated the passenger transport market (light-duty), moreover, the application of heavy-duty diesel vehicles such as buses, trucks, trains and ships for transportation of goods cannot be replaced.

Although the first on-road vehicles emissions standards were promulgated in 1971, however no legislation has been structured. Such guidelines only provide the concept of a green environment and promote the reduction of potentially harmful emissions (i.e. NO_X, PM, CO and HC) from diesel engines (DieselNet, 2010). Therefore, automotive industries were unwilling to invest in R&D in this sector (ACEA, European Automobile Manufacturers Association, 2009). Thus, the diesel user in the period 1980 ~ 1990 contributed a significant amount of environmental pollutants. The exhaust gas was released directly to the atmosphere without any control or treatment. This contained a large amount of toxic chemical compounds, among these; the particulate matter (PM) emission is perhaps the most important as linked to deleterious heath effects.

PM can be separated into three categories based on the size distribution, as shown in the following (Kittelson, 1998):

- Coarse particles 2.5 ~ 10 μm (PM 10)

- Fine particles 1.0 ~ 2.5 µm (PM 2.5)
- Ultra fine < 1.0 µm (PM 1.0)

Figure 1.1 provides an illustration of size ranges of diesel PM and a comparison with human hair (Tiward and Colls, 2009). Although the black smoke emission can be visible with the naked eye, and thus constitutes the first impression of air pollution, however, the more serious problem is the fine particles that form more than 90% of diesel PM which cannot be visualized.

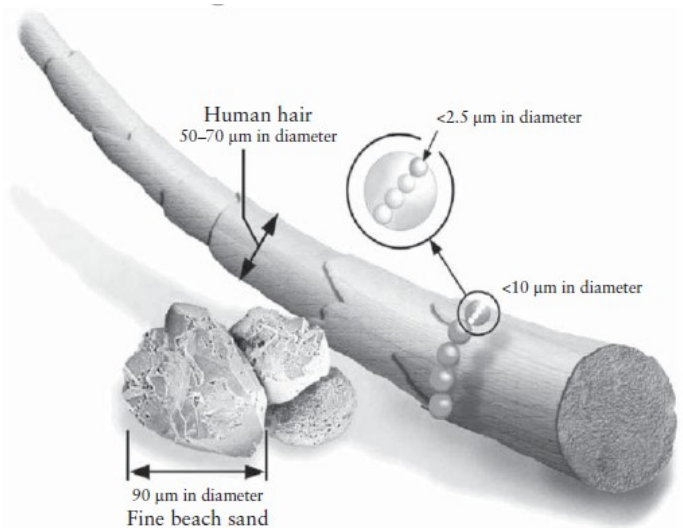


Figure 1.1: Illustration of particulate sizes. (Taken from: Tiward and Colls, 2009)

Under the pressure of several organizations among the European Union countries (e.g. Environmental Protection Agency (EPA), World Health Organisation (WHO)), the first series of efforts to control the pollution of on-road diesel engines was initiated in 1992, in the form of a collaboration with the European car manufacturers and the oil industry. It was deemed that new vehicles should meet the emissions requirements set before being licensed on the road.

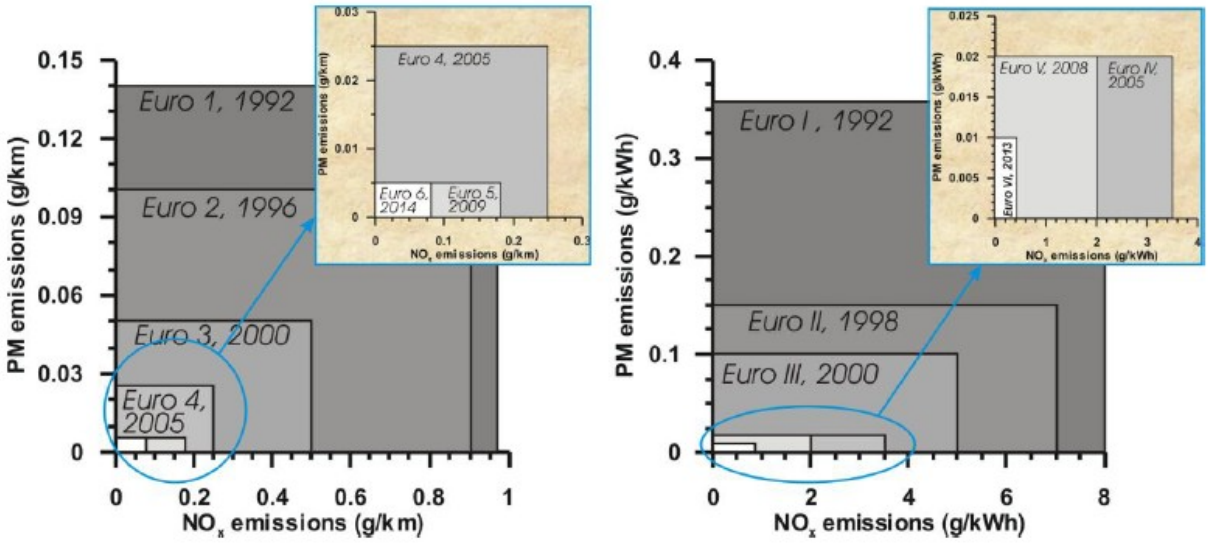


Figure 1.2: European PM and NO_X emissions legislation for light duty diesel vehicles (g/km) and heavy duty applications (g/kWh). (Taken from Sitshebo, 2010)

In subsequent years the environmental groups have continued to lobby for stricter legislation on vehicles emission limits. Figure 1.2 presents major emission standards for diesel engines (NO_X and PM) regulated by the European Union. The continued raising of the emission standards has driven R&D efforts to achieve clean emissions for the successive diesel vehicles, which have achieved more than 90% of NO_X and PM reduction compared to the early 1990. (IMO, International Maritime Organisation, 2007).

To date, diesel engines are cleaner and more efficient. According to an Economic Report elaborated by the ACEA (European Automobile Manufacturers Association) in 2009, more than half of new passenger cars registered in the European Union are powered by diesel engines. Moreover, the future emission legislation aims to progress strict emission guidelines. Modifications to the combustion systems, in the form of common rail, high injection pressure, multi injection strategies cannot achieve these standards. As a consequence, all of the vehicles produced today are equipped with diesel particulate filters (DPF).

When the particles in the filter are accumulated, this can result in filter blockage leading to a reduction of filter efficiency. Therefore, it is essential to clean the filter through a regeneration process (e.g. soot oxidation). There are several competing techniques to regenerate particle filters. These regeneration techniques can be divided into active and passive regeneration processes. The main principles of the active methods are based on temperature control strategies, which actively increase the exhaust temperature through auxiliary systems (Khair, 2003) (e.g. fuel-fed burner, electrical heating, microwave, post injection, etc.) to generate sufficient heat energy burning off the collected particulate matter with oxygen at or above approximately 600°C (York *et al.,* 2007). However, a possible drawback of this method may occur during the high temperature regeneration process, in which uncontrolled temperatures that arise from the soot oxidation process can cause damage to the DPF. The frequent short travel distances and/or stop/start driving patterns may fail to regenerate the DPF resulting in malfunctioning. Furthermore, an extra space is required for an additional system to increase the regeneration temperature which is less attractive for light-duty vehicles.

Passive regeneration methods are based on increasing the NO_2/NO_X ratio in the exhaust gas to reach the required NO_X/soot ratio (e.g. greater than 8:1 or preferably above 20:1) (Khair, 2003) by installing an oxidation catalyst upstream of the DPF (CTR system). Using the recommended ratio, the active oxidative agent (NO_2) produced in the DOC will reduce the thermal energy required to initiate the regeneration, allowing the trapped particulate matter to burn off at lower temperatures (<300°C) (York *et al.,* 2007). However, the unsteady state of the exhaust temperature, caused by the variety of driving conditions, generates a challenge in regenerating the filter efficiently, subsequently, increasing the difficulty of both the active or passive regeneration process.

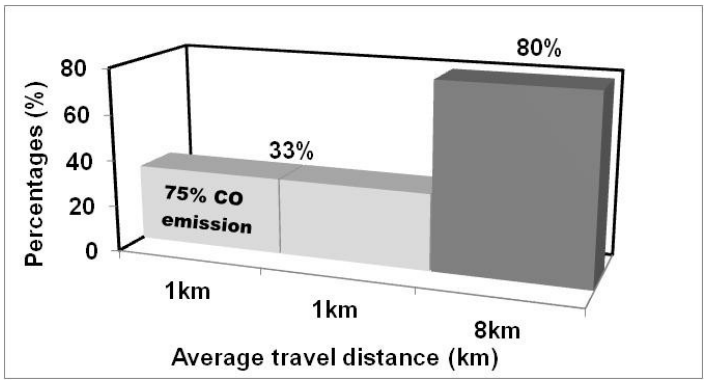


Figure 1.3: Average driving distance and CO emission. (Adapted from Tiward and Colls, 2009)

Recently, surveys (Tiward and Colls, 2009) have shown that, approximately 60-70% of the total annual mileage is completed without the engine having achieved its warmed-up operating conditions, 80% of car journeys are less than 8km and 33% of them are below 2km. Subsequently, it has also been estimated that 75% of total CO is emitted from the first km of a 10 km journey; the data is summarized and re-plotted in Figure 1.3. In other words, in most of the actual driving conditions the DOC has not achieved its highest performance and as a consequence nearly 90% of CO that is typically reduced after the light-off temperature is not actualized, thereby, inhibiting the NO-NO_2 oxidation process. In this respect, the challenge remains to achieve passive DPF regeneration especially operating at low temperature conditions.

Alternatively, the application of Non-Thermal Plasma (NTP) creates a low temperature chemically active media for the exhaust gas and the plasma reactions to take place. In this process the highly active oxidation species (e.g. free radicals, O_3) strongly promote the NO to NO_2 oxidation under the low exhaust temperature conditions. Thus, providing an alternative solution for cold start emissions treatment which cannot be easily achieved by thermal or catalyst processes.

1.1 Objectives and Approaches

The aim of this study is to focus on the enhancement of NO_2/NO_X ratio in the exhaust gas in order to promote low temperature on-board Diesel Particulate Filter (DPF) regeneration. Several methods have been examined to promote the NO-NO_2 oxidation over a wide range of exhaust temperatures (low, moderate and high) under real diesel engine exhaust operating conditions and are summarized below.

- DOC is currently commercially available and represents the most common catalytic devices used of the NO into NO_2 oxidation. In this study, it was used as a reference for investigating the NO-NO_2 oxidation activity at moderate exhaust gas temperatures conditions. Propane was added within the system to study the influence of HC.

- A thermal process was used prior to the introduction of the catalyst. A thermal reactor was designed in this study to investigate the NO-NO_2 oxidation activity at high exhaust gas temperatures. Propane was added within the system to study the influence of HC.

- (Ag/Al_2O_3) HC-SCR has shown promising results for NO_X reduction. In this case, the NO to NO_2 oxidation was studied in the presence of H_2. H_2 was added to the EGR to form a reformate EGR and introduced to the combustion process. The HC-SCR is later installed downstream to obtain the benefit of H_2 remaining from the REGR combustion process.

- Plasma technologies are believed to act as a panacea and are widely applied in modern technology (e.g. plasma screens, plasma cutters, plasma medicine). An atmospheric-pressure non-thermal Dielectric Barrier Discharge (DBD) plasma reactor was designed here for

investigating the NO-NO_2 oxidation activity at low exhaust gas temperatures. Propane was added within the system to study the effect of HC.

To a significant extent, the objectives were met in the present study. The completed work has resulted in one journal paper, presented in SET for BRITAIN 2011, two patents registered and two journal papers are under preparation.

1.2 Research Outline

Health problems caused by diesel Particulate Matter (PM) have been presented in the introduction section. Moreover, the particular challenges current DPF regeneration methods are facing have been outlined. The remainder of the thesis is presented as follows:

Chapter 2: Literature review

The overview of Particulate Matter (PM) from diesel engine emission and the controlled techniques of DPF will be initially presented. As the main research topic focuses on low temperature DPF regeneration and promotion of NO_2 formation over a DOC in the exhaust gas, the author re-collated the active regeneration to O_2 based and passive regeneration to NO_2 based regeneration. This allows the focus of the review articles to be based on the soot oxidation agent applied in the regeneration process. Finally, relevant methods introduced for oxidising NO to NO_2 in the exhaust gas are also presented, including thermal oxidation, catalytic oxidation and non-thermal plasma oxidation.

Chapter 3: Experimental facilities

This chapter presents the details of experimental facilities which include the engine test rig, engine instrumentation, exhaust emissions measurement, plasma power measurement,

specification of monolithic catalysts (DOC, SCR, DPF), and the fuel properties used for this research work. For the purpose of clarity the details of the reactor design along with the experimental setup will be presented separately within the individual chapters.

Chapter 4: The effect of thermal oxidation and diesel oxidation catalyst for enhancing the NO_2/NO_X ratio in diesel engine exhaust gas.

In this chapter, the design of the thermal reactor and the experimental setup used to study the thermal oxidation are presented. The thermal reactor was used for the temperature ramps study to investigate the temperature ranges of NO-NO_2 oxidation associated with the highest NO_2 produced from the diesel exhaust gas. The same process was applied to the DOC. Propane was also used as an additive to study the promoting effect for both oxidation methods. Information of the reaction mechanism under the effect of propane was provided from the literature review, to better understand the important roles of major radicals. Both pre-oxidation systems were later installed upstream of the DPF, to exam the regeneration processes over the temporal evolution of the pressure drop across the filter.

Chapter 5: Influence of hydrogen and reformate combustion on NO to NO_2 oxidation in the engine combustion chamber and HC-SCR

The research work presented in this chapter was carried out in two sections; in which the primary goal was to enhance the NO_2 formation after the combustion process through adding H_2 into EGR to simulate a reformate EGR process.

Secondly, the HC-SCR catalyst was installed in the engine exhaust. This provided the opportunity of utilising the hydrogen that remained after the combustion process in promoting the NO-NO_2 oxidation in HC-SCR. The final part of the chapter studied the regeneration

processes over the temporal evolution of the pressure drop across the filter. The combination systems REGR-SCR-DPF obtained good results, simultaneously removing the NO_X and PM from the diesel emission. The details of the experiment setup are also provided.

Chapter 6: Preliminary study of NO-NO_2 oxidation in the Dielectric Barrier Discharge (DBD) plasma reactor

Application of the DBD plasma technology to the exhaust treatment represented the initial research work in the Future Power System Group at the University of Birmingham. This chapter was used as a preliminary investigation of NO-NO_2 oxidation on the new reactor and plasma circuit. The full experimental setup is provided in this chapter. Several combination of O_2, N_2, NO, and C_3H_8 from bottled gas were used as synthetic gas mixtures to study the NO-NO_2 oxidation process over the DBD plasma reactor. The results obtained compared with other similar published research to confirm the performance of this reactor.

Chapter 7: The applications of Dielectric Barrier Discharge (DBD) plasma for enhancing the NO_2/NO_X ratio in diesel engine exhaust gas to improve low temperatures DPF regeneration

This chapter extends the work from the studies in the previous section. The performance of DBD plasma reactor on the NO-NO_2 oxidation process was evaluated under real diesel exhaust gas conditions. The engine was tested at different conditions to provide different compositions of exhaust gas for the study. In addition, propane was used as the additive to enhance the NO_2/NO_X ratio in the exhaust gas. This provided an enhancement for the DPF which was installed downstream from the DBD plasma reactor. The regeneration processes over the temporal evolution of the pressure drop across the DPF will be investigated in the final section.

Chapter 8: Conclusions

This chapter summaries and outlines the research works that has been covered in the thesis, and provides suggestions for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Particulate Matter (PM) from Diesel Engines

The incomplete combustion of hydrocarbon fuel contributes to the emission of PM. However, the formation of PM is relatively complex involving chemical and physical processes, and many details of the mechanisms still have not been understood (Zhao & Ladommatos, 1998), which creates major challenges for diesel designers and environmentalists to understand the PM species over different regions (e.g. in-cylinder, exhaust tail pipe, atmospheric).

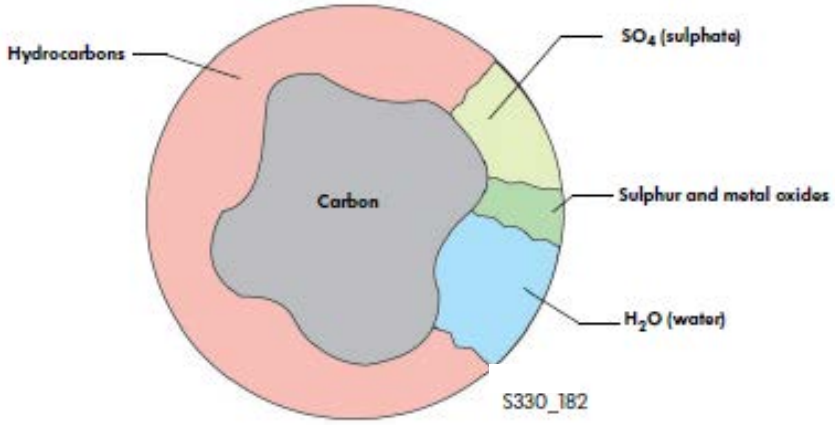


Figure 2.1: Diesel Particulate Matter (PM) compositions. (Source: Volkswagen AG, 2005)

As illustrated in Figure 2.1, the diesel PM consists of several compounds. The main core of PM is made up of soot particles, in which they are adsorbed with different layer of species such as metal oxides and sulphur. However, the exact structure of the PM changes depending on the engine technology, operating conditions and the type of fuel (Broome and Khan, 1971).

In general, PM can be separated into three categories: (a) solid carbonaceous fraction, (b) volatile organic fraction, and (c) sulphur compounds fraction which are summarised as below (Eastwood, 2000).

(a) Solid carbonaceous fraction

Primarily consisting of carbonaceous soot and include small portion of incombustible ash derived during the combustion in locally fuel rich regions in the combustion chamber. It is also considered as an insoluble fraction because the majority of elements appear in the solid phase.

(b) Soluble organic fraction

Is a complex mixture of high molecular weight organic compounds derived from the unburned fuel and evaporated lubricant oil which is partly oxidised in the combustion chamber and appears as volatile organic fraction (VOC).

(c) Sulphur compounds fraction

This is derived from the sulphur compounds presented in the diesel fuel. In the high temperature combustion chamber, the fuel sulphur components are combusted to form sulphur dioxide (SO_2), and some of this species is oxidised into sulphur trioxides (SO_3). This contributes to the formation of sulphate (SO_4^{2-}).

2.2 Diesel Particulate Filter

The invention of the Diesel Particulate Filter provides the best solution in eliminating Particulate Matter (PM) in diesel engines. The most common and popular DPF presented these days are formed in wall-flow monolithic structures as shown in Figure 2.2. The exhaust gases flow through the monolithic wall of the filter with alternate channels plugged at both ends; this design inhibits the exhaust flow that exits the cell directly from the same channel,

and forces it to exit the adjoining channel before being released to the atmosphere. This process contributes to more than 90% (Prasad & Bella, 2010) of the soot particle emissions trapped within the porous walls of the filter. When the accumulated particles in the filter are allowed to amass, this can result in a significant reduction in the filter efficiency in a short period of time. This continual depositing behaviour increases the exhaust backpressure. This is detrimental to the engine's performance, as it leads to increased fuel consumption (Khair, 2003). Therefore, it is essential to clean the filter through the regeneration process.

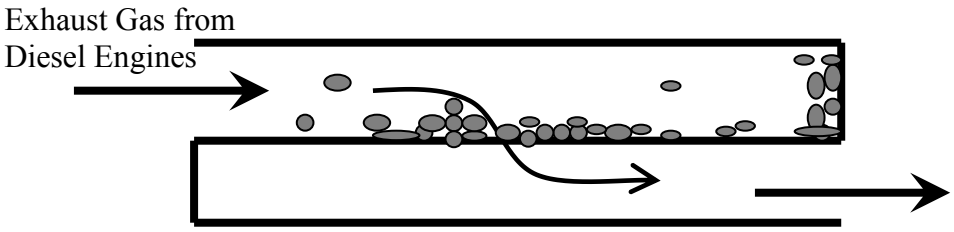


Figure 2.2: Schematic view of a wall-flow Diesel Particulate Filter (DPF).

There are several competing techniques to regenerate the particle filter. These regeneration techniques can be mainly divided into active and passive regeneration processes (Fino, 2007). Within active regeneration O_2 forms the oxidation agent, and DPF regeneration process functions under higher temperature conditions. Conversely, NO_2 is more reactive compared to O_2, which can operate within the regeneration process passively at lower temperatures. For this reason, the author re-classified the regeneration processes through the type of oxidation, and replaced the 'active regeneration' as 'O_2 based regeneration' and 'passive regeneration' as 'NO_2 based regeneration' respectively.

2.2.1 Oxygen (O_2) Based Regeneration

According to Kim *et al.* (2010), the general reaction scheme of carbon oxidation by oxygen in the exhaust gas can be expressed as follows:

$$C + \alpha_1 O_2 \rightarrow 2\,(1-\alpha_1)\,CO + 2\,(\alpha_1 - 0.5)\,CO_2 \qquad (2.1)$$

where the values of α_1 is between 0.55 to 0.9 (Zhang *et al.*, 2002), which is used as an index of the completeness reaction between C and O_2, and CO and CO_2 are the final products of the reaction.

Based on the reaction mentioned above, there are two general requirements that have to be satisfied for oxygen based regeneration, which are the temperature to be 550˚C or higher and the oxygen concentration to constitute at least 5% of the exhaust gas (Swiss Agency, 2000). Normally, it consists of 7% to 22% vol. of oxygen concentration in the diesel exhaust gases (Kim *et al*., 2010), and the value varies according to engine operating conditions. In the case of temperature, however, most of the engine exhaust temperatures are lower than the temperature required for soot oxidation, especially for the operation of light-duty vehicles.

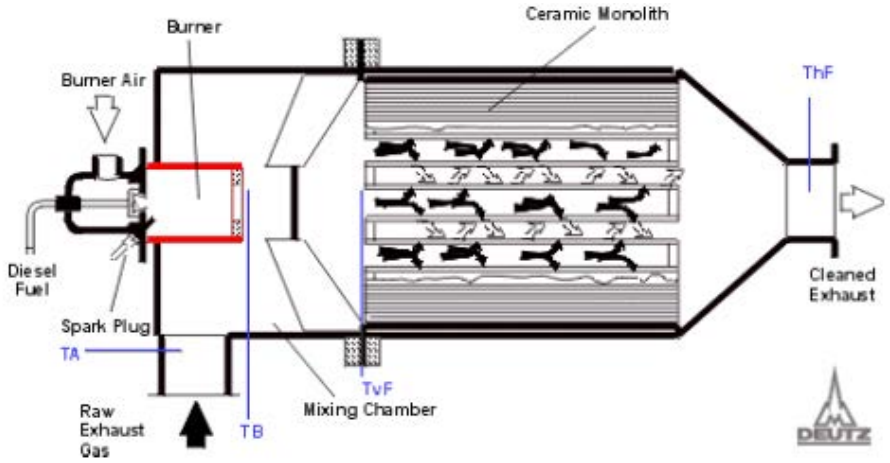


Figure 2.3: Fuel Burner Regenerating Filter. (Source: DG ENTR).

For this reason, several techniques to raise the exhaust temperatures have been reported in order to reach the threshold temperatures for oxidising soot directly on-board the vehicles. These technologies can either be controlled though the addition of auxiliary systems or by the engine management itself. As the previous example used in active regeneration, the former included fuel-fed burner, electrical heating, and microwaves, while the later control is mostly

applied in modern diesel engines, which employ the flexible fuel injection system. Some commercially available retrofitting devices have been reported by auto industries, for example, Deutz AG developed a fuel burner regeneration device (Figure 2.3), which has successfully passed the VERT field durability tests for over 2000 hours. Gillet and FEV (Swiss Agency, 2000) have developed a system which allows the soot to be burned off by electrical heating only, however this technique is associated with a higher energy penalty. This was also confirmed by the research group from Ford Motor Co. *et al*. (1985), in that they agreed that the higher energy efficiency of fuel burners are more favourable compared to electrical heaters applied in O_2 based filter regeneration, however it suffered secondary emissions problems.

More recently, ArvinMeritor developed a filter regeneration device called ActiveClean^{TM} Thermal Regenerator (Kong *et al.*, 2004). Comprehensive results have demonstrated that this device is able to regenerate the filter at any engine condition, and has increasingly captured market attention. Another attempt has been made to increase the exhaust temperature by controlling the fuel injection strategy. Gantawar *et al.* (1997) has proposed a filter regeneration skill by controlling the engine operation, and boosting the exhaust temperature by temporarily increasing the engine to full load condition. Bouchez and Denenthon (2000) also confirmed that retarding the injection timing can increase the exhaust temperature, and only a less than 2% fuel penalty is required under the steady-state engine conditions. In general, more accurate and efficient control can be reached by retarding the injection timing, injecting the fuel at the top end of the cylinder's expansion stroke, at that combustion phase, in which no additional work can be done; the energy of the fuel is then released to the exhaust to provide sufficient heat for filter regeneration.

Another O_2 based regeneration is presented by Garner and Dent (1990), in which about 40 ~ 80% of regeneration efficiency is recorded by the microwave regeneration. Henrichsen and Popuri (U.S. Department of Energy) also reported that, this technology is still in the development stage, and it may possibly be another useful tool for future filter regeneration.

Alternatively, the introduction of fuel-borne additives enables the reduction of the soot burn-out temperature, and lower exhaust temperature is required to regenerate the filter. Lepperhoff *et al*. (1995) studied the effectiveness of fuel additives between cerium-based, copper-based and ferrocene-based fuel additives over the steady-state engine condition, and cerium-based fuel additive is suggested to be the best candidate as allowed for a lower the soot ignition temperature to 200˚C. In addition, the mature development of the cerium-based additives technique was also successfully announced by PSA Peugeot-Citroen (2000), who introduced the first commercialized vehicle adopting these technologies.

2.2.2 Nitrogen Dioxide (NO_2) Based Regeneration

According to Kim *et al*. (2010), the general reaction scheme of carbon oxidation by NO_2 in the exhaust gas can be expressed as follows:

$$C + \alpha_2 NO_2 \rightarrow (2- \alpha_2)\, CO + (\alpha_2 - 1)\, CO_2 + \alpha_2 NO \qquad (2.2)$$

where the values of α_2 is between 1.2 to 1.8 (Opris and Johnson, 1998), which is used as an index of the completeness reaction between C and NO_2, CO, CO_2 and NO are the final products of the reaction.

The higher oxidation potential of NO_2 with soot has gained growing interest, for considering it to be the main oxidising agent for DPF regeneration. In particular the advantage of low temperature soot oxidation of NO_2 (around 250˚C) (Ehrburger *et al.*, 2002) is more

acceptable for applications in current passenger vehicles. However, the amount of NO_2 concentration presented in the exhaust gas is still low and not sufficient to oxidiser the soot under such conditions. The application of an oxidation catalyst over the exhaust gas provides a solution of this limitation; the oxidation catalyst with higher level of NO_2 can be used in the soot oxidation process.

Johnson Matthey was the first industrial company who combined the oxidation catalyst (DOC) with DPF and patented it as a passive regeneration called Continuously Regenerated Diesel Particulate Filter (CRT) (Cooper *et al.*, 1990). A new innovation has been developed, namely Coated Diesel Particulate Filter (CDPF), directly coating the oxidation catalyst on the DPF surface itself, in order to improve the compactness of the system. Although CDPF has the advantages of installation space, the efficiency of the soot regeneration process within the DPF was reduced. This is because when the soot loading is faster than the regeneration process, the architecture designed catalyst coating within the DPF, induced the NO_2-soot reaction underneath the soot layer (Görsmann, 2005), and the regeneration process becomes less sensitive. As a result, more NO_2 was measured downstream the DPF. The latest commercialized NO_2 based regeneration device for DPF regeneration, also created by Johnson Matthey, is believed to be the most promising method currently available. This system combines DOC and CDPF, providing two reaction pathways to oxidise NO into NO_2, which is called Catalysed Continuously Regenerating Technology (CCRT^{TM}). Three systems were compared at low temperatures (< 270˚C) for their performance in DPF regeneration which was reported by Görsmann (2005). The schematic diagram of these devices is shown in Figure 2.4, and it is concluded that, CCRT system combines the benefits of CRT and CDPF and shows better performances in every aspect of the DPF regeneration process (ex. operate

temperature, pressure drop) and the performance of these systems are ranked in the order: CCRT > CRT > CDPF.

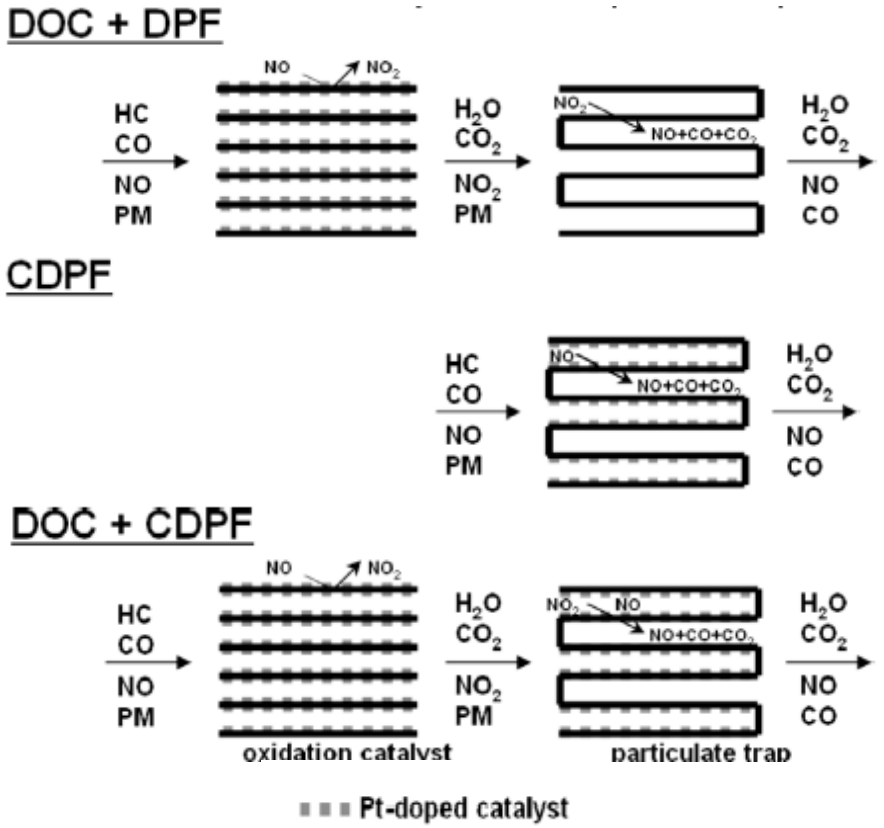


Figure 2.4: CRT, CDPF and CCRT systems on filter regeneration. (Source: Deutz).

Some general principles have to be considered in order to improve the efficiently in applying the NO_2 based regeneration methods over the DPF. Ultra low sulphur fuel (<10ppm) is required to run the systems, however it is believed this limitation can be neglected, due to its widespread application in the future (Allansson *et al.*, 2000). Hawker *et al.* (1997) reported that, self regeneration process (no intervention required/ without manual control or external support) was produced over the DPF itself under the temperature range 200 – 450˚C.

Additionally, NO_X emission is also another important factor for passive DPF regeneration control, which has been presented by York *et al*. (2007). It requires at least 8:1 or preferably above 20:1 of NO_X/soot ratio for the NO_2 based regeneration process (Khair, 2003).

Kim *et al*. (2010) numerically investigate the NO_2 assisted soot regeneration over the heavy-duty diesel engine; similar parameters called NO_2/soot ratio has been reported. It is suggested that the most reasonable range for continuous regeneration is $7 \leq NO_2/soot < 8$. More recently, the ratio of NO_2/NO_X has also been examined (Chong *et al.*, 2010; Gill *et al.*, 2011). The research focuses on the effect of pre-oxidiser (catalytic oxidation) on promoted NO_2 formation in the exhaust gas, in order to improve the NO_2 based regeneration. It is observed that, for all the parameters mentioned above, it is always associated with the EGR (Exhaust Gas Recirculation) control strategy, which is the typical technique applied in NO_X emission control (Tsolakis *et al.*, 2005; 2007).

2.2.3 Oxygen (O_2) + Nitrogen Dioxide (NO_2) Based Regeneration

Little attention has been focused on the combined effect of O_2 and NO_2 on commercialized DPF regeneration devices. Among most of the theoretical and experimental studies it is concluded that the mixture of O_2 and NO_2 provided the highest advantages for soot oxidation, compared to the regeneration with O_2-only and NO_2-only. The accumulative effect of both oxidisers can also be observed.

According to Jacquot *et al.* (2002), the mechanism reaction of carbon oxidation by O_2 and NO_2 can be expressed in the following:

$$C \leftrightarrows (\text{int. species}) \leftrightarrows CO_2 + CO + NO + NO_2 \qquad (2.3)$$

The soot oxidation is initiated by the NO_2 that reacts with soot and creates an intermediate species called surface oxygen complexes (SOCs). These intermediates later react with oxygen to form CO_2, CO, NO and NO_2, which leads to the largest increase in the rate of carbon consumption. It is observed that, although NO_2 is involved in the reaction, it is not

fully consumed after the reaction. More discussion of oxygen complexes and the complex reaction with oxygen has been published by Setiabudi *et al*. (2004).

Moreover, another accumulate effect can be found in the mixture of O_2 and NO_2 that shifts the carbon oxidation profiles to lower temperatures compared to the condition with O_2-only and NO_2-only (Setiabudi *et al.*, 2004). This observation has also been confirmed by Schejbal *et al.* (2010) through modelling studies of soot oxidation by NO_2 over different regeneration systems (CRT, CDPF and CCRT). At a temperature of 300˚C, the reaction rate of carbon oxidation in O_2 and NO_2 mixture is approximately double compared to NO_2-only, and no significant carbon gasification was recorded for the condition O_2-only. It has also been supported by Jeguirim *et al*. (2005), that O_2 and NO_2 mixture oxidises soot particles faster than the oxidation rates with O_2-only and NO_2-only. A more comprehensive study of carbon oxidation with other possible oxidisers in the exhaust gas has been reviewed by Stanmore *et al*. (2008).

In reality, different regeneration modes can be achieved by applications to passive regeneration methods (CRT, CDPF and CCRT). Regeneration processes either can be triggered into 'direct NO_2 mode' or 'cooperative NO_2-O_2 mode'.

The author defined the 'direct NO_2 mode' as self-regeneration, in which the exhaust gas reached the catalyst (DOC) light-off temperature and allowed the DPF to be continuously regenerated. However, it is reported that self-regeneration will not completely remove the soot within the DPF, and off-board regeneration is always required to maintain the filter performances after a long period of travel.

For this reason, the concept of 'cooperative NO_2-O_2 mode' is suggested, which requires external intervention to increase the exhaust temperatures, in order to have the accumulative

benefit of both oxidisers. Under this regeneration condition, more complete soot oxidation can be done on-board the vehicles. Closely related work has been conducted by Görsmann (2005) who observe that more complete regeneration is obtained in the temperature range of 540 - 640˚C under the CDPF.

2.2.4 Control Strategies of Regeneration

Figure 2.5 shows the trade-off of fuel penalties for DPF regeneration over a passenger car. It shows that, there is no gain from regenerating the filter below the travel distance of 200km, which is the highest fuel penalty, paid to increase the exhaust gas temperature for the regeneration process.

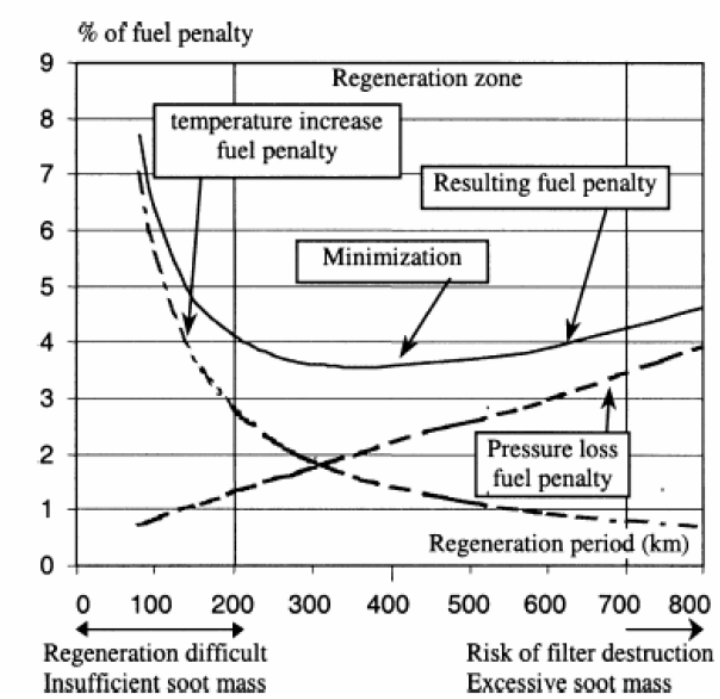


Figure 2.5: Fuel Penalty Tradeoff for DPF Regeneration. (after: Salvat *et al.* 2000).

This is because the soot accumulated on the filter is proportional to the fuel required to initiate the regeneration process. At short travelling distances, only a small layer of soot is accumulated on the filter, and a higher investment of energy is required to initiate the

regeneration of the DPF. However, if the regeneration process is initiated after a long travelling distance (after 700km), the over loading of soot may cause the risk of damage to the filter, due to the unprotected heat released from the exothermic reaction of soot combustion.

For this reason, it is suggested the regeneration process for diesel passenger vehicles is between the travel distance of 300km ~ 500km, which is believed to be the best control strategy for DPF regeneration in considering the fuel economy and filter maintenance (Salvat *et al.,* 2000).

Additionally, Ford Research Center (taken from SAEFL, 2000) provided engine operation mapping and the exhaust gas temperatures employed for different current commercially available regeneration methods (Figure 2.6). The maps show that, to initiate the low temperature regeneration process the addition of the fuel burner and electrical heater allows for an increase in the exhaust temperature to 200˚C and 250˚C, respectively. The fuel-born additives, can be applied when the exhaust temperature is between 350 to 500˚C. Lastly, although the CRT system represents the most promising regeneration methods in this figure, a wider operating temperature range (235 - 500˚C) can be used, however, improvement for low temperature regeneration is required to fulfill future emission legislation.

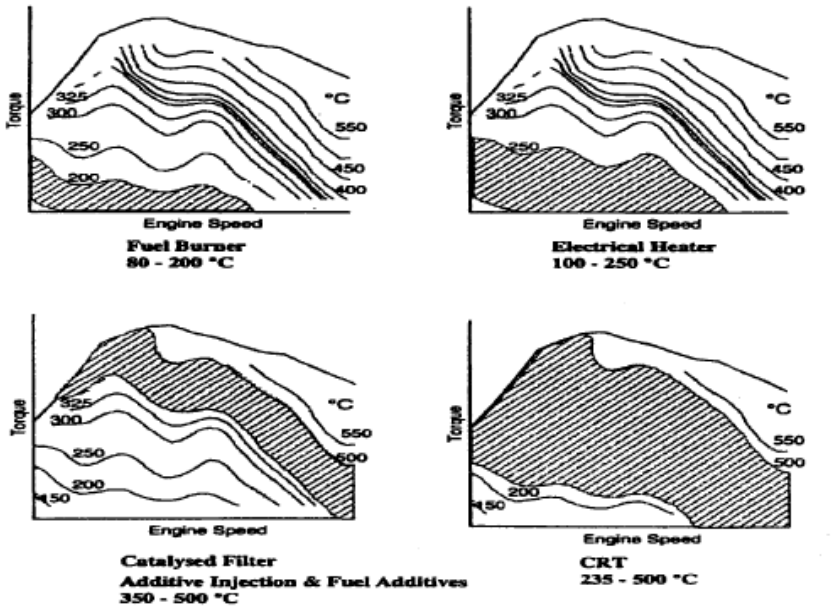


Figure 2.6: DPF Regeneration Methods for Different Engine Operation and Exhaust Temperature Ranges. (Source: SAEFL, 2000).

2.3 In-Cylinder NO-NO_2 Oxidation Process

The high oxidation property of NO_2 allows DPF regeneration at lower temperature and be successfully applied on-board the vehicle. However, the NO_2 (only 5-15% of overall NO_X emission) in the diesel engine is not sufficient in the actual regeneration application. The oxidation of NO to NO_2 process is observed during the combustion process (in-cylinder) or after the combustion process (exhaust pipe). According to the literature studied, there are very few papers focused on the method of promoting the NO-NO_2 oxidation process in-cylinder, and more discussion is given to the formation of NO_2 during the combustion process. Conversely more studies have been carried out to investigate the NO-NO_2 oxidation in the exhaust gas through several oxidation methods, which include non-catalytic, catalytic, and non-thermal plasma. Van Setten *et al*. (2001) has named this process as a preoxidiser when applied with other aftertreatment devices such as SCR and DPF.

The NO_X is formed in the combustion chamber under high temperature conditions (> 2000 K) (Bacha *et al.*, 1998) over the oxidation process of atmospheric nitrogen (N_2) contained in the fuel-oxidant mixture. Due to this, the thermal NO_X mechanism is believed to mainly contribute to the formation of NO_X in the combustion process. The reaction of the thermal NO_X mechanism governs the N_2 molecule in the formation of NO over the three reactions processes, which can be explained via the extension of the Zeldovich mechanism:

$$O + N_2 \leftrightarrow NO + N \quad (2.4)$$

$$N + O_2 \leftrightarrow NO + O \quad (2.5)$$

$$N + OH \leftrightarrow NO + H \quad (2.6)$$

From there, it provides the initial opportunity of producing the NO_2 in the combustion. Many researchers have established that the hydroperoxyl radicals (HO_2) play an important role in producing NO_2 through the oxidation process of NO into NO_2 and produces the following reaction:

$$NO + HO_2 \leftrightarrow NO_2 + OH \quad (2.7)$$

The first reference to this concept was associated with the research in the 1970s by Merryman and Levy (1974) that studied the NO_2 formation in the combustion process. Although it is difficult to justify the local formation of HO_2 in the combustion chamber, however, HO_2 has been found to occur in regions where high concentration and temperature gradients, cause the diffusion of radicals (H, O, and OH) into cool boundary layers or eddies exist (Hargreaves *et al.*, 1981).

Similarly research carried out by Jones and Leng (1996), confirmed that the HO_2 radicals are formed during the rapid cooling process in the hot combustion gas. Sano (1984) provided

numerical simulation of combustion, in which a higher amount of NO_2 formation was found within the mixing region of cool air with the combustion gases. In addition, Arcoumanis and Jou (1992) concluded that NO_2 is a transient intermediate species that exists only at flame conditions, but is possible to convert back into NO within the post flame region, unless quenched with other cooler fluids. Therefore, a higher NO_2 formation in the combustion process can be achieved by operating the engine at low fuelling rates (greater cooling effect is formed by a higher amount of input air to the combustion chamber).

2.4 Exhaust Gas NO-NO_2 Oxidation Process

2.4.1 Non-catalytic Oxidation Process (Thermal Oxidation)

Before the invention of the catalytic converter, the thermal oxidation process was one of the most common methods applied in environmental pollution control, especially in the successful application of removing Volatile Organic Compounds (VOC) (Kim, 2011). The thermal oxidation process also can be categorised as part of a non-catalytic oxidation process due to the absence of catalysts in which only heat is provided during the process.

The research of applying thermal oxidation in the NO to NO_2 oxidation process was popular in the 1990s. The main objective is to provide an alternative solution for improving the performance of NO_X reduction over the Selective Catalytic Reduction (SCR) process. However, NO_X can also be removed with scrubbing techniques. This is because enhancing the proportion of NO_2 in the NO_X emission can improve the catalyst surface absorption processes, and induce a higher solubility of NO_2, making the scrubbing technique feasible in the aftertreatment application. The degree of NO_2 formation can be quantified from measuring the NO_2/NO_X ratio at the exit of the thermal reactor, and analysing the NO_2/NO_X ratio in the

exhaust gas also provides useful information for environmental pollution and indoor behaviour (Hori, 1988a).

Hori *et al*. (1992) has extensively contributed to the understanding of thermal NO to NO_2 oxidation. NO_2 formation was attributed to the HO_2 kinetic mechanism, and the research demonstrated that the roles of HO_2 radicals are dominant in the NO to NO_2 oxidation process, and are not limited to the in-cylinder combustion process, which also contributes to the exhaust gas.

To achieve the rapid formation of HO_2 radicals throughout the exhaust gas, several studies have suggested the supply of HC additives to the engine cylinders or exhaust gas. A kinetic and experimental study of thermal oxidation were carried out by Hori *et al*. (1992), demonstrating the interaction of NO/Air mixture with seven types of hydrocarbon fuels (C_1 to C_4 hydrocarbons), in which hydrogen and carbon monoxide were studied. The results show that the effectiveness of additives in promoting NO to NO_2 oxidation in the following order $(H_2/CO) < CH_4 < C_2H_6 < C_2H_4 < C_3H_8 < i\text{-}C_4H_{10} < n\text{-}C_4H_{10}$. Similar results were presented by Jasma and Boreman (1980), H_2 and CO show a similar pattern in promoting the NO oxidation process, but the effect was not significantly strong.

Additionally, research shows that the effect of hydrocarbon additions not only promote the NO to NO_2 oxidation, but a mutual oxidation effect was found between NO and hydrocarbon. Bromly *et al.* (1992) carried out a study on mutually sensitised oxidation of NO and $n\text{-}C_4H_{10}$ in the mixture with air. He found that the influences of low concentrations of NO in the mixture will promote the oxidation of $n\text{-}C_4H_{10}$; conversely, the only trace of $n\text{-}C_4H_{10}$ to the mixture promotes the NO oxidation. Also Hjuler *et al*. (1995) reported that NO and organic compounds mutually promoted the oxidation process under thermal conditions.

Subsequently, different types of additives were presented by Kundu and Deur (1991). Kinetic studies of aliphatic compounds included methanol, ethanol, ethane and butane. The presence of all the above additives promoted the formation of NO_2; however, the effectiveness of additives was not included in that discussion. In addition, Lyon *et al*. (1990) also confirmed the benefits of methanol in promoting NO to NO_2 oxidation.

More recently, Hori *et al*. (2002), has extended the research on temperature dependence of NO to NO_2 oxidation. A new oxidant fuel was introduced (*n*-C_5H_{12}). The results show that *n*-C_5H_{12} has the greatest effect in promoting NO oxidation compared to his previous findings. However, for temperatures higher than 900K, the NO_2/NO_X ratio was decreased. This is because at higher temperature, a counter reaction of NO is promoted by HO_2 radical that are formed, and NO_2 is converted back into NO.

2.4.2 Catalytic Oxidation Process

A catalytic device was designed in order to remove the harmful emissions from diesel exhaust gas, which is called catalytic converter. The first diesel catalytic converter was introduced in the 1970s, which was used to reduce the CO and HC emissions from underground mining. These days, the increasingly stringent emissions standards have driven the demand for stimulated research of catalytic converters.

As illustrated in Figure 2.7, the application of catalysts is able to decrease the activation energy of the reaction, and/or provide a new reaction pathway between reactants and products. In other words, under the same reaction temperature conditions, the reaction rate with a catalyst applied is faster than a non catalytic reaction. Generally speaking, catalysts do not participate in the chemical reaction nor consume themselves, though they may be inhibited, deactivated or poisoned as from the reaction.

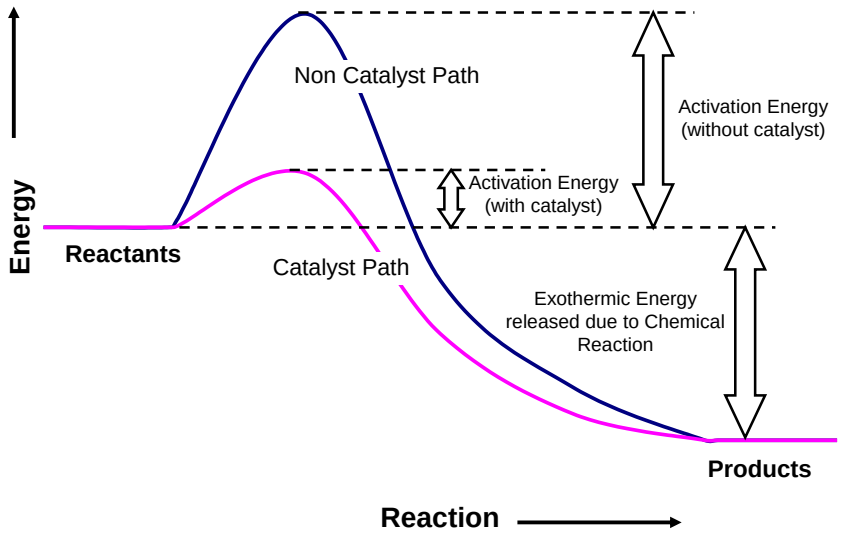


Figure 2.7: Effect of Catalyst in Chemical Reaction. (Source: Banerjee, 2007).

The key component of a catalytic converter is the monolith block located inside the converter. When the exhaust gas flows into the catalytic converter, the physical (mass transfer) and chemical (kinetics reaction with catalyst) processes take place within the monolith channels.

Monolith catalysts consist of three major substances (Figure 2.8), (1) substrate, (2) washcoat and (3) catalyst. To accomplish in diesel emission application, the substrate is designed from high mechanical properties (low thermal expansion coefficient and high temperature resistance) and the ceramic materials were firstly applied (Cybulsko and Moulijn, 2006). The catalysts were dispersed in the washcoat, in order to increase the catalyst loading area; the washcoat was designed as a porous structure and was composed of gamma-alumina (γ-Al_2O_3) (Bennett *et al*, 1992). Lastly, the catalyst itself was coated in the washcoat. The selection of the catalyst depends on its role in exhaust gas treatment. For example, a noble metal catalyst such as platinum (Pt) coating is commonly applied for oxidiser NO into NO_2.

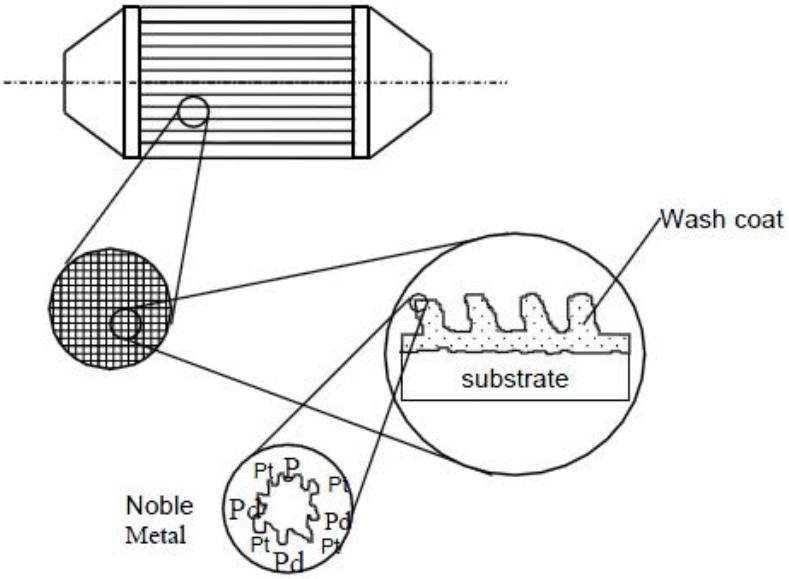


Figure 2.8: Structure of the Monolithic Catalytic Converter. (Source: Stratakis, 2004).

In general, a broad variety of different catalytic converters are introduced to the diesel aftertreatment. Concerning the catalytic oxidation process converting NO to NO_2 in the diesel exhaust, the most successful devices that appear in production vehicles include:

- Diesel Oxidation Catalyst (DOC)
- Hydrocarbon-Selective Catalytic Reduction (HC-SCR)
- NO_X Storage Catalyst

2.4.2.1 Diesel Oxidation Catalyst (DOC)

Compared to other exhaust gas aftertreatment devices, Diesel Oxidation Catalyst (DOC) had the longest history and successful record in vehicle applications. The early development of DOC aimed to abate CO and HC. Under the pressure of new regulated emission standards for highway diesel engines in the 1990s, the second generation of DOC was announced and had the further task to regulate particulate emissions control.

In the 21st century, a multi-discipline DOC has been introduced to the market, effectively converting the CO, HC and PM (consists of carbonaceous, Soluble Organic Fraction (SOF), and Volatile Organic Fraction (VOC)) emission into H_2O and CO_2. When the DOC light-off temperature is achieved, high conversion efficiencies were found and Prasad *et al*. (2010) reported that, around 60~90% for the HC and CO and 20~40% for PM.

More recently, the promising results shown in the NO_2 based DPF regeneration (required a pre-oxidiser installed upstream DPF) has introduced a new task for DOC, which is expected to improve the NO oxidation process of the exhaust gas, in order to increase the NO_2 proportion for DPF regeneration. Though the NO_2/NO_X ratio in the exhaust gas has the potential to reach the value of 0.40 ~ 0.45, by applying a Pt based DOC to the exhaust gas, however, higher temperature is required (about 310 ~ 390˚C) (Sadler Consultants, 2006)

Several studies have focused on the oxidation process of NO to NO_2 over different metal-based catalysts. Després *et al*. (2004) carried out tests of the Pt/SiO_2 catalyst by different combinations of mixtures (NO, NO_2, O_2, H_2O and N_2), and the result implicated that increasing the oxygen concentration in the mixtures rapidly promoted the NO to NO_2 oxidation, however, this observation reached a plateau for O_2 concentration of 10%.

Majewski *et al*. (1995) and Kawanami *et al*. (1998) have confirmed that Pt based catalysts had a better operation temperature advantage compared to the conventional Palladium (Pd) based catalyst. Lower HC and CO conversions were found at lower temperature in applying the Pt catalyst to the DOC. Katare *et al*. (2007) studied the conversion performances for a new and aged DOC. The result shows that, for the temperature below 200˚C, NO oxidation process will not begin before HC and CO were fully oxidised. A new developed catalyst which combined the Pt/Pd was established by Watenabe *et al.* (2007),

in which further improvements of oxidation activity for unburned diesel fuel under the low operating temperature was achieved.

In addition, there also exist other methods to improve the oxidation process of NO to NO_2 through the addition of additives. H_2 addition was reported to be the most effective additive to improve the DOC performance. Salomons *et al*. (2006) studied the mixtures of CO and H_2 (bottle gas was used) over a Pt based DOC. The researchers reported only a little amount of hydrogen (500ppm) addition shifting the CO oxidation to lower temperature. This was also confirmed by Tsolakis *et al*. (2009) with a real diesel exhaust gas which provided more realistic experiment result. Gill *et al*. (2011) reported that H_2 addition also promoted the NO to NO_2 oxidation as well as CO and HC, and raised the NO_2/NO_X to a higher ratio. Theinnoi *et al*. (2012) suggested that the increased NO to NO_2 oxidation by H_2 addition is attributive to the reaction of H_2 over the DOC, which provided an exotherm to increase the DOC temperature.

2.4.2.2 Selective Catalytic Reduction (SCR)

SCR catalyst is designed to reduce the NO_X emission for the lean operated engines (high excess of O_2). Hydrocarbon Selective Catalytic Reduction (HC-SCR) is one type of SCR catalyst which utilised hydrocarbons as a reducing agent. Other kinds of SCR catalyst using different reductants have been reported which mainly included Ammonia-SCR and Urea-SCR catalyst. The feasibility of applying diesel fuels as the reductant over HC-SCR (Eränen *et al*., 2003), has received much attention in developing this technology due to the on-board reductant available.

The selective catalytic reduction mechanism of using diesel fuels as reductant can be expressed as:

$$C_nH_m + \left(2n + \frac{m}{2}\right) NO \rightarrow \left(n + \frac{m}{4}\right) N_2 + nCO_2 + (\frac{m}{2})H_2O \qquad (2.8)$$

The reaction utilises the available NO in the exhaust gas reducing it into N_2, CO, and H_2O. Yet it also appeared to compete with oxygen, which reduced the NO_X conversion efficiency. Therefore, several kinds of catalytic compositions (e.g. zeolite catalysts, noble metal catalysts, metal oxide catalysts) have been studied to increase the selectivity of NO_X reduction to N_2 in the process. The high activity and selectivity of silver-alumina metal oxide catalysts (Ag/Al_2O_3) have been reported (Burch *et al.*, 2002; Satokawa *et al.*, 2000), and successfully applied over full scale vehicles tests (Klingstedt *et al.*, 2004).

Additionally, the contribution of H_2 also appeared in Ag/Al_2O_3 catalyst (Shimizu *et al*., 2006; Golunski *et al*., 2005), especially the improvement of low temperature (<200˚C) NO_X reduction process (Satokawa *et al*., 2003) and preventing catalyst deactivation by the formation of soot on the catalyst surface (Houel *et al*., 2006) have been reported.

Houel *et al.* (2006) suggest the improvement of catalyst deactivation at low operated temperature is due to the formation of NO_2 (strong oxidant agent) in the process which effectively remove the carbon layer formed on the catalyst surface. The effect of H_2 promotes the NO to NO_2 oxidation over the Ag/Al_2O_3 catalyst was also confirmed by Shibata *et al*. (2004). Moreover, compared to the experiment results preformed over the feed synthetic mixture gases presented above, a more practical study has been carried out of a diesel exhaust gas (Chong *et al*. 2010) and obtained similar results.

2.4.2.3 NO_X Storage Reduction Catalyst

Another commercially available device that enabled the NO oxidation process within the reaction is the NO_X Storage Reduction Catalyst, or referred to as NO_X adsorber catalyst (NAC). NAC provides an alternative method to reduce the NO_X emission under lean burn exhaust gas.

The operating principle for $DeNO_X$ process of NAC slightly differs to the SCR process. The latter requires a continuous supply of reductant to the system (can be achieved by active or passive) in order to maintain the optimum operation condition for the catalyst (Mital *et al.*, 2002); conversely, the former initially stores the NO_X in the catalyst under the lean operation and later releases it under rich operation.

NAC consists of three major processes, and the examples of the components are presented in blanket, which can be divided into:

I. Oxidation process (i.e. Platinum, Pt)

II. Adsorption process (i.e. Barium carbonate, $BaCO_3$)

III. Reduction process(i.e. Rhodium, Rh)

Several studies have compared the storage ability of NO and NO_2 over the NAC. Different mixtures of (NO, NO_2, O_2, and N_2) gas were fed into a commercial NAC by Mahzoul *et al*. (1999), that found the storage capacity was increased by enhancing the NO_2 level in the mixture. Fremerey *et al*. (2011) applied the directly monitored in situ and microwave-based method to observe the NO_X loading on the NAC, and the result shows NO_2 can be stored more easily and at a higher capacitance than was recorded over the catalyst, compared to NO. Therefore, the pre-oxidation process is important in NAC treatment, as the

NO_2 proportion has to be increased before the storage process begins in order to improve the NO_X reduction efficiency.

2.4.3 Advance Oxidation Technologies (Non-thermal plasma oxidation)

Compared to the challenges facing the conventional oxidation methods (thermal and catalyst) it has led to an interest in alternative NO oxidation on low temperature processes, high energy efficiency and without catalyst poisoning issues. Advance oxidation technologies (AOTs) have shown the potential for simultaneously oxidising NO into NO_2 through the production of highly active species (e.g. free radicals, O_3) in the reaction. The AOTs were initially applied in recalcitrant water pollutants (Glaze *et al*., 1987) and expanded to hazardous wastes control (Munter, 2001). There are several methods included in AOTs (Liu *et al*., 2011): plasma oxidation, photochemical oxidation, sonochemical oxidation and Fenton oxidation. Beyond these methods, the plasma oxidation process is suggested to be more suitable in the application of mobility emissions control (Rosocha and Korzekwa, 1999).

In general, there are two types of plasma technologies found in industrial applications, which are classified through the operated temperatures and input energy as Thermal Plasma (TP) and Non-Thermal Plasma. In the Thermal Plasma, the electrons and other heavy particles (ions, radicals and neutrals) are in the thermal equilibrium conditions. In other words, the gas temperature (Tg) is close to the electron temperature (Te), typically working at temperatures greater than 10,000K, which applied in arc discharge or plasma torch. Conversely, the NTP can be generated at ambient temperature, in that the electrons have higher energetic energy than other heavy particles, and as a result, a non-equilibrium condition is created. For example, the plasma TV displays and UV lamps, both works at the ambient temperature, but the temperature of electrons in the system are greater than 10,000K.

Various types of NTPs technology have been reported for potential industrial applications, such as electrical corona discharges, radio frequency discharges, microwave discharges, or electron beams, however, not all of them are suitable for applications for vehicles emissions treatment. A less complicated process that requires no external vacuum equipment for atmospheric discharge plasma is more favourable for applications to onboard vehicles. It is also reported by Whealton *et al*. (1997), that the atmospheric pressure available for NTPs technologies which obtained the highest feasibility for engine exhausts gas treatment are listed as follows:

- Corona Discharge (CD) Plasma
- Surface Discharge (SD) Plasma
- Dielectric Barrier Discharge (DBD) Plasma
- Dielectric Packed Bed (DBD-Packed) Plasma
- Electron Beam (E-Beam) Plasma

It is noticeable that, although some researchers have shown that high reduction efficiency was achieved by E-Beam on NO_X emission control from coal fired power plants (Frank and Hirano, 1988; Li *et al*., 1997), however, the large installation space required makes them impractical for mobile applications.

Additionally, the working principle of SD and DBD-Packed are closely related to DBD, which are special modifications from the originally operated concept of DBD. Hence, only Corona Discharge (CD), Dielectric Barrier Discharge (DBD) and attaching them with the new plasma concept allowed the latter discovery - Pulse Discharge (PD) Plasma, which is discussed herein.

2.4.3.1 Corona Discharge Plasma

During electrical storms, a natural phenomenon in crown-like luminous discharge can be captured nearby the high voltage transmission lines, lightning rods, or antennas. This phenomenon is called corona discharge which is taken from the Latin word 'Crown' (Chang *et al.*, 1991).

The corona discharge can also be created artificially in the laboratory by connecting either AC or DC voltage between two electrodes. As illustrated in Figure 2.9, an inhomogeneous electrode geometries design is usually applied in the reactor for the corona discharge, which requires at least one of the electrodes to be connected to a small diameter of wires, needles, or in sharp tips. When a high voltage is applied, a small curvature is formed in a close vicinity of the electrode edges, in which a high electric field is created and an initial corona is formed.

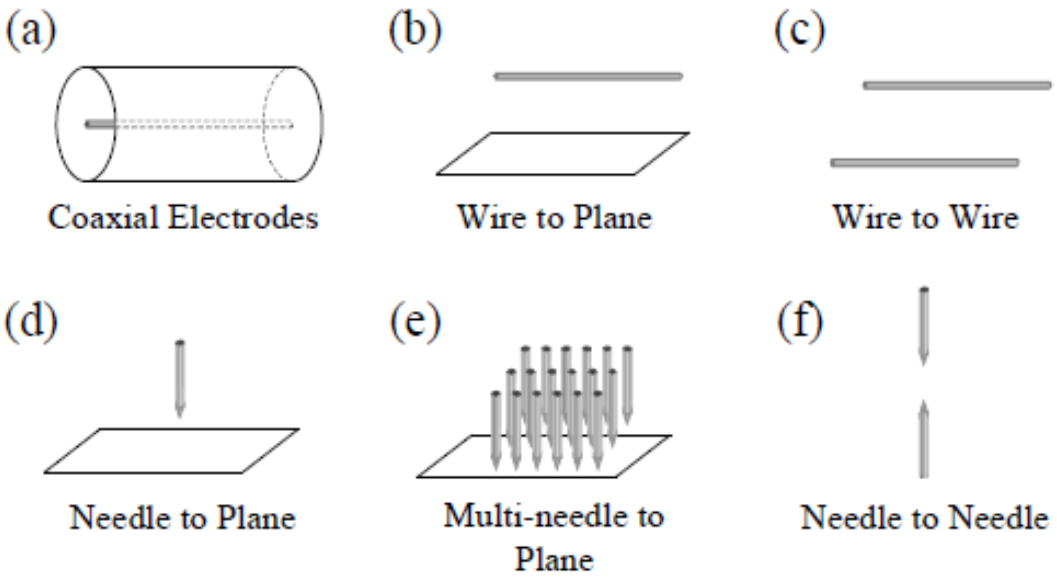


Figure 2.9: Typical Electrode Configurations of Corona Discharge.

Compared to other NTPs processed at atmospheric pressure condition, the discharge power in the Corona Discharge Plasma is relatively weak, and possesses a low electron and

ion density, as a result producing a low rate treatment of the exhaust gas. Thus restriction is due to the electrode configuration and the design of the power sources. When the current and discharge power exceed a certain value, the gases within the reactor are completely broken down and an arc is formed that bridges the discharge gap, thus turning the corona discharge into a spark discharge (Chang *et al.*, 1991).

For example, a synthetic flue gas was used by Yang and Chen (2000) to study the two-stage chemical scrubber process. A DC Corona Discharge Plasma was applied in the initial stage process to oxidise the NO to NO_2. It is reported that a highly efficient oxidise process was performed for the initial NO value under 600ppm, in which more than 90% of NO converted into NO_2, however, the NO oxidation failed when the spark discharge was observed.

In addition, A DC power generator was used to generate the corona plasma by Yan *et al*. (1999), to study the NO to NO_2 conversion over the mixtures of $N_2/O_2/CO_2/H_2O/NO_X$. It is reported that, almost 100% of NO was converted to NO_2 at the discharge voltage of 27 kV, corresponding to the corona energy density of 4.8Wh/Nm^3, but the NO_X concentration is not affected in the discharge process which remained constant. The author concluded that, it is less efficient to apply a DC power source to produce Corona Discharge Plasma for a large volume gas cleaning process; other types of power source are required to avoid the corona-to-spark transitions at high discharge power. Oda *et al*. (1998) also supported the finding that the Corona Discharge Plasma plays a crucial role in NO to NO_2 oxidation process, instead of converting the NO_X into N_2.

2.4.3.2 Pulsed Discharge (PD) Plasma

As previously stated, the limitation of the Corona Discharge Plasma at a high energy discharge is due to the transformations of corona into a spark discharge. This can be avoided through the improvement of electrical or geometrical design of the system. Pulsed Discharge Plasma is one innovation of corona discharge which prevents the spark formation through the modification of the electric system.

In PD plasma, the electric energy is not directly transferred to the reactor. The electric energy is initially stored in the intermediate storage devices (e.g. capacitors, inductors, batteries), and later releases the accumulated energy to the reactor over a very short interval time (normally 100 ~ 300 nanosecond (Fridman, 2008)), subsequently, a large amount of energy is delivered. The whole energy storage-and-released cycle are produced in a nanosecond duration, yet the high energy discharge will not cause local heating in the reactor, therefore no extra energy is wasted in the molecule vibration excitation process. This provides better efficiency of plasma-chemical processes and it is believed to be one of the most promising atmospheric-pressure NTPs for future exhaust emissions control.

There are several pulsed power modules that have the potential to generate PD plasma, which include Marx generators, rotating spark gaps, thyratrones, thyristors, high performance transistors, magnetic compressor and others. It is clear to see that, the switching process plays a critical role in PD plasma. A review of switch technology for pulsed repetition control has been undertaken by Schoenbach *et al*. (1984), together with the comparison of reliability, lifetime, cost, and sizes.

Rotary spark modular PD plasma was used by Mok *et al*. (2001) to study the remediation of NO_X; the result suggested that NO_X removed over the PD plasma is dependent on the gas

composition. Most of the NO was reduced to N_2 in the absence of O_2; whereas, with small concentration of O_2 addition, the reduction process was transformed to oxidation process and large amount NO_2 was formed. Yankelevich *et al*. (2007) used a magnetic compressor switching process to generate the PD plasma. An actual diesel exhaust gas was used to study the NO_X treatment over the PD plasma. Similar results were obtained, in which the increased pulsed repetition leads to the rapid formation of O_3 concentrations, which contributed to the dramatically increased NO oxidation process. Other evidence also can be found to evaluate the feasibility of PD plasma for vehicles exhaust emissions treatment (Puchkarev *et al*, 1998; Mohapatro and Rajanikanth, 2011).

2.4.3.3 Dielectric Barrier Discharge (DBD) Plasma

Dielectric Barrier Discharge (DBD) plasma is another type of corona discharge which modifies the geometric configuration in order to provide an alternative solution for Corona Discharge Plasma to prevent the formation of an arc. The working principal of DBD plasma places a dielectric barrier layer (e.g. ceramic, quartz, or glass) (Cal and Schleup, 2001) in between the discharge gap to limit the excess current bridges of the electrodes and prevents the spark formation. Several DBD electrode configurations that are frequently applied in industry are illustrated in Figure 2.10.

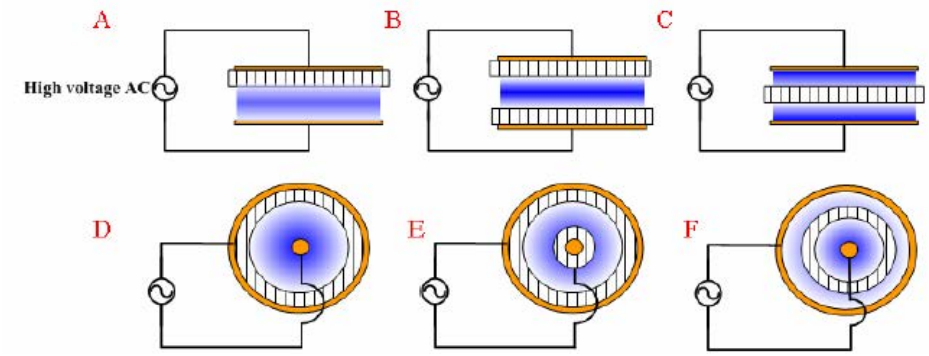


Figure 2.10: Typical Electrode Configurations of Dielectric Barrier Discharge. (Source: Liu Lu, 2011).

The dielectric layer(s) also function as a capacitor, similar to the initial process in the PD plasma. When the AC voltage is applied across the electrodes, the energy is accumulated within the dielectric layer. Once the gas is broken down, the energy is discharged into the reactor channel and produces a number of filamentary microdischarges. This behaviour continuously occurs and the microdischarges are reformed under the frequency of the AC power supply. It is suggested by Koelschatz *et al*. (1999) that, the frequency applied in DBD plasma is in the range from 50Hz to 500kHz, and the formation of microdisharges is twice that of the applied frequency, this increases the probability of free electrons interacting with other background gas molecules to promote the plasma-chemistry processes.

Compared to other atmospheric pressure NTPs, DBD plasma has the advantages of high energy efficiency, reliability and cost effectiveness (Chirokov *et al.,* 2005). The technique to produce NTPs by DBD is relatively mature, which has a long history in industrial applications. The first DBD plasma was introduced by Siemens in 1857 to create ozone, and later widely applied in UV sources, polymer treatment, biological, and CO_2 lasers; the most successful product is the plasma display.

Although, there are also some examples (Lepperhoff, *et al.,* 1999; Song, *et al.,* 2009) that shows DBD plasma is able to remove pollutant gases from diesel emission, however the energy required is a lot higher compared to the catalyst treatment. Thereby attention has focused on plasma-assisted aftertreatment systems to provide an alternative solution for NO_X and PM control. A high frequency DBD plasma reactor was developed by Mohammadi *et al*. (2003) for simultaneously reducing the NO_X and PM from diesel emission. Both simulated and actual diesel emission were studied, and the results show that direct DBD plasma treatment did not significantly affect the NO_X and PM emission, in contrast, the NO_2 was

generated from the NO-NO_2 oxidation process. It is suggested that the DBD reactor can be a powerful tool for the pre-oxidation process.

Despite that there is a large number of publications that argue stand-alone DBD plasma treatment is difficult and less efficient in removing NO_X and PM from diesel engine emission. However, DBD plasma has a potential application for future exhaust gas treatment or alternative methods of four-way catalysts when applied in conjunction with other aftertreatment devices (e.g. SCR, NO_X traps, DPF).

CHAPTER 3

EXPERIMENTAL FACILITIES

Experimental Facilities

The engine test bench for the research is described in this chapter. It also includes the equipment used for exhaust gas analysis and measurement instrumentation, plasma power monitor and measurement instrumentation, specification of catalysts, DPF configuration, as well as the properties of the fuels used for the research work in this thesis.

3.1 Engine Test Bench

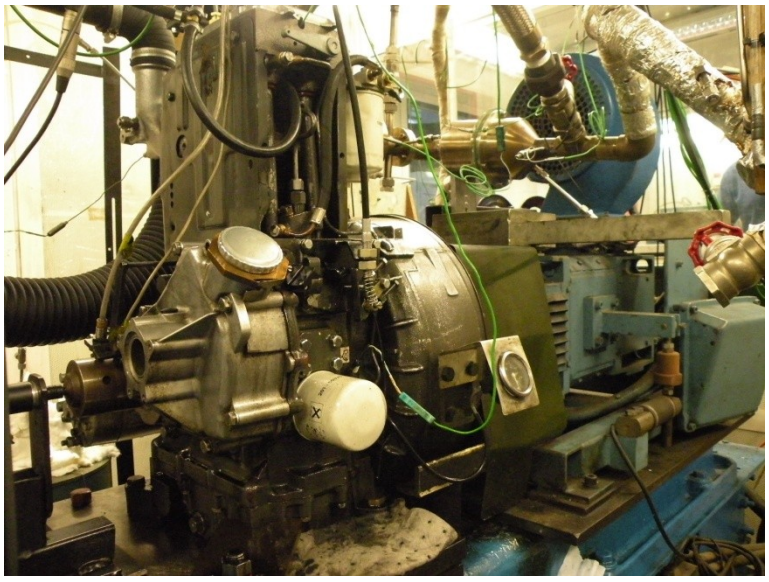


Figure 3.1: Lister Petter TR1 diesel engine test rig.

The experimental study was carried out in a naturally aspirated, direct injection single cylinder research diesel engine. The engine was maintained on the original settings from the manufacturer; standard injection timing was set at 22 Crank Angle Degree (CAD) before top dead centre (BTDC). The engine was used as an emissions generator to develop

aftertreatment studies. The main engine specifications are given in Table 3.1. And the general output of torque/power as a function of different engine speeds powered by the ULSD fuel is illustrated in Figure 3.2.

An externally cooled EGR system was designed and installed as part of the engine system. An external pipe was connected to the engine exhaust pipe and linked through to the intake airflow channel in which a rotary valve was inserted between them. Manually controlling the valve (opened or closed) allowed the engine to operate either in 'EGR ON' or 'EGR OFF' mode. During the test with 'EGR ON', the EGR level was determined volumetrically by the percentage of the volumetric flow rate of intake airflow that was reduced. The total intake air flow into the engine is measured by a Romet G65 rotating airflow meter.

Table 3.1: Test engine specifications.

Engine specification	Data
Model	ListerPetter-TR1
Number of cylinders	1
Bore/stroke	98.4mm/101.6
Connecting rod length	165mm
Displacement volume	733 cm^3
Compression ratio	15.5:1
Related power (kW)	8.6@2500rpm
Peak torque (Nm)	39.2@1800rpm
Injection system	Three holes pump-line-nozzle
Engine piston	Bowl-in-piston

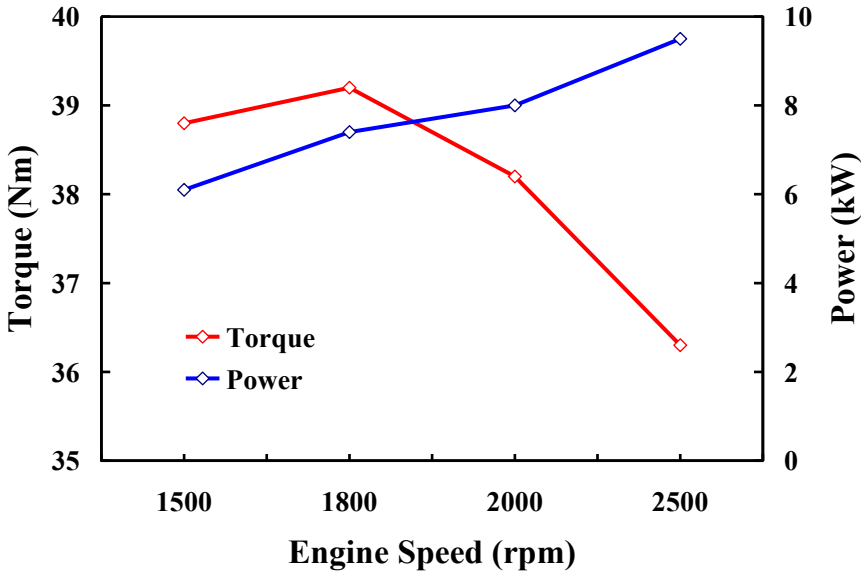


Figure 3.2: Lister Petter TR1 engine characteristics.

3.2 Engine Instrumentation

The dynamometer used to drive and load the engine in the test was a thyristor-type DC electric generator produced by Thrige Titan. An in-cylinder pressure transducer KISTLER 6125B was mounted on the cylinder head and a digital shaft encoder (Baumer BDK) was installed at the crank shaft positions. During the combustion process the signal of the in-cylinder pressure was amplifier by a KISTLER 5011 pressure transducer, and the signal of the crankshaft position was recorded by computer through a National Instruments data acquisition card.

The engine test rig also included other essential instrumentation for research purposes, such as thermocouples (to measure inlet, exhaust and oil temperatures). Atmospheric conditions, such as humidity, pressure, temperature were also monitored and recorded during the tests.

3.3 Catalyst/Filter

3.3.1 Diesel Oxidation Catalyst (DOC)

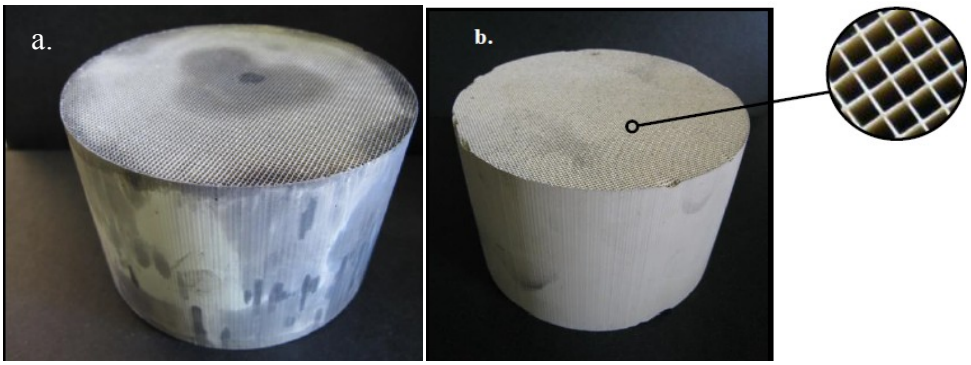


Figure 3.3: a) Diesel Oxidation Catalyst (DOC) b) Hydrocarbon Selective Catalytic Reduction (HC-SCR) catalyst.

This was a prototype DOC prepared by impregnating a low loading supported Pt based catalyst that was coated onto a cordierite honeycomb monolith substrate with a cell density of 600 cells per square inch (cpsi). Figure 3.3a shows the appearance of the DOC used in this study, having a diameter and length of 25mm and 65mm respectively.

3.3.2 Hydrocarbon Selective Catalytic Reduction (HC-SCR)

The HC-SCR catalyst used in this study was composed of a 2 wt.% silver dispersed on γ-alumina (surface area ~150 m^2/g) with aqueous silver nitrate ($AgNO_3$). Before impregnating the silver onto the support, it was dried and calcined in the air for 2 hours at a temperature of 500˚C. The catalyst was later made into an aqueous suspension, which was then uniformly coated on ceramic monolith substrates with a cell density of 600cpsi. The HC-SCR had a similar appearance with DOC (Figure 3.3b), given the dimensions of diameter and length of 115mm and 75mm respectively.

3.3.3 Diesel Particulate Filter (DPF)

The DPF used in this study is a non catalyst coated silicon carbide (SIC) DPF. The newly developed silicon carbide has the advantages of high thermal resistance and conductivity, and the uniform pore structure designed has been widely used to replace the traditional usage of cordierite DPF (MECA, Manufactures of Emission Controls Association, 2007). A non-coated mini-SIC-DPF was studied in this thesis, given the dimensions of 25mm diameter and 76mm length.

3.4 Emissions Measurement and Analysis

The gas analyser together with the operation principle used to measure the exiting gaseous compositions in this thesis is presented in the following. During the measurement in the tests, the gaseous were passed through a temperature control heating line from the sampling point to the analyser. The temperature of the heating line was set to 190˚C to avoid condensation of hydrocarbon. The rest of the details are presented below.

3.4.1 FTIR and AVL Emissions Analysers

A MKS MultiGas 2030 FTIR (Fourier Transform Infrared Spectroscopy) analyser was employed to measure all major exhaust gas species concentrations of CO, CO_2, NO, NO_2, N_2O, C_2H_4, C_3H_6, formaldehyde, C_2H_4 and H_2O during the tests. The FTIR measure technique exploits the comparison of sampling gaseous with standard spectra within a manufacturer predetermined database (set for diesel exhaust compounds) to validate the material being analysed. The quantitative analysis is based on the phenomenon of molecular IR absorption, as every compound have a characteristic region of its IR spectrum. FTIR measurement provides the extra benefit and convenience for the research in the thesis, especially in respect

of the on-line monitoring of the rapid process of NO to NO_2 oxidation. The measuring range, resolution and accuracy of the equipment are listed in Table 3.2.

Table 3.2: Technical data for the MKS Type MultiGas Analyzer Model 2030.

Measurement Specifications	
Measuring Technique	FT-IR spectroscopy
Gases and Vapor Measurable	Most molecules with dipole moments except for N_2, H_2, and O_2
Ranges	Concentration between low ppb and 100 ppm scale
FT-IR	2102 Process FT-IR
Spectral Resolution	0.5-128 cm-1
Scan Speed	1 scans / sec @ 0.5 cm-1
Scan Time	1-300 sec
Infrared Source	Silicon Carbibe at 1100°C
Reference Laser	Helium – Neon (15798.2 cm-1) – dependent upon detector
Detector	LN_2-cooled MCT; TE-cooled MCT
Pressure Transducer	MKS Baratron (0-1000 torr 0-3000 torr standard; consult model code)

An AVL DiGAS 440 analyser was used to measure O_2 concentrations through an electrochemical method. This is a diffusion type gas detection system that works on the principle of O_2 sensor. During the measurement process, the O_2 molecule is initially dissolved and the free electron is passed from anode to cathode to build an external circuit. The amount of the electrons passed is proportional to the oxygen content in the exhaust gas. The measuring range, resolution and accuracy of the equipment are listed in Table 3.3.

Table 3.3: Technical data for the AVL Digas 440 analyzer.

Gas	**Measuring range**	**Resolution**	**Accuracy**
CO	0-10% vol.	0.01% vol.	<0.6% vol.: ±0.03% vol. ≥0.6% vol.: ±5% of ind. val.
CO_2	0-20% vol.	0.1% vol.	<10% vol.: ±0.5% vol. ≥10% vol.: ±5% of ind. val.
HC	0-20000ppm vol.	≤2000 ppm: 1ppm vol. >2000 ppm: 10 ppm vol.	<200 ppm vol.: ±10ppm vol. ≥200 ppm vol.: ±5% of ind. val.
O_2	0-22% vol.	0.01% vol.	<2% vol.: ±0.1% vol. ≥2% vol.: ±5% of ind. val.
NO	0-5000ppm vol.	1 ppm vol.	<500 ppm vol.: ± 50ppm vol. ≥500 ppm vol.: ±10% of ind. val.

3.4.2 Gas Chromatograph (GC)

A Hewlett-Packard (HP) gas chromatography model 5890 Series II equipped with a thermal conductivity detector (TCD) was used to measure the hydrogen concentrations (in ppm) remaining in the combustion process. Before the measurement began, the GC was initially calibrated at a certified span in order that gases contained 30% H_2 in N_2. When the sampling gas (the exhaust gas contained H_2) was introduced, the H_2 was separated in a 2 m long 1/8 inch diameter molesieve 5Å (MS5A) column installed within the GC. Since most of the compounds have their own thermal conductivity, the sampling gas that elutes from the column was then compared in the TCD. In this case, higher TCD sensitivity to H_2 was achieved by using Argon (Ar) as the carrier gas since argon's thermal conductivity is less similar to that of hydrogen compared with other typical carrier gases such as He and N_2. The signals produced were then processed and recorded by HP 3395 integrator.

3.4.3 Horiba PM Analyser

A Horiba Mexa 1230PM was used to measure soot by a diffusion charging (DCM) method. During the measurement process, the soot concentration is calculated by measuring the electrical current of ions attached onto the surface of charged particles. Hot dilution was considered to prevent nuclei mode, with the dilution ratio of the soot diluter set to approximately 40.

3.5 Fuel

The ultra low sulphur diesel (ULSD) fuel used in this study was supplied by Shell Global Solution UK, and the hydrocarbon additive (propane) was supplied by BOC UK. The

main physical and chemical of fuel and propane properties are shown in Table 3.4 and Table 3.5 respectively.

Table 3.4: Fuel properties.

Fuel Analysis	Method	Diesel (ULSD)
Cetane Number	ASTM D613	53.9
Density at 15^{o}C (kg/m^{3})	ASTM D4052	827.1
Viscosity at 40^{o}C (cSt)	ASTM D445	2.467
50% distillation (^{o}C)	ASTM D86	264
90% distillation (^{o}C)	ASTM D86	329
LCV (MJ/kg)		42.7
Sulphur (mg/kg)	ASTM D2622	46
Aromatics (% wt)		24.4

Table 3.5: Propane properties.

Property	propane
Relative density (15.6 ^{o}C, 1 atm)	1.5
Boiling point (^{o}C)	-42.1
Latent heat of vaporisation at 15.6 ^{o}C (kJ/kg)	358.2
Flammability range (%vol. in air)	2.2 – 9.5
Autoignition temperature (^{o}C)	470
LCV (MJ/kg)	46.3
Theoretical air requirement (m^{3}/m^{3})	24

3.6 DPF Pressure Measurement

A DPF located inside a mini-reactor was designed to study the filter regeneration. A pressure transducer (Cole-Parmer High-Accuracy Compound Transmitters model EW-68073-00) was installed at the inlet and outlet of the reactor to measure the pressure drop across the DPF to assess the filter regeneration.

3.7 Plasma Power Measurement

The electric characteristic in the DBD plasma reactor consisted of short rise-time pulse and the micro-discharge, which is difficult to obtain accurate power measurements by using the method of multiplying the voltage and current across the reactor.

For this reason, a more accurate and reliable Lissajous Method was adopted to measure the electrical discharge power dissipated in the DBD plasma reactor in this study which was initially created by Manley in 1943 (Manley, 1943). This step is necessary in order to establish an energy balance of the process, as well as to monitor and control the energy consumption.

This method requires the AC output voltage (V) from the power supplier and the voltage reading from the capacitor (Vc) connected in series with the grounded electrode. The discharge power can be calculated by a Q-V Lissajous diagram, through plotting the accumulated charge ($Q(t) = C \times Vc(t)$) of the capacitor against AC output high voltage ($V(t)$) on the y-axis and x-axis respectively, under the full cycle of the AC sine wave operation. The example of the Lissajous figure is shown in Figure 3.4 presented in a parallelogram.

These electrical characterisations were made using a 1000:1 reduction high voltage probe (Tektronix 6015A), and the probe capacitors were connected to a high resolution Tektronic (TDS-2000B) oscilloscope. The signals obtained were connected to a PC by USB cable and launched through the NI LabVIEW SignalExpress TektronixTM driver. The read-out of the Lissajous diagram was used to analyze an energy balance of the process, monitor and maintain the constant power consumption in the DBD plasma reactor under the specific test condition. All the measurements were taken at stabilised discharge plasma conditions.

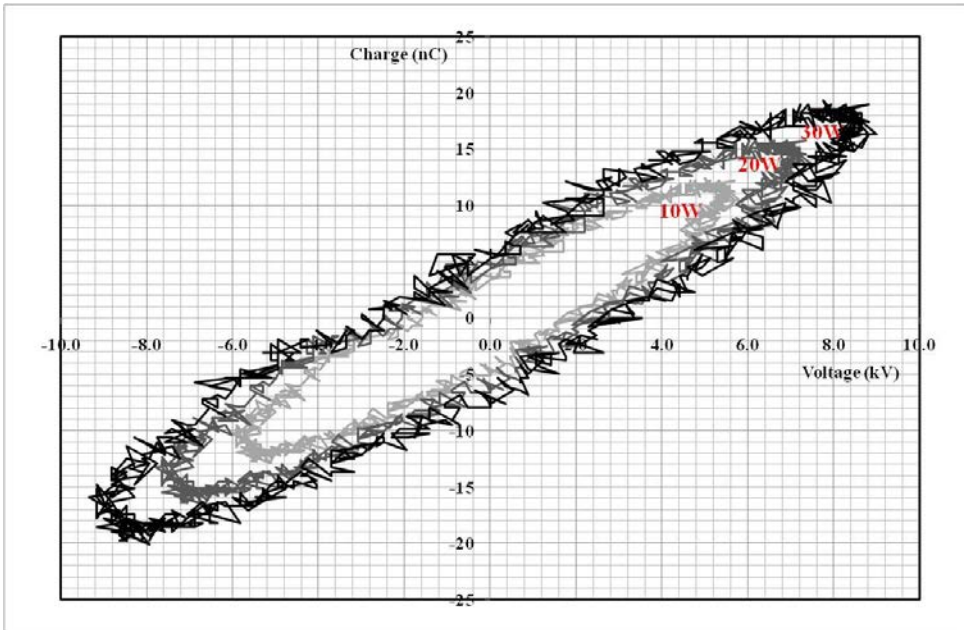


Figure 3.4: Lissajous diagram for the discharge power of 10, 20, 30W.

CHAPTER 4

THE EFFECT OF THERMAL OXIDATION AND DIESEL OXIDATION CATALYST FOR ENHANCING THE NO_2/NOX RATIO IN DIESEL ENGINE EXHAUST GAS

The NO_2 has the advantages of low temperature DPF regeneration and also induces the SCR to a faster reaction rate under the equal molar of NO/NO_2 condition. Unfortunately, the NO_2 concentration present in the diesel exhaust gas is relatively low, and without increasing the level, it is difficult to function efficiently for the aftertreatment devices installed downstream of the engine exhaust gas.

DOC is currently the most common device applied to diesel exhaust gas to remove HC and CO emissions, and also functions as a pre-oxidiser to promote the NO-NO_2 oxidation used in DPF regeneration.

However, in the real application, challenges remain in the NO-NO_2 oxidation process. Under the cold catalyst condition, kinetically restrictions at low temperatures limit the NO oxidation process; in the case of thermal oxidation, the NO demonstrates a thermodynamic limitation at high temperatures to be converted into NO_2.

Thus, the introduction of additives to the systems (combustion/aftertreatment), could provide a solution to overcome these temperature sensitive behaviours of NO oxidation characteristics. The additives are expected to decrease the DOC light-off temperature and produce the reactive radicals (such as OH, O) over the thermal process enhancing the formation of HO_2 radicals which is useful in the NO-NO_2 oxidation process.

In this Chapter, two different oxidation methods were compared. The NO_2/NO_X ratio under real exhaust conditions was analysed using a thermal reactor and a DOC under the effect of temperature. Propane was adding to improve the NO_2/NO_X ratio in order to enhance DPF regeneration. Propane was chosen not only because of its ability in promoting NO_2, but also as propane can be used as a fuel in both spark ignition (Badr *et al.,* 1998) and compression ignition engines (Saleh, 2008). The optimal propane concentration to promote NO_2 can be used as a feedback and incorporated into the engine management strategies making the regeneration process more accurate.

4.0.1 Test Conditions and Procedure (specific to Chapter 4)

Thermal Reactor: A stainless steel thermal reactor was designed to study the effect of thermal oxidation on NO-NO_2 oxidation in the diesel exhaust gas. The design of the reactor was similar to the folk-like structure reactor previously used by Duo *et al*. (1991), Hulgaard and Dam-Johansen (1993) in their nitrogen chemistry oxidation and combustion study. The reactor consists of three major parts: a major channel was placed in the bottom centre of the reactor, where all the gases mixed and the reactions took place. The propane is injected from the top of the reactor and mixed with the exhaust gas in the cross-stream through the small jet holes. Engine exhaust gas flow was used to pre-heat the reaction channel. These separated flow systems offer the advantage of maintaining the separation of reactive species during the heat-up process. A K-type thermocouple was installed inside the reactor covered by a thin jacket (stainless steel) with no access to the reactant gases. The design detail of the thermal reactor is shown in Appendix A.

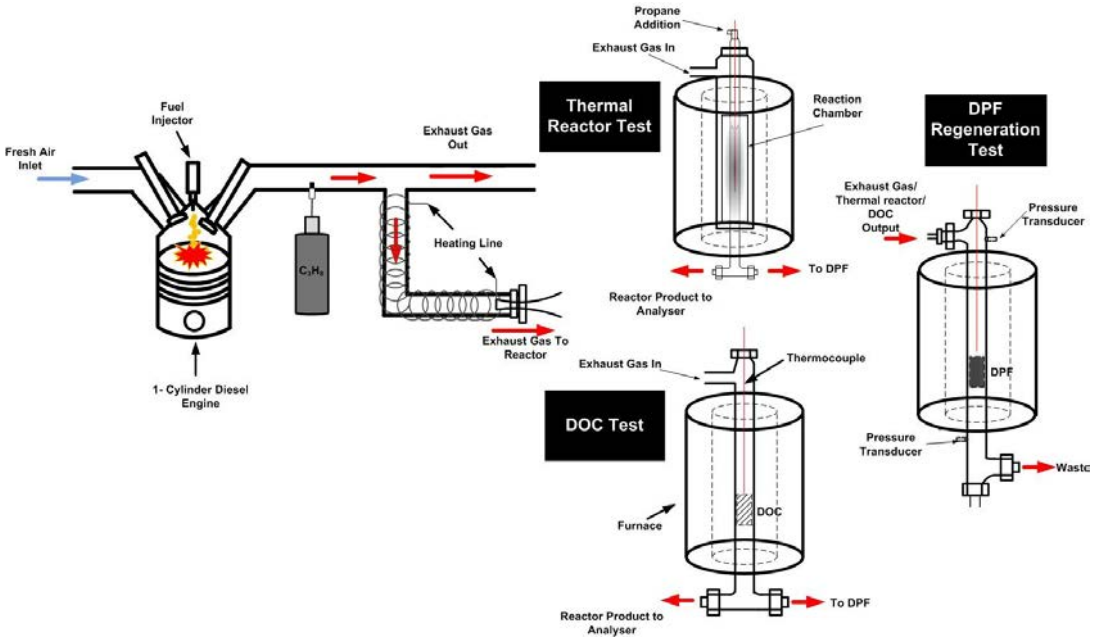


Figure 4.1: Schematic of the engine, DOC, thermal reactor and DPF system.

Experimental procedure: The experiments were performed at an engine speed of 1500rpm, with an engine load of 3 bar indicated mean effective pressure (IMEP). Part of the exhaust gas was then fed through the reactor with a residence time of 1.5s. This residence time was chosen based on the study of Mori *et al.* (1998). The reactor is positioned inside a tubular electric furnace and the temperature was controlled by means of a temperature controller. A K-type thermocouple was used to record the temperature profile along the reactor with PicoLog software. The temperature ramps for catalytic and thermal oxidation were selected from 150 to 500°C and 150 to 900°C, respectively. As mentioned above, propane concentrations (in volume) were selected to simulate HC-doses, those were controlled by a flow meter before they were added to the exhaust gas to study the effect of C_3H_8/NO_X ratio in promoting NO-NO_2 oxidation. As shown in Figure 4.1, a DPF was located inside a mini-reactor downstream from the thermal reactor and the DOC in each specific test.

The mini-reactor temperature was chosen as the outlet temperature of the thermal reactor and the DOC in each condition.

4.1 The Effect of Thermal Oxidation

The concentration of NO_2 as a function of inlet temperature and propane addition is shown in Figure 4.2. The results of two different engine exhaust NO to NO_2 oxidation methods, using a diesel oxidation catalyst and a thermal oxidation reactor, were compared and collated as explained in the following sections. Non-catalytic thermal oxidation process is presented in the first section, while the DOC results are outlined in the next section to study the catalytic oxidation process. The effect of the propane addition over these two methods was also included in the discussion.

4.1.1 Exhaust gas treatment without propane addition

Little attention has been paid in the literature to the non-catalytic oxidation process, especially applied to exhaust gas treatment. The results of temperature ramp over the reactor are shown in Figure 4.2 (curves on the right), while the results corresponding to NO and NO_2 are showed in Figure 4.3. Additionally, the NO_2/NO_X ratio over the reactor is depicted in Figure 4.4. At the inlet of the reactor, the NO_2/NO_X ratio is relatively low (around 0.1). This value is in agreement with the literature, where it is reported that diesel engines emit 5-15% of NO_X as NO_2 (Soltic and Weilenmann, 2003).

The NO oxidation process is limited to a narrow temperature window, in which approximately 70ppm of NO_2 is generated at 700°C. The NO_2 concentration later declines to the initial value (40ppm) when the temperature further increased to 900°C. The free radicals

derived from the engine-out hydrocarbons does not sufficiently change the NO_2/NO_X ratio even at the temperature (700°C) which obtained the highest NO-NO_2 oxidation. Hence, the limited value of NO_2 produced through the thermal oxidation process without additives, is not effective in the application to aftertreatment systems.

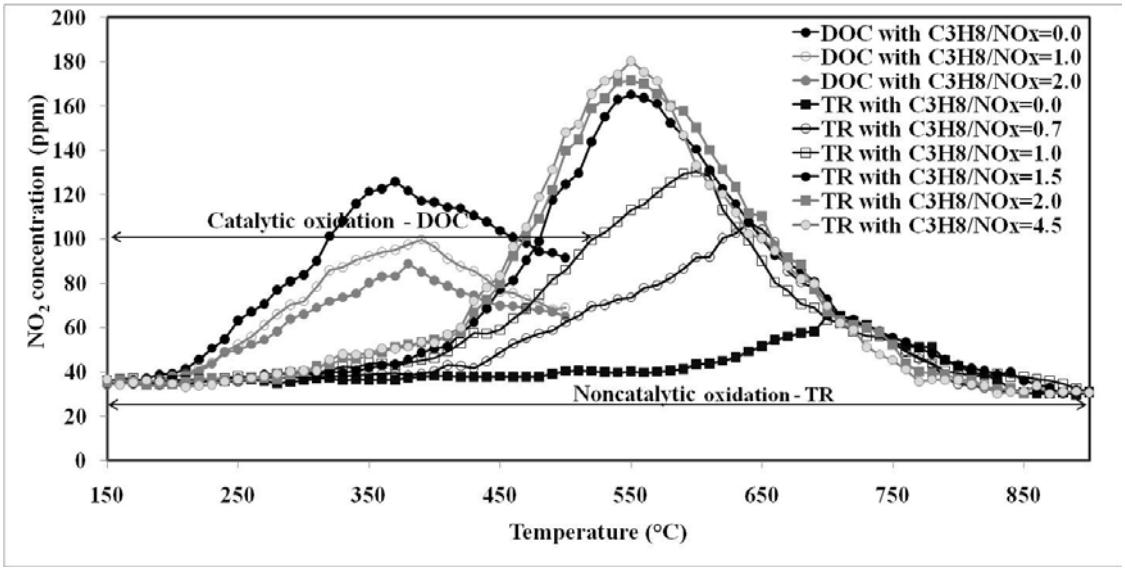


Figure 4.2: Concentration of NO_2 emissions as a function of temperature over the diesel oxidation catalyst (DOC) and thermal reactor (TR).

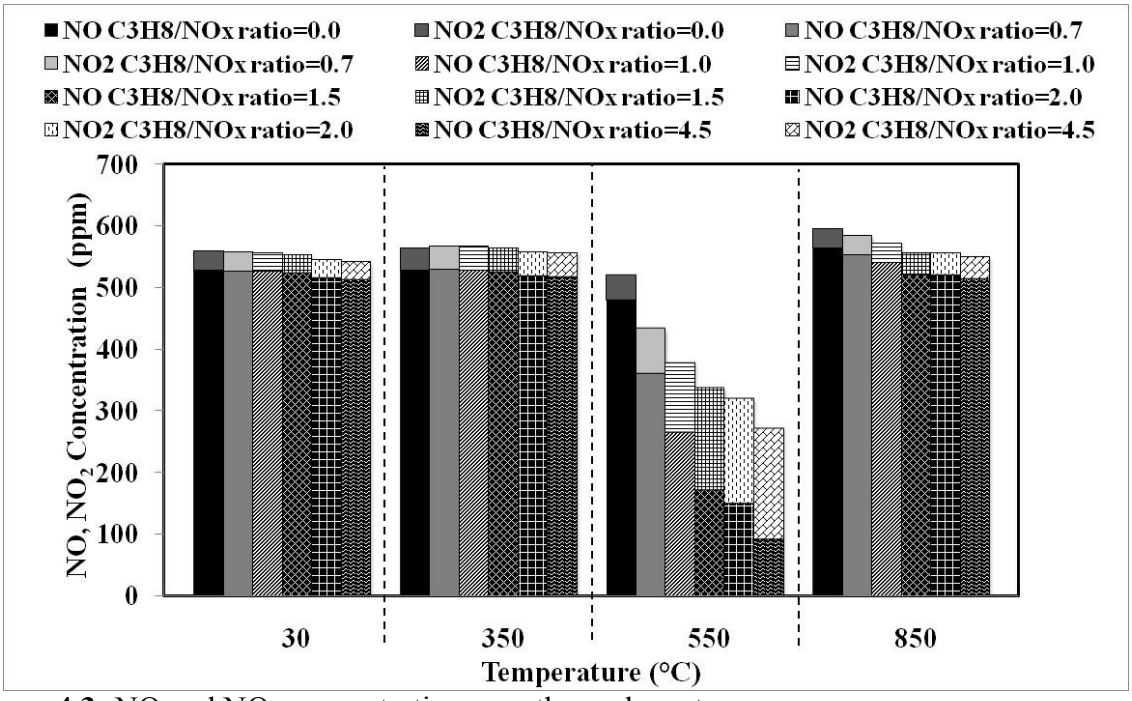


Figure 4.3: NO and NO_2 concentration over thermal reactor.

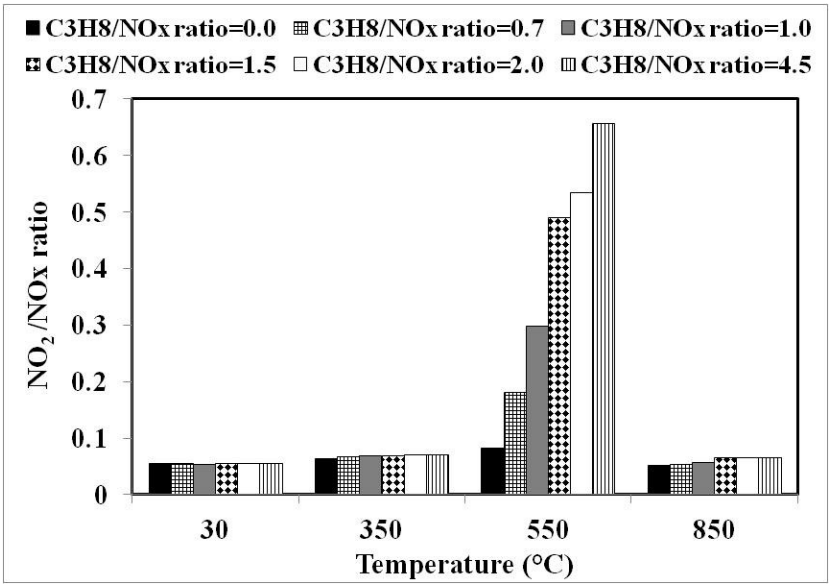


Figure 4.4: Effect of NO_2/NO_X ratio over thermal reactor

4.1.2 Exhaust gas treatment with propane addition

Selective non-catalytic reduction (SNCR) is another technology that utilises the advantages of thermal oxidation and additives (e.g. urea (Lin *et al.,* 1995), ammonia (Lyon, 1987) cyanuric acid (Caton and Siebers, 1990)) which are used as reductants to control the NO_X emission from stationary plants. Apart from the NO_X reduction, Hori *et al.* (1998) have focused on the fuel effect in promoting the NO-NO_2 oxidation over the mixture of NO (20ppm) / HC (50ppm) / air. Several types of fuels were studied within the research. The results show that the effectiveness of propane is greater than methane, hydrogen and CO. Comparable results have been obtained in this study under actual exhaust gas conditions, where the influence of the exhaust components (soot, CO, oxygen, high NO concentrations, etc.) is taken into account. As can be observed in Figure 4.2, in the temperature range from 400 to 700ºC, the addition of propane increases the NO to NO_2 oxidation process. This resulted in an increase of the NO_2 concentration at each temperature and a shifting of the NO_2 production peak towards lower reactor temperatures, when the C_3H_8/NO_X ratio was increased

up to 1.5. Further propane additions do not significantly increase NO_2 production. Generally, it is accepted that the oxidation of NO to NO_2 proceeds mainly through the HO_2 mechanism.

$$NO + HO_2 \leftrightarrow NO_2 + OH \quad (4.1)$$

$$RO_2 + NO \leftrightarrow RO + NO_2 \quad (4.2)$$

The addition of propane under certain temperatures produces reactive radicals such as OH and O atoms that allow the promotion of hydrocarbon oxidation and generate the HO_2 radical in the system (Hori *et al.,* 1998).

4.1.3 The effect of different C_3H_8/NO_X ratios

To overcome the high temperatures which are needed in non-catalytic thermal NO to NO_2 oxidation, the effect of temperature for various propane addition concentrations was examined. From the temperature ramp results, four independent temperatures (30°C, 350°C, 550ºC and 850°C) were chosen to analyse NO, NO_2, carbon containing products and the NO_2/NO_X ratio. The lowest temperature (30ºC) was considered as a reference of the dilution caused by propane addition and 350ºC was chosen because it is the temperature at which maximum NO to NO_2 oxidation is obtained using the DOC. The temperature of 550ºC was selected as it is a reference temperature for DPF regeneration and is close to the temperature at which the maximum NO_2 production is obtained. Lastly, to ensure a high decomposition rate of hydrocarbons, the propane was added into the reactor at 850°C.

At 350°C propane does not enhance the oxidation process and total NO_X emissions remain similar with the different propane concentrations (Figure 4.3). At 550ºC, the addition of propane (until a C_3H_8/NO_X ratio of 1.5) increases the NO_2 concentration and decreases the

total NO_X emissions, while increasing the NO_2/NO_X ratio (Figure 4.4). At the highest temperature (850ºC) total NO_X was slightly decreased when the C_3H_8/NO_X ratio was increased (Figure 4.3).

a) NO_X reduction with propane addition

The NO_X reductions that are observed when propane is added might be the result of the NO re-burning process over the reactor, which is commonly applied as the post-combustion treatment in coal combustion systems for controlling the NO_X emission. The addition of hydrocarbon-containing fuel into the downstream combustion zone will lead to hydrocarbon species (mainly CH, CH_2 and possibly CH_3) reducing NO to HCN (equation 4.3) (Hill and Smoot, 2000).

$$CH_i + NO \rightarrow \text{products (e.g., HCN, CN . . . .)} \qquad (4.3)$$

Figure 4.5, depicts the temperature profile with (dashed lines) and without (solid lines) propane addition along the reactor for the different reactor temperatures. This temperature profile corresponds to a C_3H_8/NO_X molar ratio and is equal to 1.5 when the reburning process is noticeable (to avoid repetition, the rest of the temperature profiles for the remaining propane concentrations are not shown). These temperature profiles remained stable during the residence time of the exhaust gas within the oxidation chamber in the reactor. By comparing the temperature profiles with and without propane addition, these remained similar for each reactor temperature. Therefore, the heat released in the NO reburning process, did not affect significantly the global temperature at each sampling point. This confirmed that the formation of NO_2 (shown in Figure 4.2) is not affected significantly by the potential thermal effect

derived from propane combustion. In the following section, the enhancement of propane in the NO oxidation process is justified.

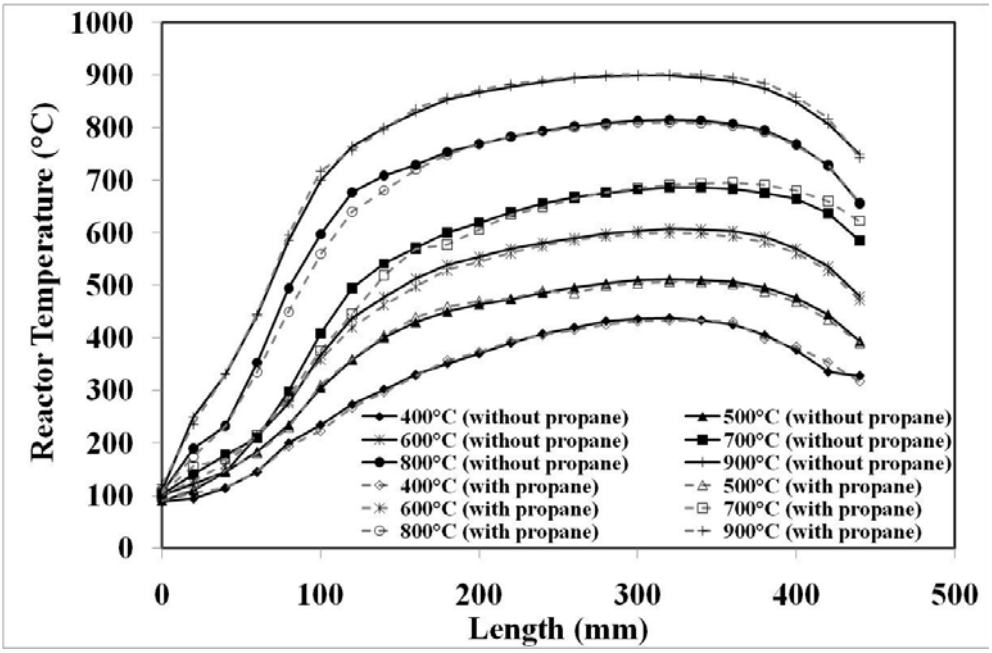


Figure 4.5: Effects of propane addition (C_3H_8/NOx =1.5) on the thermal reactor temperature profile for thermal oxidation process.

b) NO_2 enhancement through propane addition

The enhancement of the NO_2/NO_X ratio results in evident benefits in DPF regeneration (as it is explained in the Introduction section). However, the toxicity and ozone-forming potential of NO_2 is far greater than NO. Therefore, the proportion of NO_2 to NO_X should be optimised in order to facilitate the matching between the requirements of the exhaust gas treatment systems (e.g. NO_X traps, SCR, DPF regeneration) and the environmental concerns of elevated NO_2 emission level.

Evidence to support the fact that propane promotes NO to NO_2 oxidation in the reactor can be found in the work of Hori *et al* (1998). They analysed the kinetics of hydrocarbons on the NO-NO_2 oxidation pathways. It was found that the ability of propane to promote the

oxidation reaction was primarily due to the hydroperoxy-propyl radical plus O_2 reactions that led to the production of oxygenates and the HO_2 radical.

The OH radicals consume propane through:

$$C_3H_8 + OH \rightarrow i\text{-}C_3H_7 + H_2O \quad (4.4)$$

and

$$C_3H_8 + OH \rightarrow n\text{-}C_3H_7 + H_2O \quad (4.5)$$

The generation of propyl radicals will further react with O_2, and this leads to two possible general outcomes:

$$i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \quad (4.6)$$

and

$$n\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \quad (4.7)$$

Or

$$i\text{-}C_3H_7 + O_2 \leftrightarrow i\text{-}C_3H_7O_2 \text{ followed by } i\text{-}C_3H_7O_2 \leftrightarrow C_3H_6 + HO_2 \quad (4.8)$$

and

$$n\text{-}C_3H_7 + O_2 \leftrightarrow n\text{-}C_3H_7O_2 \text{ followed by } n\text{-}C_3H_7O_2 \leftrightarrow C_3H_6 + HO_2 \quad (4.9)$$

For this reason, the availability of propane allowed the production of the HO_2 radical via the reaction, as suggested above, which promoted the NO-NO_2 oxidation process.

From the discussion above, it is clear that the HO_2 radical played the main role in promoting the NO-NO_2 oxidation. In the process of generating the HO_2 radical, C_3H_6 was the main reaction product in the reaction of propane with the OH radical (equations 4.6-4.9). Similar results were also discussed in Nelson and Haynes (1994), in the mixture of

$C_3H_8/NO/O_2$. Most of the NO to NO_2 oxidation occurs at less than 10% of the C_3H_8 conversion. In fact, over 75% of the reacted C under these conditions appears as CO, HCHO, C_2H_4 and C_3H_6. Therefore, the analysis of the carbon-containing products over thermal oxidation will provide essential knowledge in the selection of adequate additives, which instantly promotes the HO_2 radical.

Although, the components in the diesel emissions is rather complicated compared to the mixture of $C_3H_8/NO/O_2$, the results are similar to those obtained in ideal conditions. Figure 4.6 illustrates that before the addition of propane, almost none of these olefins products were detected downstream from the reactor. The highest propylene and ethylene concentration at 550°C are coincidental with the temperature at which the highest NO-NO_2 oxidation was achieved.

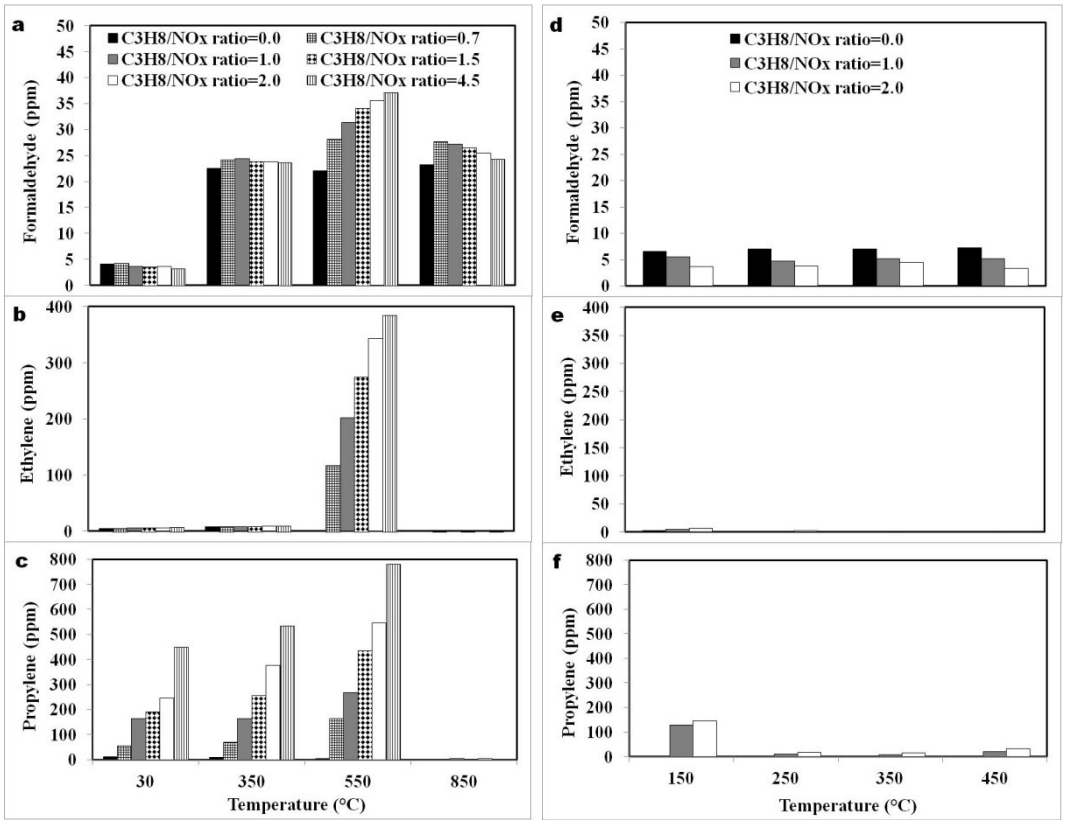


Figure 4.6: CO and CO_2 concentration over thermal reactor (left) and DOC (right).

The highly complex process consisted of several reaction pathways of ethylene promoted the HO_2 radical formation, as published previously (Doughty *et al.,* 1996). This, allowed us to assume that the formation of ethylene, provided another reason for the highest NO-NO_2 oxidation at 550°C. The net overall reaction of the process is as follows:

$$C_2H_4 + 2OH + 3O_2 \rightarrow 2CO + 2H_2O + 2HO_2 \qquad (4.10)$$

High correlation of the evidences for CO emission and the olefin by-products are shown in Figure 4.6 and Figure 4.7 respectively. From Figure 4.7, it can be seen that at the highest temperature, the major carbon-containing species were then fully oxidized and transferred into CO_2.

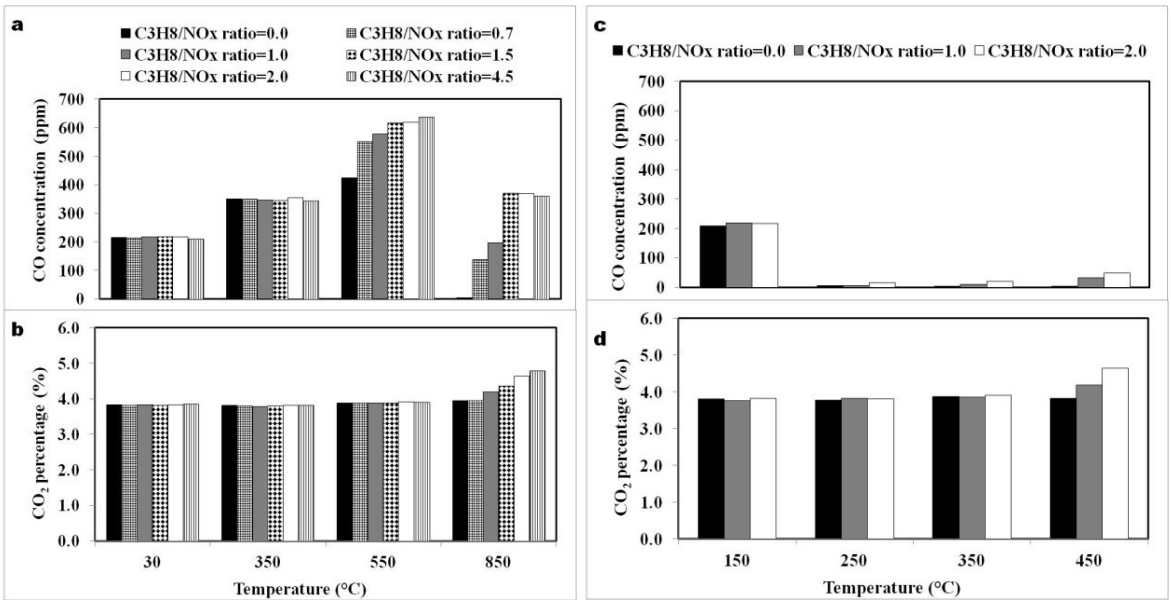


Figure 4.7: Carbon-containing products over thermal reactor (left) and DOC (right).

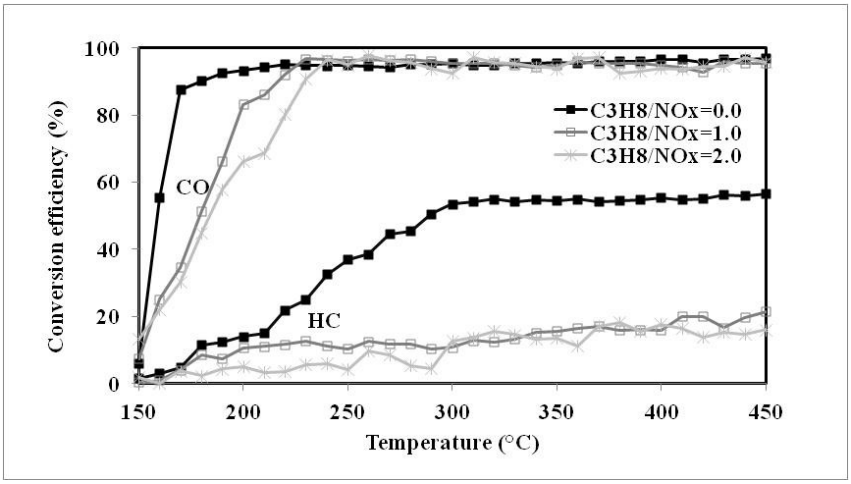


Figure 4.8: Conversions of carbon monoxide and hydrocarbon over DOC.

4.2 The effect of DOC

4.2.1 Exhaust gas treatment without propane addition

The performance of the DOC presented here is comparable to the commercialised DOCs that commonly are installed in vehicles today for CO and HC reduction. Generally, it is accepted that the ability of the CO conversion over the DOCs is more efficient compared to other emissions (HC, NO_X, PM) (Zervas, 2008). The result in Figure 4.8 shows that CO oxidation takes place prior to HC oxidation. The maximum conversion efficiency of carbon monoxide was 90% being obtained at 170°C, while the maximum conversion for hydrocarbons takes place at 300°C and is the conversion efficiency is only around 50%. Additionally, the lean operation in diesel engines (excess of oxygen according to the stoichiometric) results in an oxygen environment over the exhaust gas, allowing the DOCs to promote NO to NO_2 oxidation through the reaction:

$$NO + \frac{1}{2}\, O_2 \leftrightarrow NO_2 \qquad (4.11)$$

The results in Figure 4.2 show that the NO_2 concentration reached the highest level (around 125ppm, doubling the initial NO_2 concentration) when the DOC temperature was increased up to 370ºC. Apart from CO, HC and NO oxidation, small amount of NO_X reduction across the DOC can also be observed from Figure 4.9, which has been attributed to the HC effect through the following reaction:

$$C_nH_m(g) + \left(2n + \frac{m}{n}\right)NO(g) \rightarrow \left(n + \frac{m}{4}\right)N_2(g) + nCO_2(g) + \left(\frac{m}{2}\right)H_2O\ (g) \quad (4.12)$$

The activity of the DOC to reduce CO and THC is reasonable at low exhaust temperatures. However, the use of additives has been studied in which a shift of the NO to NO_2 oxidation towards lower temperatures (reducing the activation energy of the reaction) and/or enhance NO_2 concentration at each temperature (increase the rate of reaction) has been observed.

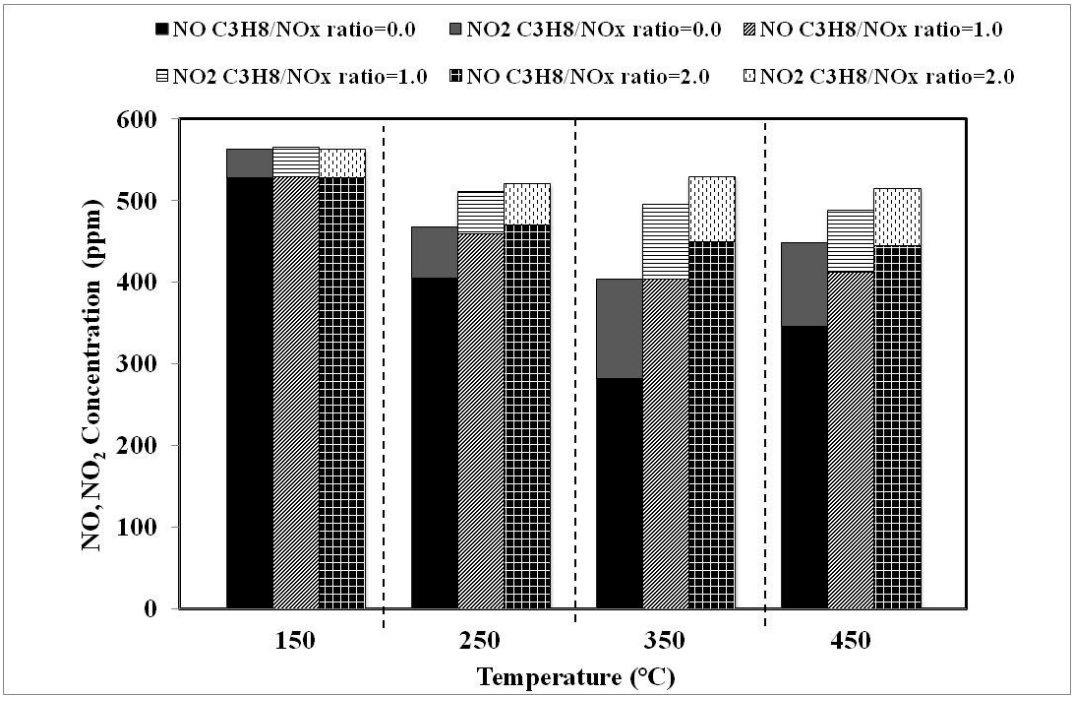


Figure 4.9: NO and NO_2 concentration over DOC.

4.2.2 Exhaust gas treatment with propane addition

Over the wide range of aftertreatment systems, a device/system that could effectively work independently under real exhaust conditions to reduce NO_X and PM emission could not be identified. In practice, these technologies required active agents, for example, the presence of ammonia in NH_3-SCR catalysts (Hums, 1998), hydrogen and hydrocarbons additions over lean NO_X reduction platinum-based catalyst (Abu-Jrai and Tsolakis, 2007; Burch *et al.,* 2002) and NO_2 to regenerate the particulate filter (Kandylas and Koltsakis, 2002). Recently, the introduction of H_2 (Theinnoi *et al.,* 2012) and reformed EGR (REGR) (Gill *et al.,* 2011) have also been applied to the DOC to promote NO to NO_2 oxidation, in order to improve the DPF regeneration process. As a result and taking into consideration the literature review discussed earlier, the additive applied here could play a different role over the DOC and the thermal reactor in the NO-NO_2 oxidation process.

As the hydrogen effects on the DOC have been previously studied in our research group, it is worthy to study the effect of other HC additives in enhancing the NO to NO_2 oxidation. To be comparable with thermal oxidation, the propane was selected as an additive being added upstream the DOC to study the NO-NO_2 oxidation process over DOC.

The effect of propane on DOC oxidation activities is included in Figure 4.8. The results show that the CO conversion was not affected. However, the HC performance on the DOC was sensitive to propane addition reducing the conversion efficiency by about 50%. At low temperature, the NO to NO_2 oxidation with propane addition has a similar trend than without propane, but this desisted when the temperature increased to 300°C.

Several reasons may account for the negative impact of propane over the DOCs. Katare *et al.* (2007a) found that an excessive presence of CO, hydrocarbons, and NO in the engine exhaust gas leads to a competition in the oxidation process between each element. Therefore, the NO_2 production was reduced and the HC conversion efficiency was hindered over the DOC. In a subsequent study (Katare *et al.,* 2007b), the performance of NO oxidation over aged DOCs was investigated. The results found that NO_2 concentration is reduced by the reductants (e.g. HC, CO, C) in the exhaust gas, facilitating the complete reduction of the produced NO_2 back to NO, as the reaction shown below:

$$NO_2 + [HC] \leftrightarrow NO + CO + H_2O \quad (4.13)$$

$$NO_2 + CO \leftrightarrow NO + CO_2 \quad (4.14)$$

$$NO_2 + C \leftrightarrow NO + CO \quad (4.15)$$

Another possible reason of the inhibition of NO oxidation over the DOC is attributed to the adsorption of oxygen on the metal surface (Burch and Watling, 1997), dominating the reaction surface. The over load of propane will then compete with the oxygen in the diesel exhaust gas to process the oxidation reactions over the limited active sites. Consequently, this is suggested as one of the reasons of this inhibition effect of HC addition on NO to NO_2 oxidation or HC oxidation. Henry *et al.* (2011) explained this inhibition effect as 'HC-affected' and 'nearly HC-free' zone according to HC species at different conditions within the DOC, where the former ('HC-affected') consumes the incoming NO_2 and inhibited NO oxidation; while the latter ('nearly HC-free') promoted the formation of NO_2. For these reasons, the expectations of the role of DOCs in NO-NO_2 oxidation in some cases can be overestimated, for example under real engine operating conditions.

4.2.3 The effect of different C_3H_8/NO_X ratios

The effect of C_3H_8/NO_X ratio was analysed in more depth within the DOC tests over four independent temperatures (150°C, 250°C, 350°C, and 450°C). The lowest temperature was selected to study the dilution effect caused by propane addition before the DOC light-off temperature. 250°C was chosen as a reference of diesel exhaust temperature. 350°C was chosen as the NO_2 production peak within the DOC was reached at this temperature. Lastly, 450°C was selected for high temperature study.

NO and NO_2 emissions are presented in Figure 4.9. The increase of C_3H_8/NO_X ratio led to the reaction 4.13. A large portion of HC left over the DOC and reacted with NO_2 to form NO, CO and H_2O. As a result, the overall NO concentration increased. The NO_2/NO_X ratio decreased with the increase of propane concentration (Figure 4.10). Hence, the additive agent (propane) did not show any advantages in terms of NO_2 production.

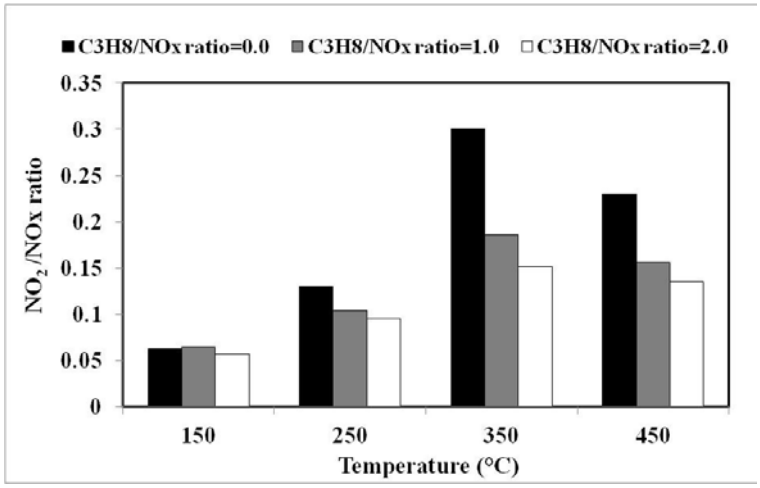


Figure 4.10: Effect of NO_2/NO_X ratio over DOC.

In comparison to thermal oxidation, the carbon-containing species after the DOC are also shown in Figures 4.6 and 4.7 to better understand the intermediate components that

participate in the NO oxidation process over different methods. Small amounts of these carbon-containing products were measured downstream the DOC at 150°C. When the DOC reached the light-off temperature, most of these products were oxidized through the following reaction.

$$C_nH_m(g) + \left(n + \frac{m}{4}\right) O_2(g) \rightarrow nCO_2(g) + \left(\frac{m}{2}\right) H_2O\ (g) \qquad (4.16)$$

From this point of view, the carbon-containing products formed in thermal oxidation created a sustainable HO_2 radical in the system to promote NO-NO_2 oxidation. However, in terms of DOC, most of these species were fully consumed. This suggests that the HO_2 radical has not been promoted with the addition of propane over the DOC, therefore, the NO to NO_2 oxidation reaction was not enhanced. Additionally, at the highest temperature, all these carbon-containing species were fully oxidized into CO_2 (Figure 4.7).

Apart from the emissions shown above, small amounts of nitrous oxide (N_2O) were detected (<20ppm) within the DOC tests. It was also reported that, under low exhaust temperatures, it is possible that Pt catalysts reduce NO_X to N_2O (Yates *et al.,* 2005). Although N_2O has not been listed in the emission regulations, attention should be paid over the formation of N_2O in the by-products after the catalyst treatment, because it has a global warming potential equal to 310 times that of CO_2 (Chang and Peng, 2010).

4.3 DPF Regeneration

Previous studies have shown that a NO_2/NO_X ratio between 0.3-0.6 is enough to enhance DPF regeneration, by noticeably reducing the pressure drop across the filter (Chong et al., 2010; Theinnoi et al., 2012). Additionally, in the literature it is suggested that a

NO_2/NO_X ratio of 0.5 (Nelson and Haynes, 1994), allows the SCR reaction to increase the NO_X conversion rate, changing from 'standard' to a 'fast' SCR reaction. However, if NO_2 fractions are above 50% of the total NO_X, the excess NO_2 will reduce the performance of the SCR resulting in a third reaction that is slower than the standard reaction. As previously commented, the use of a very high NO_2/NO_X is not recommended which could result in excessive NO_2 emissions downstream the aftertreatment system.

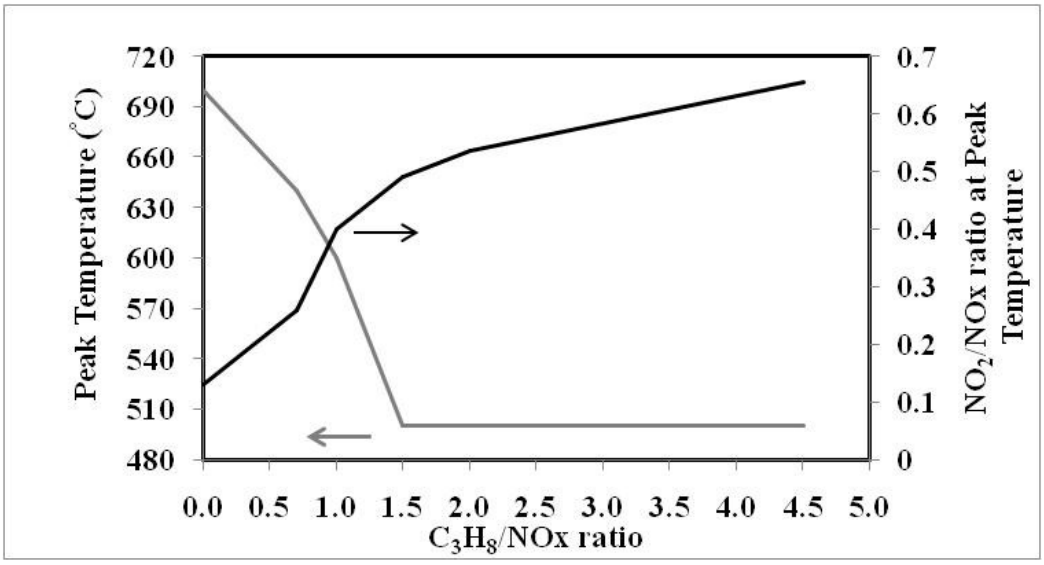


Figure 4.11: Peak temperature and NO_2/NO_X optimization with the propane addition.

Figure 4.11 shows the maximum NO_2/NO_X ratio for each propane addition and the temperature at which these maximum values are reached. Based on this information the propane addition can be optimised depending on the desired NO_2/NO_X ratio after the reactor.

In the current study and at 550ºC, a C_3H_8/NO_X molar ratio of 0.7 and 1.0 do not increase the NO_2/NO_X ratio to the levels previously suggested (0.3 ~ 0.6). However when the propane addition is increased to a C_3H_8/NO_X ratio of 1.5, the NO_2/NO_X ratio increases until 0.5. Further propane addition slightly increases NO to NO_2 oxidation, but with a considerable fuel penalty. Based on the aftertreatment requirements previously mentioned and to avoid

excessive NO_2 emission exposed to the atmosphere, the NO_2/NO_X molar ratio around 0.3-0.5 could be assumed to represent a satisfied value in this case.

According to this figure, the same NO_2/NO_X ratio can be obtained with different combinations of reactor temperature and propane addition. For example 0.4 NO_2/NO_X ratio can be obtained either using 1.0 C_3H_8/NO_X ratio and a reactor temperature of 600ºC or using a 1.5 C_3H_8/NO_X ratio with a reactor temperature of 500ºC. Further propane addition neither shifts the NO_2 production to lower temperatures nor increases the NO_2 level at each temperature, resulting in an excessive fuel penalty.

The latest condition was selected because it allowed for the required level to be reached in the regeneration process in a more adequate temperature range (less thermal stress). Additionally, it is reported that in this temperature range not only does NO_2 oxidise the soot oxidation (high soot oxidation rate between 200-500ºC (Shrivastava *et al.,* 2010; Tighe *et al.,* 2012), but also the remaining oxygen from the exhaust can oxidise the accumulated soot (starts from 400-450ºC onwards (Darcy *et al.,* 2007)), further improving the filter regeneration process.

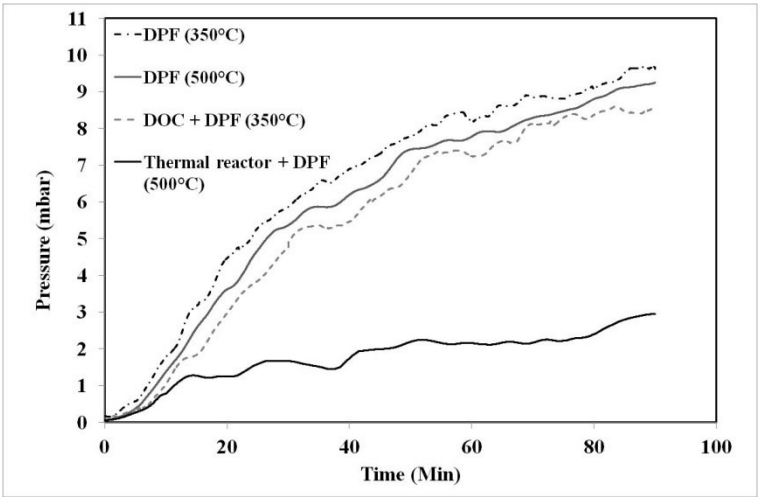


Figure 4.12: Pressure drop across the DPF.

Table 4.1: Exhaust conditions

	Thermal Reactor		DOC	
Conditions	**Inlet**	**Outlet**	**Inlet**	**Outlet**
Temp. (°C)	500	500	350	350
NO_2/NO_X	0.1	0.4	0.1	0.3
Soot (mg/m^3)	12.53	12.39	12.49	12.47
O_2 % Vol.	15.55	15.22	15.55	15.34

The results corresponding to DPF regeneration are depicted in Figure 4.12. The exhaust temperature, NO_2/NO_X ratio, soot emissions and oxygen for the regeneration conditions are shown in Table 4.1. The filter loading profiles for the baseline (exhaust gas composition without NO_2 enhancement), the DOC without propane addition and the suggested condition for thermal oxidation were compared. An additional loading profile for the DPF at 500ºC (without NO_2 promotion) was also depicted to better understand the oxygen effect.

The enhancement of NO_2 concentration within the DOC resulted in a lower rate of pressure drop across the filter. However, further reductions in soot accumulation were achieved in the case of thermal oxidation at 500ºC. These differences of the pressure drop across the DPF can be explained as follows:

- Oxygen effect. The pressure drop for the DPF at 500ºC is lower than in the case of the DPF at 350ºC. This increase in temperature promoted the soot oxidation by oxygen, as it is widely reported in the literature (Lee *et al,* 2007; Yezerets *et al,* 2005). The effect of NO_2 on soot oxidation can be neglected, as the NO_2/NO_X ratio in these conditions is not sufficient to promote soot oxidation (lower than 0.1).

- The NO_2 effect. Comparing the baseline condition (DPF at 350ºC) and the DOC at 350ºC. The pressure drop across the DPF when the DOC is used is reduced. This is

mainly a result of the soot oxidation by the NO_2 at low temperature, which has been produced in the DOC (NO_2/NO_X ratio equal to 0.3). It is suggested that at this temperature the NO_2 soot oxidation is stronger than the oxygen oxidation (Lee *et al,* 2007). This NO_2 effect is also observed when the thermal reactor at 500ºC is used upstream of the DPF. Although the oxygen effect at these conditions should be similar (similar oxygen concentration and temperature), the pressure drop using the thermal reactor is much lower than in the case of only DPF.

- The NO_2 and oxygen combined effect. The lowest pressure drop across the DPF is obtained when the thermal reactor (at 500ºC and 1.5 of C_3H_8/NO_X ratio) is located upstream from the filter. The reasons to justify this soot loading benefit are based on the combined effectiveness of two oxidant agents. The propane addition in the thermal reactor promoted the NO_2/NO_X ratio (0.4), partly enhancing soot oxidation. Also, in this temperature, the oxygen available in the system took part in the filter regeneration process. Additionally, the presence of oxygen can increase the rate of oxidation of NO_2 and a cumulative effect can be observed (Stanmore *et al.,* 2008; Jacquot *et al.,* 2002).

4.4 Conclusion

Due to the kinetic and thermodynamic limits of the NO to NO_2 oxidation process over a range of temperatures, the addition of additives has been studied. In the case of the thermal reactor, propane is oxidised producing active species such as the HO_2 radical that will promote the NO-NO_2 oxidation. Therefore, the addition of propane over the thermal oxidation process had a double benefit. The NO_2 level for each temperature is increased and the NO_2

production peak is shifted towards lower temperatures. On the other hand, propane, did not contribute to the NO oxidation process over DOC and overall the occurrence of propane reduced the DOC performance. It is concluded that the additives agents have different effects on the NO oxidation process over the diesel engine exhaust gas, depending on the oxidation method.

However, the temperatures for the NO_2 production peak in the thermal reactor occurred in a range higher than the typical exhaust temperatures, even with the addition of propane. Therefore, higher penalties (e.g. post-injection, external heating, etc.) are required to reach these levels. An optimisation process based on different propane concentrations and reactor temperatures is recommended to obtain the desired NO_2/NO_X ratio minimising these penalties.

CHAPTER 5

INFLUENCE OF HYDROGEN AND REFORMATE COMBUSTION ON NO TO NO_2 OXIDATION IN THE ENGINE COMBUSTION CHAMBER AND HC-SCR

Hydrogen and reformate addition as a supplement to diesel fuel is proposed as one of the most promising alternative strategies for improving engine performance and controlling emissions (Shirk *et al.,* 2008; White *et al.,* 2006). In an earlier investigation, other colleagues from FPS group reported that reformate can be produced on-board a vehicle using fuel reforming technologies. In parallel work other members from the group have built and integrated a mini catalytic fuel reformer within an engine exhaust, which produces a gas stream enriched in CO and H_2 that can then be directed back to the engine inlet or to the engine aftertreatment system (Rodríguez-Fernández *et al.,* 2009). In diesel engines, the combustion of this enriched gas (which also contains CO_2, H_2O and N_2) is named REGR (reformed EGR), which is a process that allows improvement in engine performance, and shifts the NO_X–PM trade-off curves to lower values (Abu-Jrai e*t al.,* 2007).

In addition, it is reported that, the effect of H_2 and REGR also contributed to the performances of HC-SCR at low exhaust gas temperatures (< 300˚C) conditions (Theinnoi *et al.,* 2007). Small amounts of H_2 (30 ~ 3000ppm) addition were prevented the catalyst from coking problem and enhanced the catalyst activity for NO_X reduction while promoted the NO converts into NO_2.

In general, engine operation with REGR has been extensively studied and the beneficial effect of engine emission and aftertreatment systems performances have been reported (Rodríguez-Fernández *et al.,* 2009). However the influence of REGR combustion on engine-out NO_2/NO_X ratio and the resultant effect on aftertreatment systems, especially diesel particulate filters (DPF), have never been reported. The objectives of this work are to 1) study the effects on NO_2/NO_X ratio of the addition of H_2 and CO in the combustion cylinder; 2) examine the effects of operational variables such as engine speed, engine load, EGR rate (%Vol. of air intake) and reformate composition on NO_2/NO_X ratio; 3) determine the influence of REGR combustion, especially on engine-out NO_2/NO_X ratio, and on an aftertreatment system (i.e. HC–SCR and DPF).

5.0.1 Test Conditions and Procedure (specific to Chapter 5)

The experiments were carried out at two different engine speeds, 1200 and 1500rpm, with two engine loads of 3 and 4 bar indicated mean effective pressure (IMEP). To run on a dual fuelled engine mode, simulated reformate was added to the engine intake at varying EGR flow rates. The exhaust gas was recycled from the engine exhaust to the inlet (external EGR) and the volumetric flow rate of the EGR was calculated according to the reduction in the air volumetric flow rate. The simulated reformate of H_2 and CO was primarily from a bottled source. The compositions of these gases were chosen based on exhaust gas-assisted fuel reforming studies published earlier (Tsolakis and Golunski, 2006). The addition of H_2 and CO was taken as the percentage volume of EGR. For example, 25%H_2 represents 25% volume of the total flow rate of EGR. For conditions with zero EGR, no H_2 and CO has been added to the exhaust gas. Test conditions that have been selected and the corresponding exhaust temperatures are given in Table 5.1.

Table 5.1: Test conditions and the corresponding exhaust temperatures

Engine Speed (rpm)	Engine Load, IMEP (bar)	EGR (%Vol.)	0	10	20	0	10	20	0	10	20
		Reformate (% Vol. EGR)	**0**	**0**	**0**	**25% H_2**	**25% H_2**	**25% H_2**	**15% H_2 + 10% CO**	**15% H_2 + 10% CO**	**15% H_2 + 10% CO**
1200	**3**	*Exhaust Temp.(°C)*	210	215	220	215	220	230	220	225	240
	4	*Exhaust Temp.(°C)*	250	255	260	275	280	300	280	290	300
1500	**3**	*Exhaust Temp. (°C)*	250	255	260	260	260	265	260	265	270
	4	*Exhaust Temp.(°C)*	300	305	310	305	310	315	310	315	320

A DPF was positioned inside a mini-reactor exposed to actual diesel exhaust gas compositions as shown in Figure 5.1. The mini-reactor was heated by a tubular furnace, whose temperature was set to simulate that of the engine-out exhaust. The exhaust gas mixture was fed through the catalyst packed bed at a rate of 15 liters per minute (space velocity of 23k h^{-1}) over a period of 30 minutes.

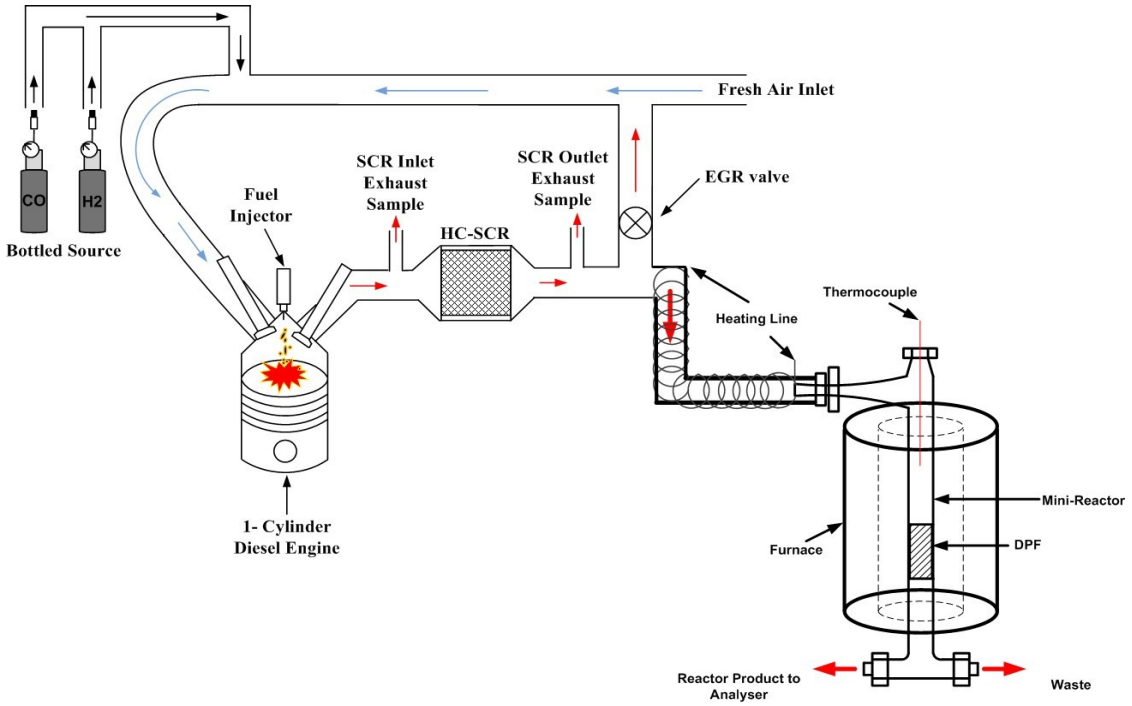


Figure 5.1: Schematic diagram of diesel engine SCR – DPF aftertreatment system.

5.1 Combustion Performance and NO to NO_2 Oxidation

5.1.1 Effects of EGR on In-Cylinder NO_2/NO_X Ratio

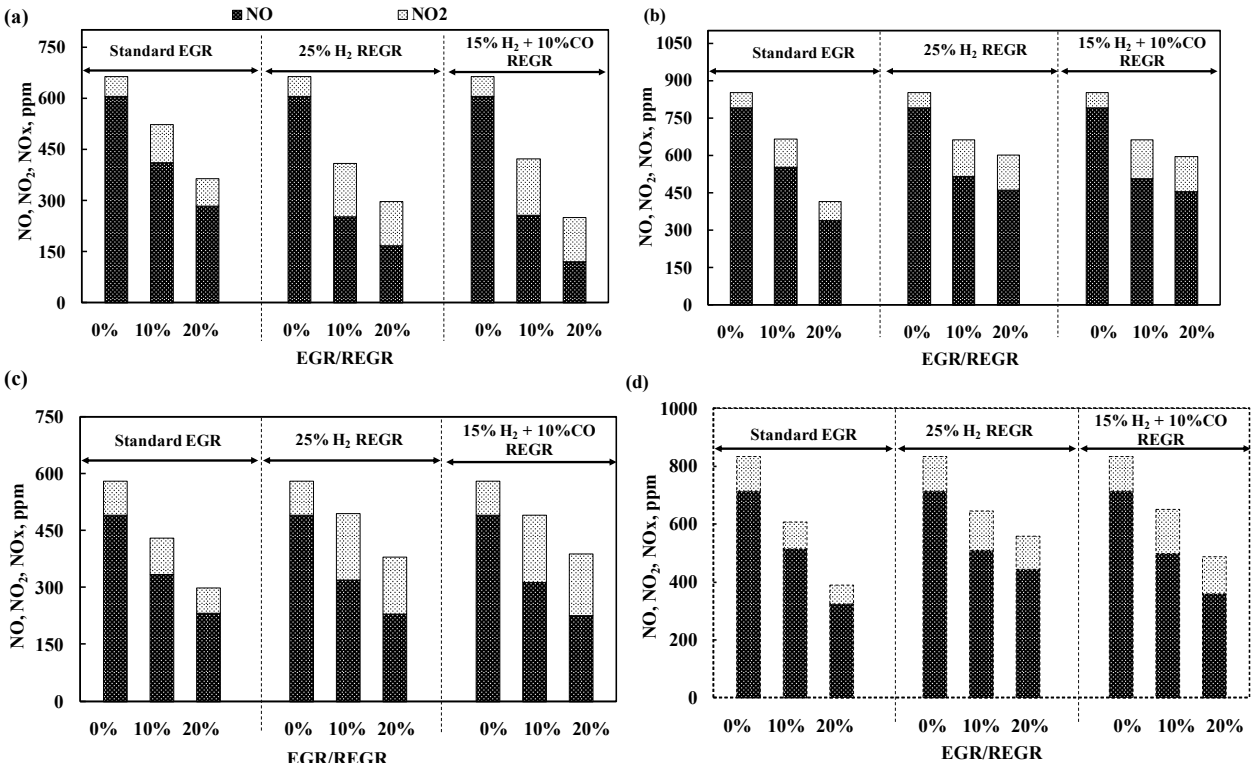


Figure 5.2: Engine-out NO_X, NO and NO_2 emissions (a) 1200rpm 3bar, (b) 1200rpm 4bar, (c) 1500rpm 3bar, (d) 1500rpm 4bar.

Nitric oxide (NO_X) emissions in a diesel engine exhaust typically consist of 85-95% nitrogen monoxide (NO) and 5-15% nitrogen dioxide (NO_2) (Soltic and Weilenmann, 2003). Although, EGR addition reduces the total NO_X emissions (Ladommatos *et al.,* 1998) it is also reduces the NO_2 concentration and therefore the NO_2/NO_X ratio as illustrated in Figure 5.2. In our tests, the EGR effect in reducing NO_2 concentration in the exhaust was more significant at high engine loads, where the fuel concentration was higher. The reduction of global in-cylinder air/fuel ratio (λ) by EGR addition and/or increased fuel concentration (higher load) influences the in-cylinder temperatures and combustion efficiencies leading to inhibition of NO oxidation to NO_2. Efficient in-cylinder air and fuel oxidation is also expected to enhance

NO oxidation, however, the localised incomplete combustion increases smoke, particulate matter (PM), CO and hydrocarbon emissions, resulting in the inhibition of the NO_2 formation.

The conversion of NO to NO_2 occurs at the same time as the oxidation of fuel or hydrocarbon, further increasing when the intermediate C-containing species (e.g. HC, soot) that are formed during combustion begin to oxidise (Nelson and Haynes, 1994). Some NO–NO_2 oxidation also occurs before the HC oxidation initiates (Bromly *et al.,* 1992). Similar trends have also been reported in several environmental catalyst research studies, with the main aim being to improve the oxidation of C-containing species (He and Yu, 2005).

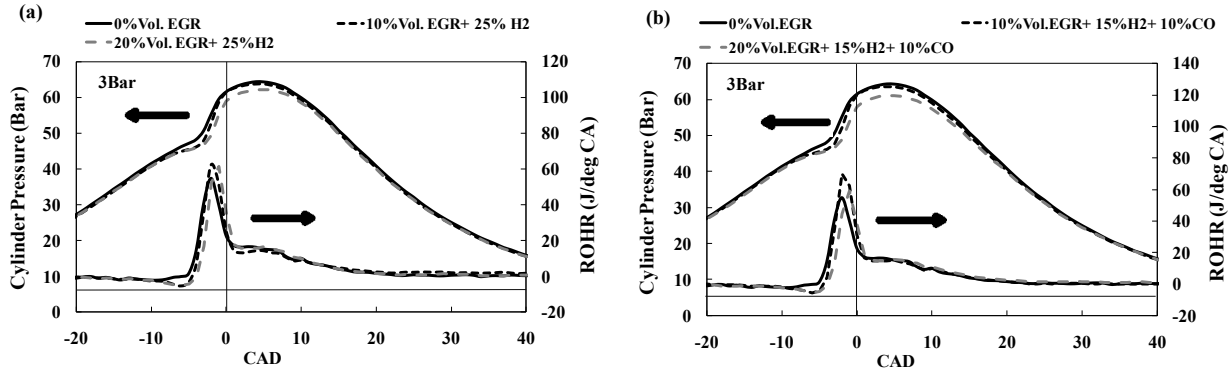
Several studies (Hargreaves *et al.,* 1981; Hori, 1988b) have reported that the formation of NO_2 is dependent on temperature and hydrocarbon presence. At low temperatures, peroxy radicals (HO_2 and RO_2) formed during combustion are crucial in promoting NO oxidation (see Equations 4.1 and 4.2). An increase in temperature results in the formation of several combustion by-products, which strongly promote NO to NO_2 oxidation. However, significant increase in hydrocarbon concentration during the combustion process prevents formation of species such as HO_2 and RO_2 which are active in NO to NO_2 conversion. This is also supported by the study carried out by Hori *et al.* (2002), where the temperature dependence of n-butane and n-pentane oxidation on the NO oxidation under a quartz flow reactor in a temperature window of 875° to 1375°C was investigated.

5.1.2 Effects of Reformed EGR (REGR) and Hydrogen on In-Cylinder NO_2/NO_X Ratio

Addition of REGR improved the NO_2 production especially at low engine loads (3bar IMEP) compared to higher engine loads (4bar IMEP). The overall NO_2/NO_X ratio at 3bar

IMEP was approximately 35-50% higher than at 4bar IMEP in either REGR compositions. Although the NO_X concentration improved with an increase in engine speed; under a constant engine load the effect was insignificant on the NO to NO_2 oxidation process as shown in Figure 5.2.

Under the same engine speed, REGR addition reduces the volumetric air/fuel ratio as air is replaced with gaseous fuel. According to the trends reported earlier, it would have been expected to reduce NO_2 production. However, the reduction of EGR flow rate (i.e. replaced by H_2 and CO) and the more pronounced premixed and completed combustion (combustion analysis shown in Figure 5.3) with a reduction in the formation of C-containing species, enhances the NO_2 production, probably due to the improved NO oxidation. Addition of H_2 and CO can significantly enhance NO oxidation at temperatures as low as 300°C, with O_2 and HC concentrations having an influential role in the reaction rates of both NO oxidation and the formation of carbon-containing intermediate species (Guo *et al.,* 2007).



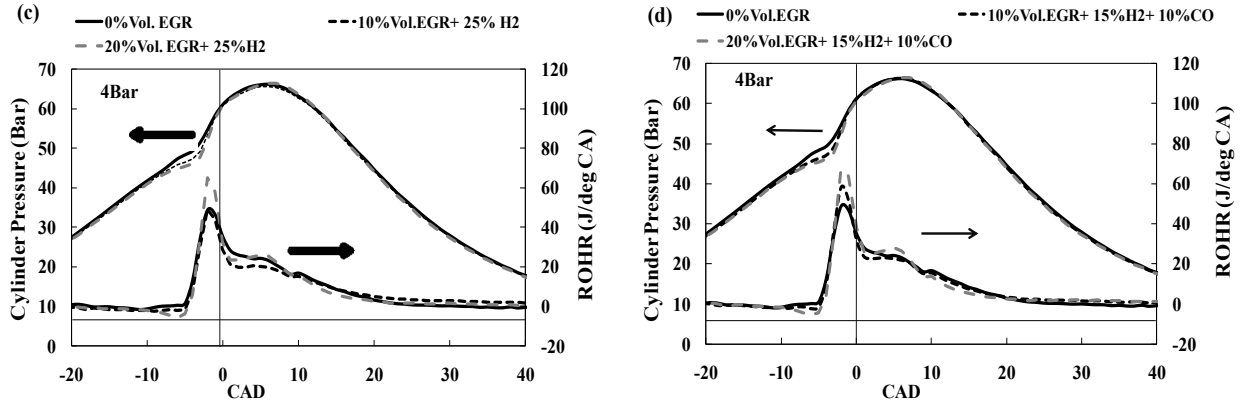


Figure 5.3: In-cylinder pressure and rate of heat release (ROHR) at 1200rpm.

Hargreaves *et al.* (1981) suggested that in order to promote NO oxidation, essentially, an increase in HO_2 radical production is required, because the 'HO_2 mechanism' is believed to be the most effective agent for this reaction. Therefore H_2, CO and possibly HC can play an important role in continuously generating the HO_2 radical.

The products formed in Equation 5.1 including the OH radical, can react further to give ⅓ ($H+O_2+H_2O$) which is illustrated in the equations below (Hargreaves *et al.,* (1981)):

$$OH + OH \rightarrow O + H_2O \quad (5.1)$$

$$O + OH \rightarrow H + O_2 \quad (5.2)$$

Alternatively, the reaction could be with H_2 or CO:

$$OH + CO\ (H_2) \leftrightarrows H + CO_2\ (H_2O) \quad (5.3)$$

This behaviour was also observed by Hori (1988) under fuel-rich conditions, where considerable levels of H_2 and CO appeared with traces of HC. The in-cylinder pressure and rate of heat release (ROHR) are presented in Figure 5.3. To avoid similar trends of repetition graphs, and further understand the in-cylinder combustion related to NO_2 production and NO

oxidation, only the test conditions for 1200rpm are presented. This specific condition showed the highest performance of NO oxidation.

The mROHR illustrated in Figure 5.3 is higher at an engine load of 4bar IMEP with the addition of EGR. Further looking at Figure 5.2, 4 bar IMEP case shows a lower portion of NO_2 compared to that of 3 bar IMEP case. Therefore at higher engine loads, with increased in-cylinder pressure and temperature the NO_2 production is limited as observed in this study. This could be associated with the HO_2 radical production. With the addition of REGR, it is possible to enhance the HO_2 mechanism as shown in Equations (5.1)–(5.3), promoting the formation of alkyl peroxy radicals, subsequently increasing NO oxidation as shown in Figure 5.2. For each engine test with REGR there was a significant smoke and PM emission reduction, however these results are not shown as part of this work.

5.2 NO_2 Effects on Aftertreatment Systems

Figure 5.4 shows the effect of NO_2/NO_X ratio at an engine speed of 1200rpm (SV of 28k h^{-1}) over the HC-SCR catalyst under 0% vol. EGR and REGR conditions. As illustrated in Figure 5.4, REGR significantly increases the ratio of NO_2/NO_X in the exhaust. Similarly, Figure 5.5 shows the effect of increasing the space velocity to 38k h^{-1} (i.e. engine speed of 1500rpm).

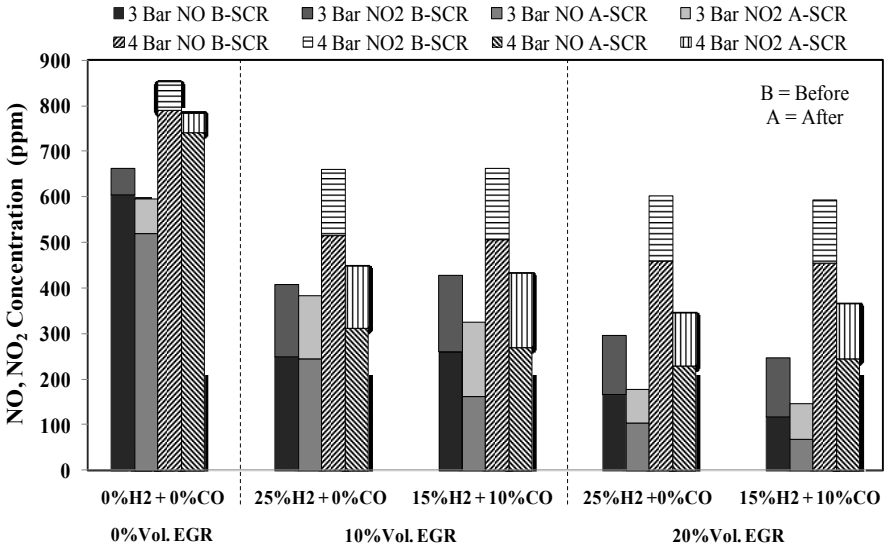


Figure 5.4: NO_2/NO_X effects over the Ag-SCR catalyst at a SV of 28k h^{-1}.

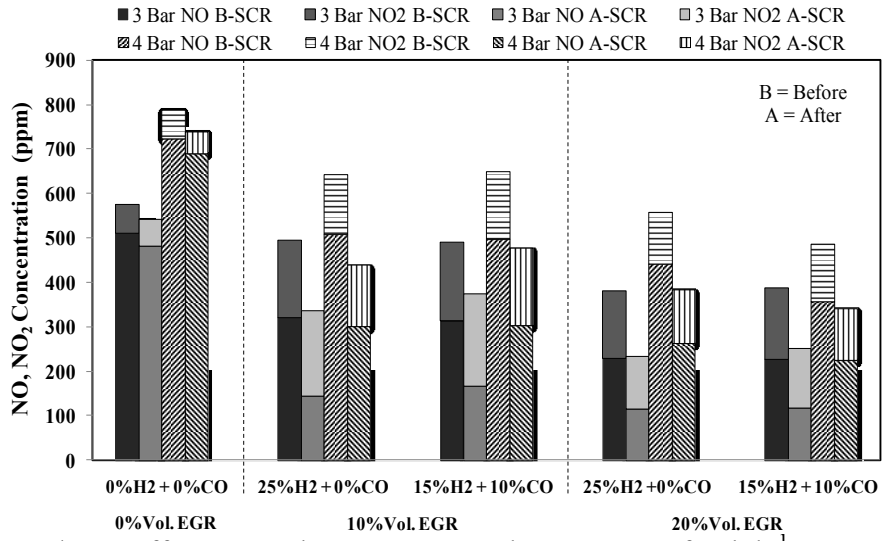


Figure 5.5: NO_2/NO_X effects over the Ag-SCR catalyst at a SV of 38k h^{-1}.

Increasing the engine load, results in higher operating temperatures over the HC-SCR catalyst, which enables further oxidation of NO. The activity of the catalyst in terms of NO to N_2 conversion is highly dependent on the ability of the catalyst to oxidise the HC chains. However from Figures 5.4 and 5.5, it was observed that the NO_2 concentration under all REGR conditions remained more or less constant with some conditions showing a small increase over the HC-SCR catalyst. In addition it can be seen that the NO was selectively

reduced over the HC-SCR catalyst instead of the NO_2. It is also known from earlier studies that the reduction of NO is enhanced by the presence of H_2 and to a lesser extent CO. The remaining H_2 after the combustion stage is illustrated in Figure 5.6. The availability of H_2 at the inlet of the catalyst suggests that the NO has reacted with H_2 to form N_2 (e.g. by dissociative chemisorption of NO, followed by removal of surface oxygen by the H_2), especially as the HC-SCR catalyst used in this study forms N_2 selectively (Theinnoi *et al.,* 2008). It is also known that H_2 retards nitrate poisoning of a clean silver surface, while NO_2 oxidises the C-containing species that can result in prolonged deactivation (Houel *et al.,* 2007). We have earlier shown that low H_2 concentrations can enhance the NO_2/NO_X ratio over the Ag/Al_2O_3 SCR catalyst.

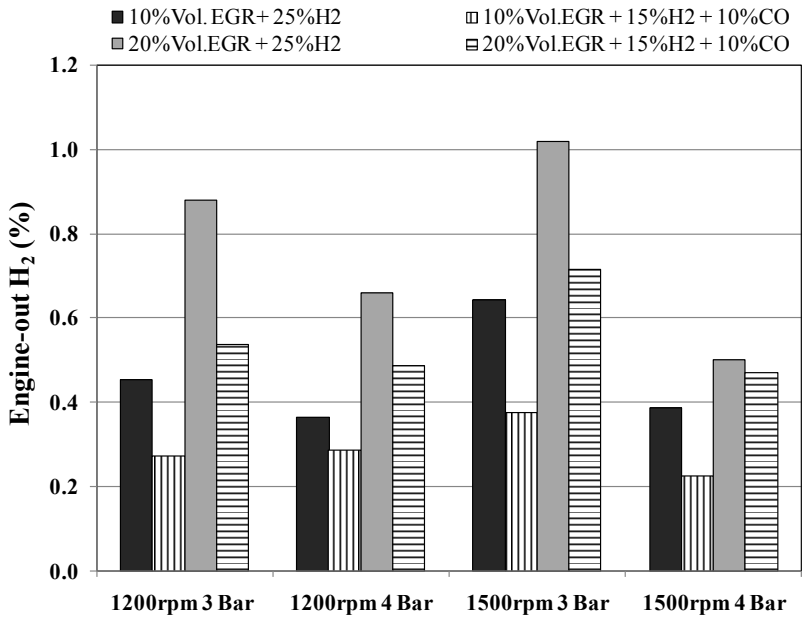


Figure 5.6: Un-combusted H_2 measured in the engine exhaust.

Figure 5.7 illustrates the NO_X conversion over the HC-SCR catalyst under various engine conditions and EGR rates. It is well known that EGR is the most effective method for reducing the NO_X produced by an engine, and for enhancing the CO, CO_2 and HC concentrations in the exhaust.

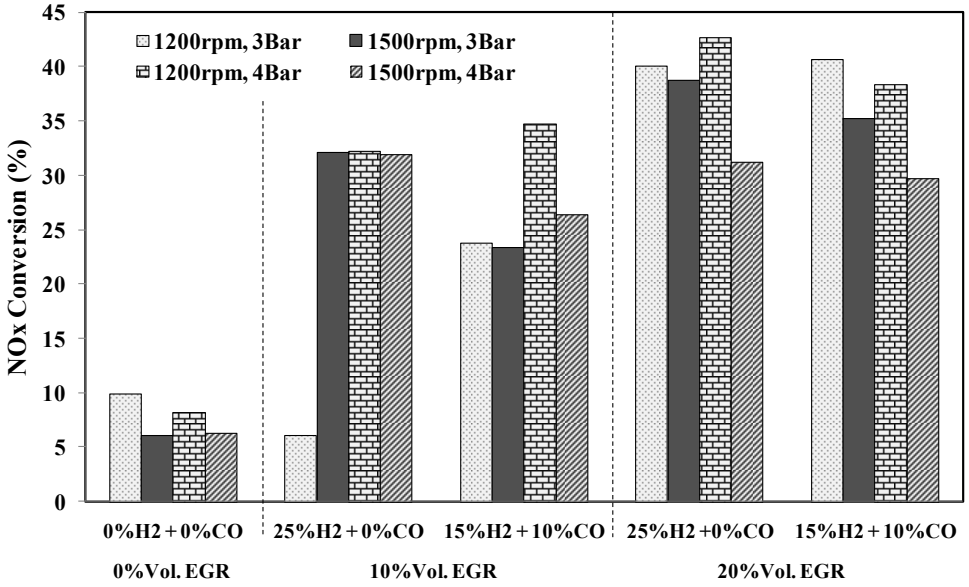


Figure 5.7: NO_X conversion over Ag-SCR catalyst.

So far we have observed that by using an HC-SCR catalyst with REGR, it was possible to reduce NO while producing about 100 ppm NO_2. Therefore, to take this study further, the beneficial effect of this NO_2 production will be utilised in a DPF system to purpose onboard continuous regeneration. NO_2 is primarily a low-temperature soot oxidation agent, enabling reduction of not only the mass but also the number of emitted particles (i.e. PM) from diesel-fuelled vehicles. Figure 5.8 shows the conditions where NO_2/NO_X ratio is the greatest, also giving an indication of how load and space velocity impact the NO_2 production.

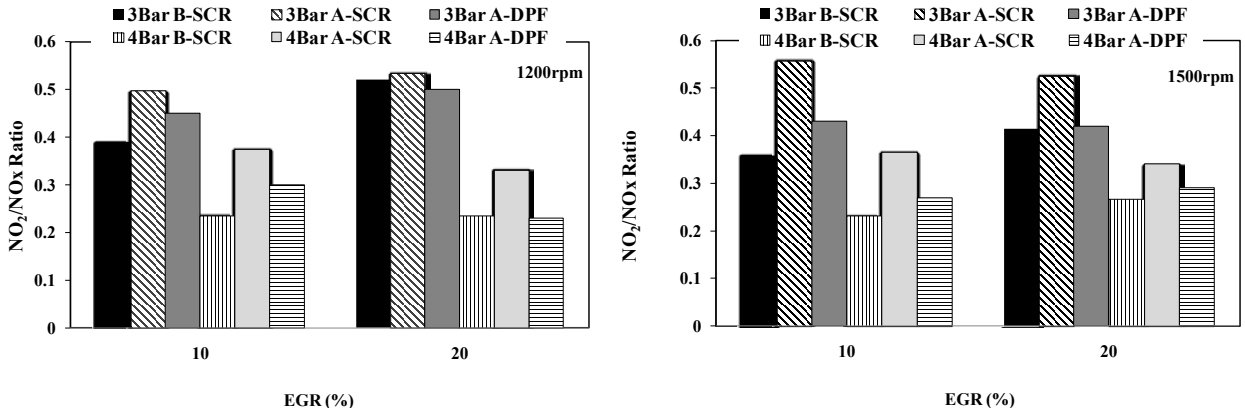


Figure 5.8: Effect of NO_2/NO_X ratio on space velocity with addition of 15%H_2 + 10%CO.

The NO_2 produced in the engine and then further enhanced over the HC-SCR catalyst was then passed through a DPF, the pressure drop along the DPF was monitor to provide an understanding of soot accumulation. The DPF regeneration was carried out at the engine conditions of 1500rpm 3bar IMEP with the REGR composition of 15%H_2 + 10%CO was shown in Figure 5.9. It is possible to see how the pressure is relieved when the HC-SCR and REGR applied catalyst is in the system. This suggests that some of the soot accumulated within the filter was oxidised by the available NO_2.

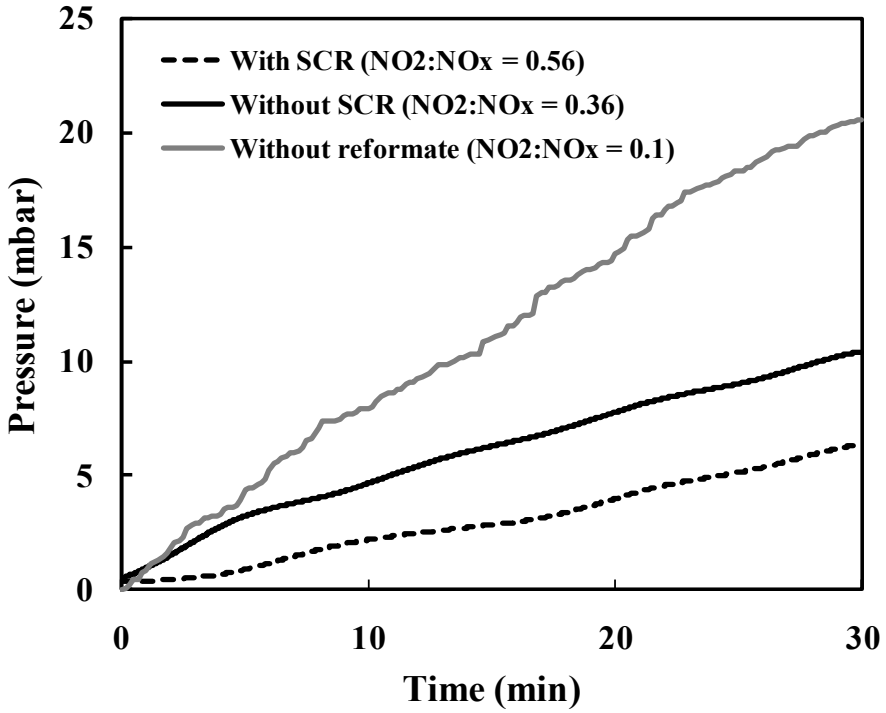


Figure 5.9: Back pressure over DPF.

This preliminary study has shown that REGR with the use of aftertreatment systems can provide sufficient reductions in NO_X and PM emissions to meet future strict legislation. As known for some time, NO_2 is better than O_2 at oxidising soot at low temperatures, and therefore its presence enables DPF regeneration. However, using REGR also allowed some of the un-combusted H_2 and CO to become available in the exhaust. Therefore, to take this further, the H_2 can be utilised with the aid of an Ag/Al_2O_3 HC-SCR catalyst, especially in

reducing NO and increasing the overall NO_2/NO_X ratio as reported in earlier studies (Houel *et al.,* 2007; Theinnoi *et al.,* 2008) which can also assist the soot oxidation in the DPF. It is also important to note that the EGR rate can have a dramatic effect on NO_2 production over an Ag/Al_2O_3 HC-SCR catalyst (Theinnoi *et al.,* 2008). As oxygen is the key reactant for NO_2 production, reducing the oxygen availability will decrease the NO_2 production.

5.3 Conclusion

The optimisation of NO to NO_2 oxidation within the engine will improve the efficiency of downstream aftertreatment devices such as SCR and DPF, by allowing them to operate at lower temperatures. The application of REGR with H_2 and CO to the combustion chamber was found not only to suppress the total NO_X concentration but also raised the NO_2 proportion in the engine exhaust. Under normal diesel conditions the NO_2/NO_X ratio in exhaust are lower than when running with REGR. Under REGR conditions the in-cylinder temperature and pressure are reduced, which effectively reduce the overall NO_X emissions. REGR type was found to be one of the influential parameters for NO_2 formation during combustion.

The combustion characteristics with REGR not only reduced the engine-out NO_X emission but also assisted in the NO_X and PM reduction over the aftertreatment systems. The presence of H_2 in the exhaust helps with the catalyst activity for NO_X reduction, whereas the NO_2 availability supports the soot oxidation over the DPF. As a whole, the system is able to simultaneously improve both NO_X reduction and DPF regeneration. It is important to note that an HC-SCR catalyst can reduce HC and NO_X emissions while increasing the downstream NO_2/NO_X ratio. The system we have described is able to contribute to improved engine

aftertreatment, aimed at achieving future emissions regulations that will require simultaneously high NO_X and PM control.

CHAPTER 6

PRELIMINARY STUDY OF NO-NO_2 OXIDATION IN THE DBD PLASMA REACTOR

The non-thermal plasma is formed when a high electrical energy is applied across the anode and cathode electrodes. Under the high electric field condition, the chemical reaction is initiated by high energy electrons, converting the input electrical energy into kinetic energy. In the non-thermal plasma exhaust gas treatment, the electrons are unable to react with NO_X molecules directly to provide the straight reduction solution. Nevertheless, the chemistry reaction process always begins with electron-impact dissociation with other background gases molecules, such as N_2, O_2, and H_2O (Penetrante *et al.,* 1995).

In the present experimental condition, the activated radicals (e.g. N, N*, O) are initially emitted over the plasma reactor through the following equation:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S, ^2D) \quad (6.1)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^3P, ^1D) \quad (6.2)$$

Where $N(^4S)$ and $N(^2D)$ are ground-state and metastable excited-state nitrogen atoms, respectively. And $O(^3P)$ and $O(^1D)$ are ground-state and metastable excited-state oxygen atoms, respectively.

These rate coefficients for electron-impact dissociation of N_2 and O_2 molecules into free radicals species strongly depend on the mean electron kinetic energy (eV) of the electrons (Penetrante *et al.,* 1995), which is defined as electron-molecule collision cross section and the

electric field experienced by the electrons. A brief explanation of these two important parameters is described as follows:

- Collision cross section
  Is a phenomenon that occurs between the interactions of molecules with the electron, which can be defined as the effective area of the molecule that overlaps, touches or collides with an electron to produce a specific reaction (e.g. dissociation, attachment).

- Electric field
  Is another important parameter to examine the plasma performance, especially at high electric field conditions; it is much easier to produce energetic electrons that initiate the excited state chemistry.

In certain conditions, the collision cross section for electron-impact dissociation of the molecule has a limit which cannot be exceeded through the improvement of reactor geometry design or electrical modification (Penetrante *et al.,* 1997). Moreover, most of the literature has confirmed, the electric field strength in the electrical discharge reactors operating at atmospheric pressure is typically between 30 ~ 60kV/cm (Raizer, 1991), corresponding to the mean electron energy of 3 ~ 6eV (Penentrante *et al.,* 1996).

According to Lee and Chang (2004) and Wang *et al.* (2011), electric field strength in co-axial DBD reactor under the atmospheric pressure can be modelled and calculated by equation based on its geometry arrangement and the voltage applied. Details of the method for electric field calculation can be found in Appendix B.

Based on the information collected, the electric field of the DBD reactor in the present work is approximately 25, 33 and 40 kV/cm for the discharge power of 10, 20 and 30W

respectively, which is adequate to produce a large proportion of the free radicals for the reduction/oxidation process.

The primary objective of this Chapter is to test the newly developed plasma system on different mixtures of synthetic gas, and understand the working principle of DBD plasma reactor on the NO-NO_2 oxidation process within this system. This included the influence of the NO concentration, oxygen concentration, propane addition, as well as the energy efficiency.

6.0.1 Test Conditions and Procedure (specific to Chapter 6)

The schematic diagram of the experimental set-up for this study is shown in Figure 6.1, which consists of five major sections: the continuous gas flow supplying system, DBD plasma reactor, AC power generator, electric and gaseous analytical system.

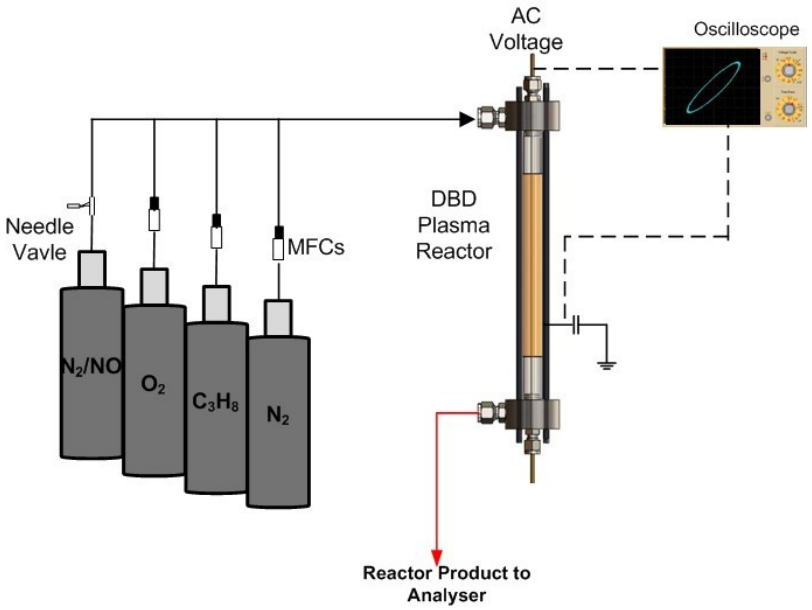


Figure 6.1: The experimental set-up diagram of synthetic bottle gases with the DBD plasma reactor system.

The synthetic gas was generated from bottled gases and fed into the DBD plasma reactor at atmospheric pressure and at room temperature. The specification of each bottled gas

was: 20% propane in nitrogen, 1% nitric oxide in nitrogen, 99.5% oxygen in nitrogen and high purity nitrogen as a balance gas. The feed flow rates were controlled by mass flow controllers, while the small amount of nitric oxide concentration in the mixture was controlled through high precision metering valves.

A custom built DBD non-thermal plasma reactor has carried out in this study. A brass round bar with the diameter of 3.18mm served as the inner discharge electrode and was installed coaxially in the middle of the reactor. The quartz with an inner diameter 16mm and the thickness of 3mm was applied as the main body of the reactor. The outer electrode was made from an aluminum foil of approximately 0.2mm thickness wrapped around the external surface of the quartz tube. The design details are shown in Figure 6.2.

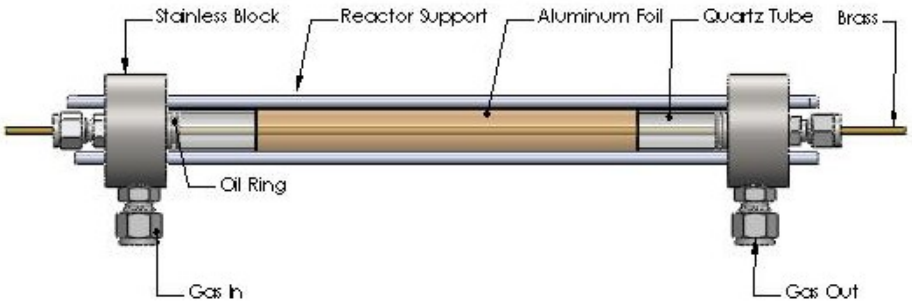


Figure 6.2: DBD plasma reactor.

A custom built AC power supply (provided by Creating Nano Technologoes, Inc.) with a variable voltage was used as the power source to generate the plasma over the DBD reactor. The voltage from the power source could be increased by 1,000 times with a high voltage transformer to give the final output voltages in the range 0 – 20kVpk-pk. The AC sine wave was driven by an electrical resonance transformer to provide the operation frequency fix at 65 kHz. The details of the electric and gases analyser were described in Chapter 3.

The specific input energy (SIE) is determined by the following:

$$\text{SIE (J/L)} = \frac{Power\ (W)}{Flow\ rate\ (\frac{l}{min})} \times 60 \tag{6.3}$$

The energy efficiency for NO conversion is determined by the following:

$$\eta\ [\text{g/kWh}] = 30 \times \frac{[NO]in - [NO]out}{22.4 \times (\frac{SIE}{3.6})} \tag{6.4}$$

where $[NO]_{in}$ and $[NO]_{out}$ mean the NO concentration in the initial gas and in the gas after the DBD plasma reactor, respectively.

This energy efficiency unit g/kWh can convert into eletronvolts per removed NO, which is frequently applied in non-thermal plasma to express the energy require for converting one mole of NO with the following:

$$\eta\ ev\ [\text{eV/NO}] = \frac{1.12 \times 10^3}{\eta} \tag{6.5}$$

where the efficiencies η and η*ev* have units g/kWh and eV/NO, respectively.

Penetrante *et al.* (1997a) emphasized, that it is important to distinguish the behaviours in the NO_X treatment processes. In this study, 'NO conversion' is used to express the de-NO_X process in which NO reduction and oxidation is accomplished; 'NO reduction' is used to define the total NO that is reduced to N_2; this mainly occurs in the absence of oxygen. 'NO oxidation' is used to express the reduction of NO that is converted into NO_2 while the total NO_X remained constant.

6.1 NO-NO_2 Oxidation in N_2/NO Mixture

The initial tests were carried out to study the effect of initial NO concentration in the N_2/NO mixture on the NO_2 formation at the discharge power of 10-30W. The mixtures were injected into the reactor under two independent flow rates of 5 l/min and 10 l/min, and four NO initial concentrations: 100ppm, 300ppm, 500ppm, and 1000ppm were selected. For all test conditions, the NO_X is reduced with minimal NO_2 observed when the discharge plasma is turned on, as presented in Figure 6.3.

This is due to the chemical reduction of NO that is initiated by the ground-state nitrogen atom form in the reaction (6.6) reducing the majority of NO into N_2 through the following reaction:

$$N(^4S) + NO \leftrightarrow N_2 + O \qquad (6.6)$$

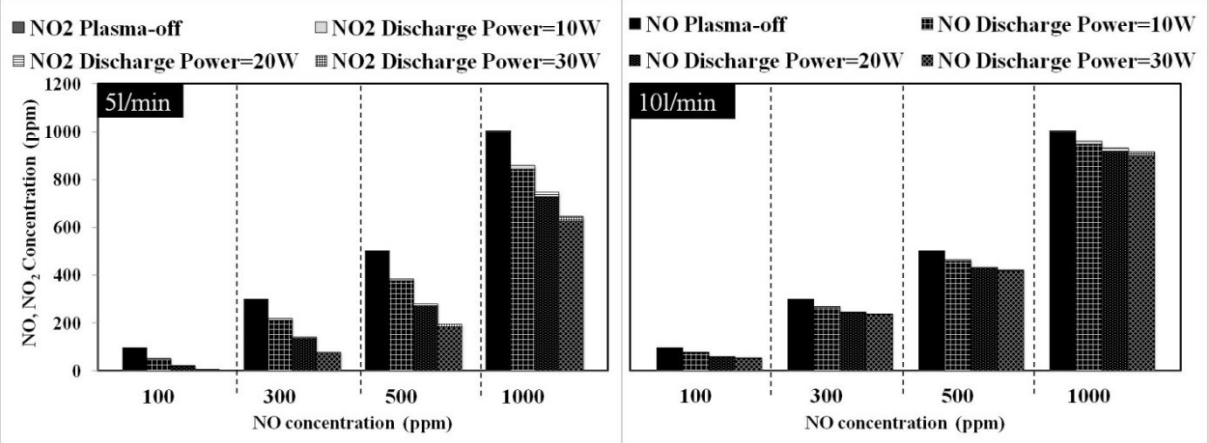


Figure 6.3: NO and NO_2 emission in the N_2/NO mixture.

The NO_X reduction efficiency and the energy efficiency of NO conversion in terms of g/kWh and eV/NO are attached in Figures 6.4 and 6.5. The results show that nearly 95% of NO_X reduction was achieved for the 100ppm of the initial NO at the discharge power of 30W. However, the overall reduction efficiency was reduced with the increased initial NO concentration to 1000ppm.

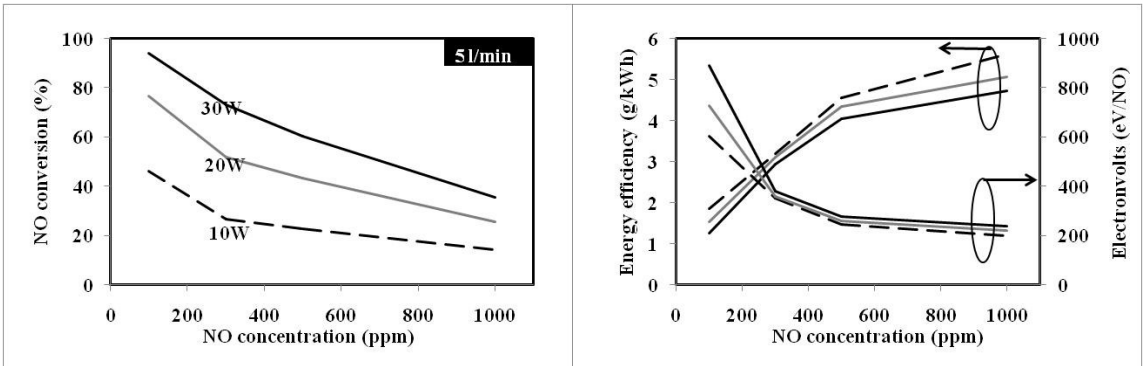


Figure 6.4: NO_X reduction efficiency and the energy efficiency of NO conversion in 5 l/min.

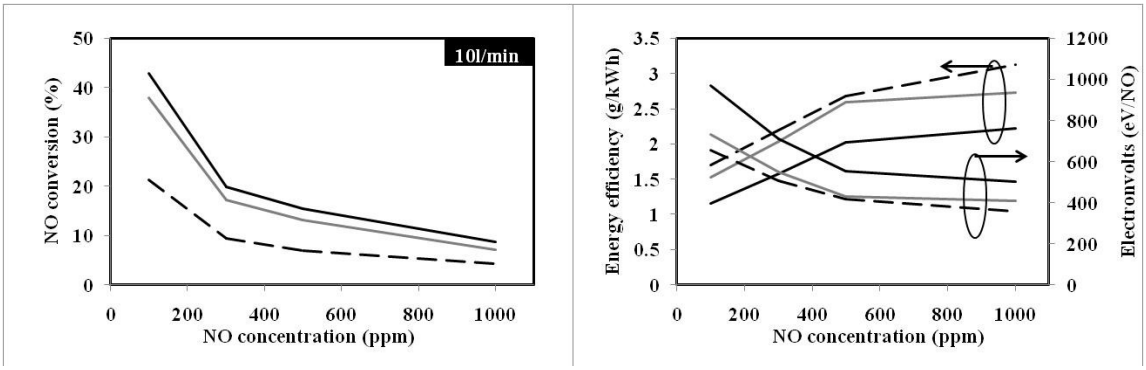


Figure 6.5: NO_X reduction efficiency and the energy efficiency of NO conversion in 10 l/min.

This can be explained by, under the same discharge power conditions, the electric field within the reactor is the same and the number of active radicals emitted to the system is constant. At this point, increasing the initial NO concentration will decrease the ratio of active species with respect to NO molecules, thereby depleting the NO_X efficiency.

In contrast, the increase of the initial NO has the advantage of energy efficiency. The highest energy efficiency was approximately 5.6 g/kWh at the condition of 10W discharge power with the initial NO of 1000ppm; this corresponds to the electronvolts of 200eV/NO (Figure 6.4). This created a challenge for obtaining a higher NO_X reduction under the condition of higher energy efficiency.

In the non-thermal plasma study, the specific input energy (SIE) (shown in Equation 6.3) is one of the important parameters that has to be considered. This directly influences the

chemical reaction in the plasma according to the changed gas flow rate or resident time over different discharge power. For example, the SIE decreased when increasing the feed flow rate under the same discharge power condition. In this section, the SIE performed in the range of 60 ~ 360 J/L.

Comparing the trends obtained in Figures 6.4 and 6.5, it is apparent, that under the same discharge power conditions, the overall NO_X reduction performance was decreased by approximately 50% when the feed flow rate was increased from 5 l/min to 10 l/min. In other words, this is affected by the reduced level of SIE, which indicates that the amount of energy required to remove a given NO concentration is not sufficient.

6.2 NO-NO_2 Oxidation in N_2/NO/O_2 Mixture

Generally, diesel engines inherently operate in the lean condition. Whereas there is a high amount of oxygen that appears in the combustion chamber during the combustion process, producing oxygen rich exhaust.

Therefore, the test condition (10W, 5 l/min) at the highest energy efficiency, obtained from previous studies, was used to examine the effect of DBD plasma on NO to NO_2 oxidation in the mixture of N_2/NO/O_2 in this section. The results of overall NO_X (NO, NO_2), NO conversion and the energy efficiency are shown in Figures 6.6, 6.7 and 6.8 respectively.

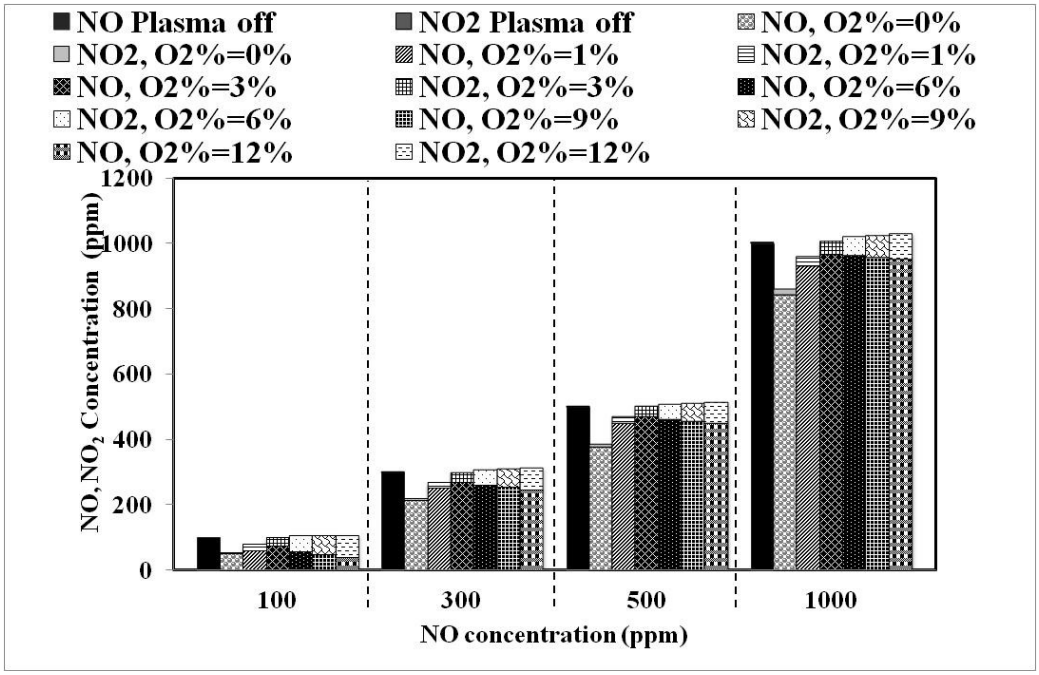


Figure 6.6: Effect of oxygen concentration on NO/NO_X ratio. Conditions: total flow rate 5 l/min, discharge power 10W.

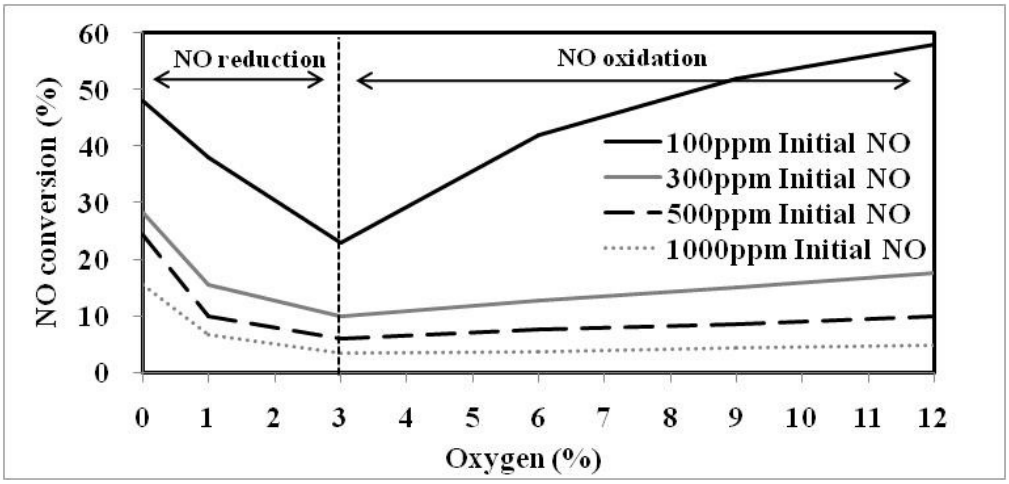


Figure 6.7: The effect of oxygen concentration on NO conversion.

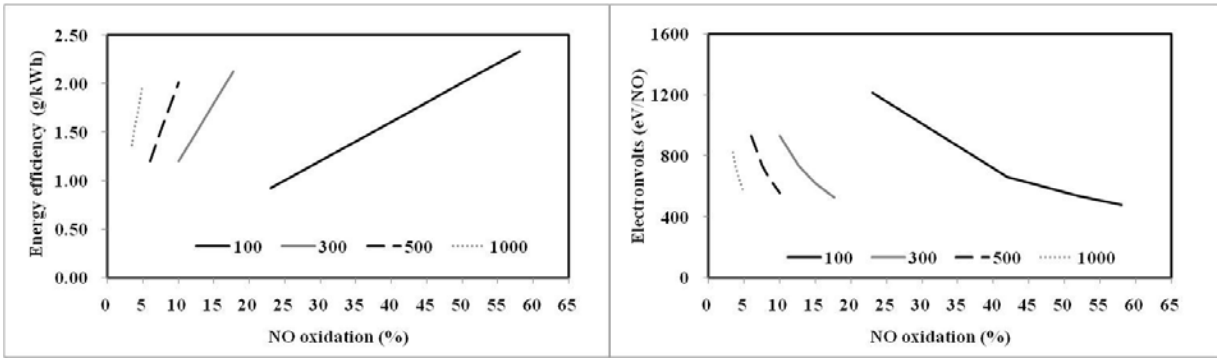


Figure 6.8: Energy efficiency of NO conversion in the $N_2/NO/O_2$ mixture.

In this study, when the oxygen concentration is below 3%, the NO reduction was the main reaction over the mixture. In contrast, the reduction process was converted in the oxidation process when the oxygen concentration is higher than 3% (Figure 6.7), the NO is oxidised to form NO_2 while the overall NO_X after the reactor remained constant. This is supported by Yan *et al.* (1999), in the mixture of $NO/N_2/O_2$; the rate of oxidation reactions was higher than the rate of reduction reactions when the O_2 concentration is above 3.6%.

In general, two possible outcomes are obtained by injecting $NO/N_2/O_2$ mixture through the DBD plasma reactor, which can be summarised in the following:

- *NO Oxidation*

  The process began with the O radicals produced from equation (6.2), the ground-state oxygen atom, $O(^3P)$ is used to convert the NO into NO_2.

  $$O(^3P) + NO + M \rightarrow NO_2 + M \quad (6.7)$$

  $$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (6.8)$$

  $$O_3 + NO \rightarrow NO_2 + O_2 \quad (6.9)$$

  (M is either N_2 OR O_2.)

- *NO Formation*

  The metastable excited nitrogen atoms ($N(^2D)$) reacted with oxygen to produce NO molecules via reaction 6.10. Thus, creating a counterbalance of NO conversion between $N(^2D)$ and $N(^4S)$ species (active in NO reduction process)

  $$N(^2D) + O_2 \rightarrow NO + O \quad (6.10)$$

Figure 6.8 shows the energy efficiency of the NO oxidation process in the mixture of N_2/NO/O_2. Compared to the energy efficiency of NO conversion (NO is converted into N_2) in the N_2/NO mixture; the energy required to convert the same amount of NO into NO_2 in the N_2/NO/O_2 mixture was slightly higher. This is because the presence of O_2 provides a counter balance between NO reduction and NO formation; part of the energy was consumed in that process.

However, if the comparison only focuses on the NO oxidation process within the N_2/NO/O_2 mixture, the energy efficiency is improved by an increased O_2 concentration. This is due to the lower dissociation energy of oxygen molecules (5.2eV) compared to nitrogen molecules (9.8eV), as a result, the rate for electron-impact dissociation of O_2 is greater than N_2. Therefore, under the higher O_2 level condition, it is much easier to produce oxidative free radicals in order to oxidise NO into NO_2.

The energy efficiency of NO conversion in this case is similar to the work carried out by Takaki *et al.* (2004) which reported that 2g/kWh NO removal energy efficiency is required over the mixture of N_2/O_2/NO containing 200ppm of initial NO. Further improvement of 8g/kWh (140eV) was achieved by changing the reactor to multipoint electrodes.

6.3 NO-NO_2 Oxidation in N_2/NO/O_2/HC Mixture

As the discussion outlined in Chapter 4, the NO_2/NO_X ratio is expected to reach the range 0.3~0.6 to obtain a better filter regeneration process. In this case, only one condition (100ppm NO) has achieved the values suggested, and the conditions provide lower values than the level assumed (Figure 6.9). This is not sufficient for the real diesel exhaust gas

application, because most of the diesel emissions have a higher level of NO emission (>100ppm) (Penetrante *et al.,* 1999).

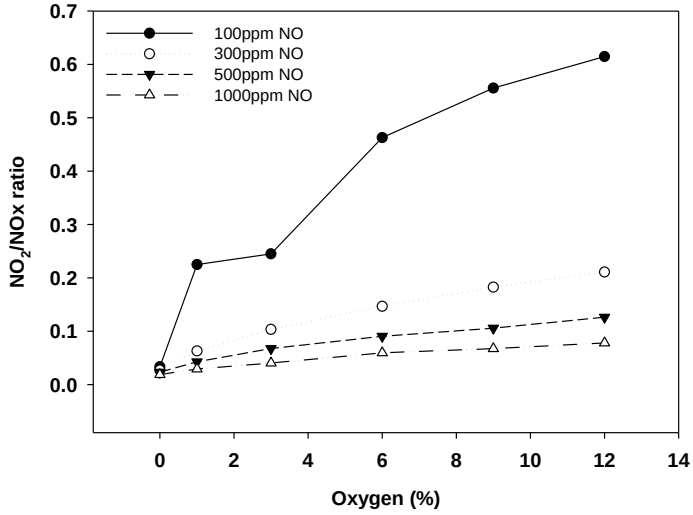


Figure 6.9: NO_2/NO_X ratio in the mixture of NO/ N_2/O_2.

Additionally, at the higher reaction temperature, the kinetic energy of the electrons is reduced; the energy transfers the background molecules into vibrational excitation and heats up the gas temperatures. For this reason, the NO-NO_2 oxidation is not favourable at high reaction temperatures, the NO_2 produced will be converted back to NO through the reaction (Penetrante *et al.,* 1997b).

$$O + NO_2 \rightarrow NO + O_2 \qquad (6.11)$$

Regarding the passenger diesel engine, the median temperatures close to the exhaust manifold are in the range of 140 ~ 250˚C (Van Setten *et al.,* 2001). The total NO_2/NO_X values achieved might be overestimated due to the fact that the test was carried out at ambient temperature.

Several studies proved the effect of HC promoting the NO-NO_2 oxidation. Furthermore, it also improves the phenomena of reverting reactions at higher temperature over the non-

thermal plasma (Penetrante *et al.,* 1997b). To be comparable with the test conditions outlined in Chapter 4, propane was selected to study the HC effect in the N_2/NO/O_2/HC mixture.

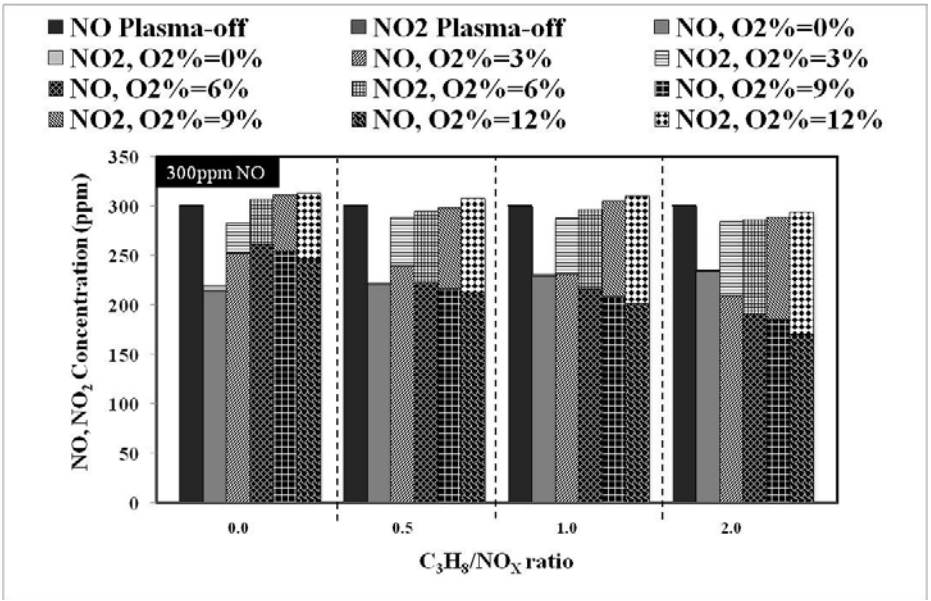


Figure 6.10: Effect of propane on NO/NO_2 emissions; (300ppm of NO with N_2 balance).

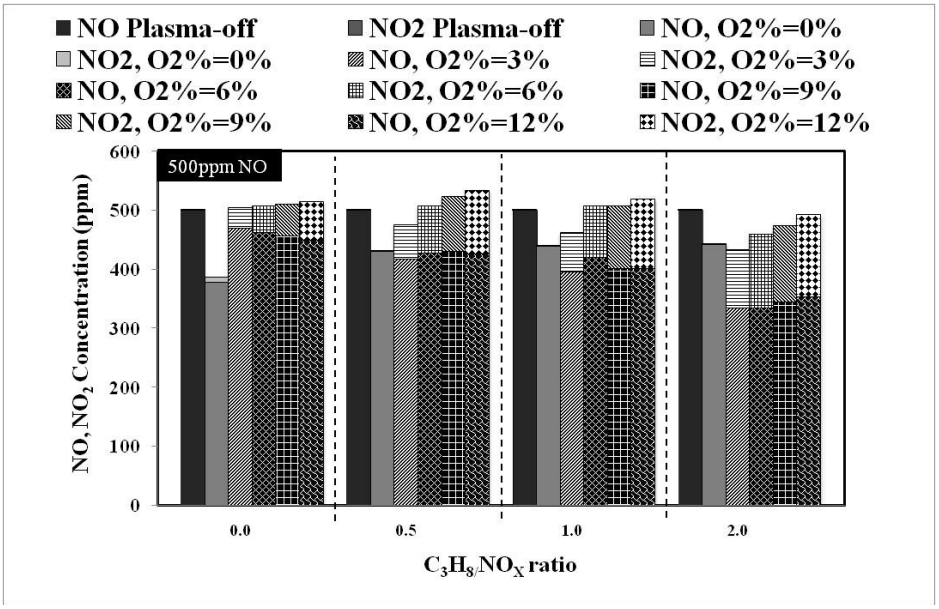


Figure 6.11: Effect of propane on NO/NO_2 emissions; (500ppm of NO with N_2 balance).

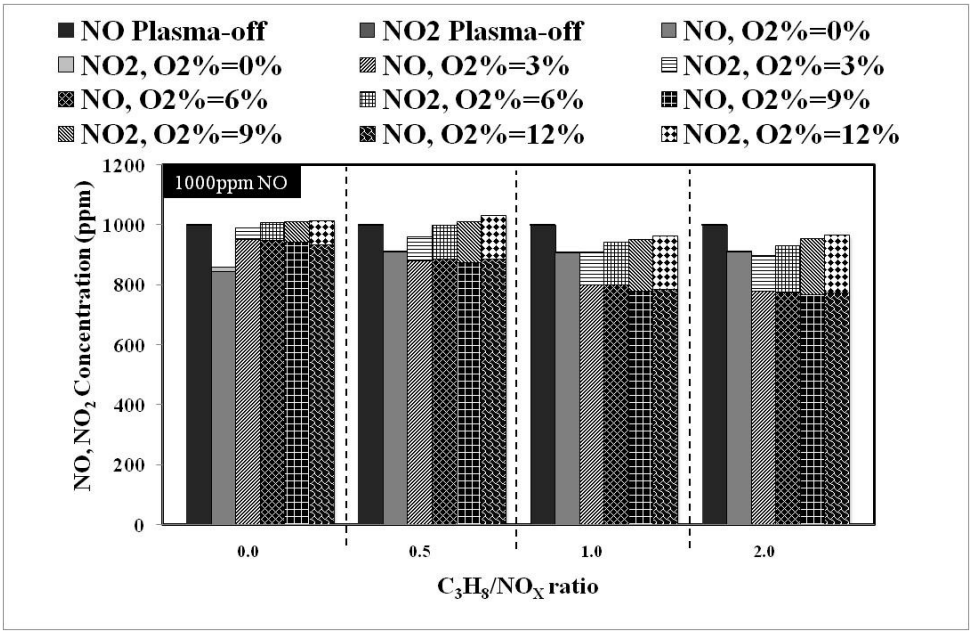


Figure 6.12: Effect of propane on NO/NO_2 emissions; (1000ppm of NO with N_2 balance).

Addition of propane (e.g. increasing C_3H_8/NO_X from 0.5 to 1.0 and 2.0) enhances the NO_2 formation as can be seen in Figures 6.10 to 6.12 for all of the three different initial NO concentrations of 300, 500 and 1000ppm.

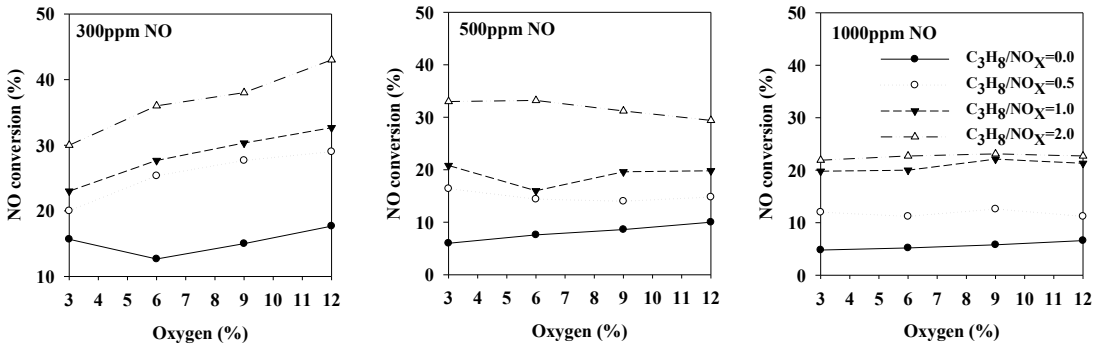


Figure 6.13: NO conversion in the mixture of $NO/N_2/O_2/C_3H_8$.

In particular, for the condition of 300ppm the initial NO provides a higher level of NO conversion as NO is oxidised into NO_2. It is suggested that, to maintain this beneficial effect, C_3H_8 has to be introduced consistently with the presence of O_2 to obtain a good NO oxidation process (Figure 6.13). This is supported by Dorai and Kushner (2001), who studied the kinetic

reaction of the effect of C_3H_8 in the NO_X treatment over the non-thermal plasma reactor. The reaction mechanism of this study is extracted and re-plotted in Figure 6.14.

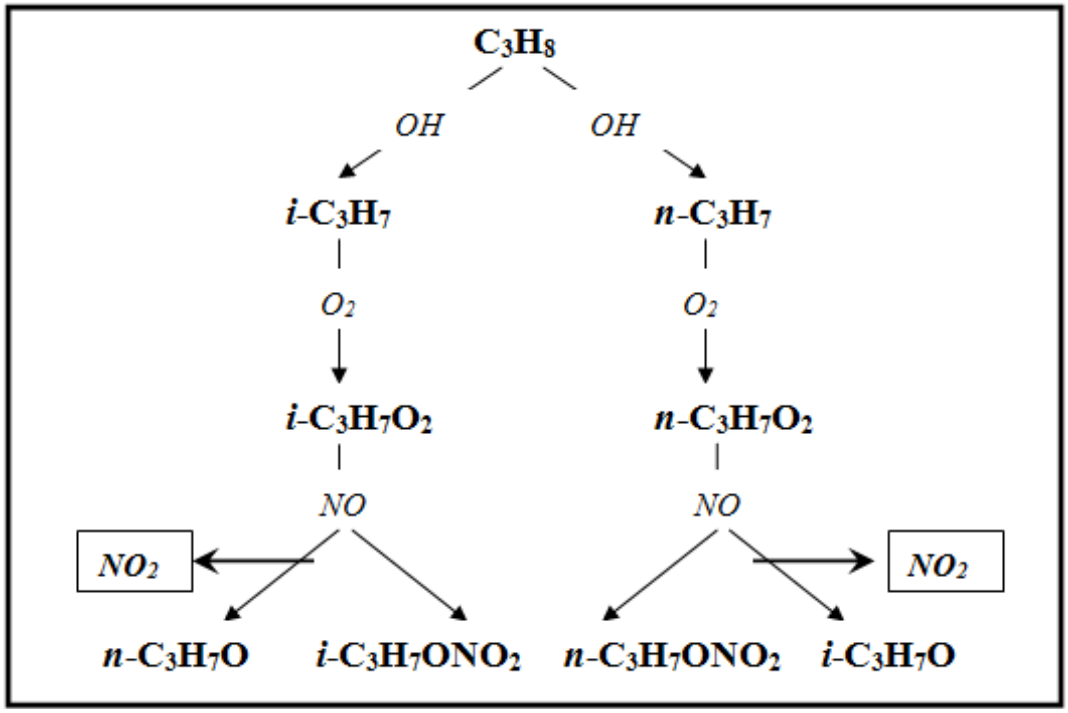


Figure 6.14: Reaction mechanism of propane promoted NO-NO_2 oxidation in the DBD plasma reactor.

This process is similar to the NO-NO_2 oxidation reaction presented in Chapter 4 (C_3H_8 effect for thermal oxidation process), which can be simplified by initiating reactions of C_3H_8 by an H-abstraction process in which OH radicals produce alkyl radicals. The alkyl radicals then react with oxygen to form peroxy radicals, which further react with NO to form NO_2.

$$C_3H_8 + OH \rightarrow i\text{-}C_3H_7 + H_2O \quad (6.12)$$

$$C_3H_8 + OH \rightarrow n\text{-}C_3H_7 + H_2O \quad (6.13)$$

$$i\text{-}C_3H_7 + O_2 \leftrightarrow i\text{-}C_3H_7O_2 \quad (6.14)$$

$$n\text{-}C_3H_7 + O_2 \leftrightarrow n\text{-}C_3H_7O_2 \quad (6.15)$$

$$i\text{-}C_3H_7O_2 + NO \leftrightarrow i\text{-}C_3H_7O + NO_2 \text{ and} \quad (6.16)$$

$$n\text{-}C_3H_7O_2 + NO \leftrightarrow n\text{-}C_3H_7O + NO_2 \quad (6.17)$$

The energy efficiency of NO conversion over the C_3H_8 addition is illustrated in Figure 6.15. Generally, the C_3H_8 addition improved significantly the energy efficiency by 2 ~ 3 orders of magnitude compared to no C_3H_8 addition for all the examined parameters. This provides the highest energy efficiency of NO conversion obtained at the molar ratio of C_3H_8/NO_X = 2.0.

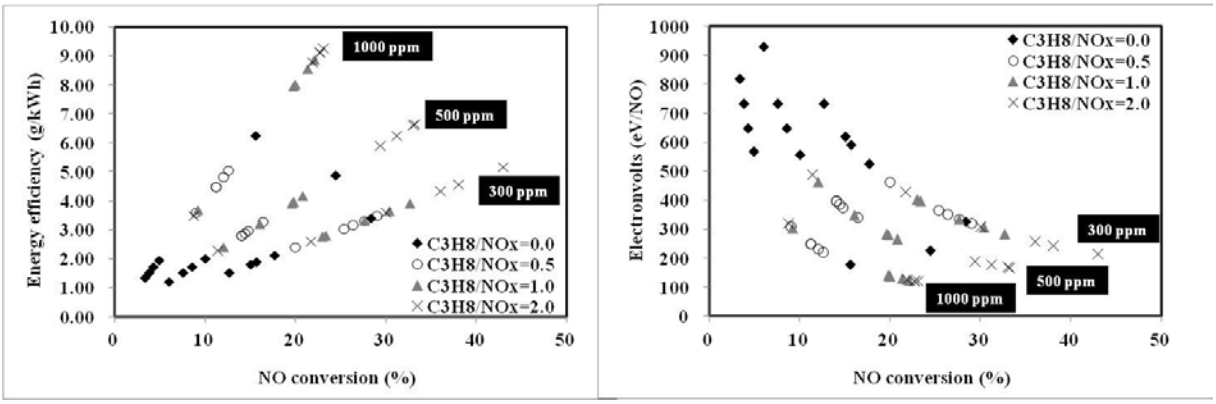


Figure 6.15: Energy efficiency of NO conversion in the $NO/N_2/O_2/C_3H_8$ mixture.

Although, a very clear improvement in the energy efficiency of NO conversion has been achieved under the C_3H_8 addition, yet the result is still not satisfactory when compared with other research (Khacef *et al.,* 2002; Niessen *et al.,* 1998).

For example, Khacef *et al.* (2002) shows the energy cost for NO oxidation was decreased from 42 to 25eV/NO by adding a 500ppm of propylene into the $N_2/O_2/NO$ mixture (initial NO 500ppm). Further energy efficiency work has been done by Niessen *et al.* (1998), which demonstrates that only the 6eV/NO molecule is required to convert NO into NO_2 when adding a 2000ppm of ethene to the mixture containing N_2, O_2, N_2O, NO (430ppm) and NO_2 (70ppm).

Consequently, the low energy efficiency of NO conversion under the C_3H_8 addition as explained in the research work of Shin and Yoon (2003). This is because the alkene

hydrocarbons have shown to better promote NO-NO_2 conversion in the NTP treatment when compared to alkane hydrocarbons. The alkane hydrocarbons are generally less effective due to their stronger sigma bonds of C-C and C-H on their stable molecular structure. In addition, the propane used in the present study required higher energy to be broken down compared to propylene and ethylene used by other studies (Hoard and Balmer, 1998; Lee *et al.,* 2003).

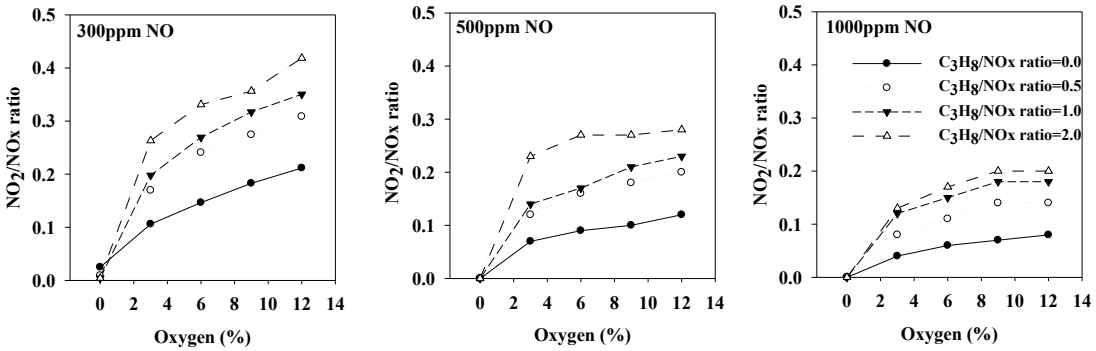


Figure 6.16: NO_2/NO_X ratio in the mixture of NO/ N_2/ O_2/C_3H_8. (Conditions: total flow rate 5 l/min, discharge power 10W).

Compared to the normal operation (without C_3H_8 addition), the NO_2/NO_X ratio is increased to satisfy values for the conditions of 300ppm and 500ppm NO, which is required in the filter regeneration process (Figure 6.16). Although it is too general to examine the DPF regeneration by studying the effect of NO_2/NO_X ratio, and further parameters such as working temperature, soot loading have to be considered, however, this provides a useful guideline for further studies using actual diesel exhaust gas.

6.4 Conclusion

The preliminary study of NO-NO_2 oxidation of the DBD plasma reactor has been established over different mixtures of synthesis gas and the findings can be summarised as follows:

- In the mixture of N_2/NO, the main reaction found was the chemical reduction of NO into N_2 by the $N(^4S)$ species. The conversion efficiency of NO at high initial NO concentration was reduced, this is because the $N(^4S)$ species generated from the reactor are not sufficient to produce the reduction process.

- In the mixture of N_2/NO/O_2, the effectiveness of the emitted N-atom or O-atom from the reactor provides different roles in the NO_X conversion process (e.g. NO oxidation/ NO reduction).

- In the mixture of N_2/NO/O_2/C_3H_8, a positive effect of C_3H_8 on NO oxidation was stronger than the presence of O_2. Larger number of NO was oxidised into NO_2 by increasing the molar ratio of C_3H_8/NO_X, this provided an improvement of the final NO_2/NO_X ratio in the exhaust which cannot be achieved by other mixtures. In addition, this mixture contained the largest value of energy efficiency, at a rate double to triple of that compared to the mixture without C_3H_8.

CHAPTER 7

USING DBD NON-THERMAL PLASMA TO ENHANCE THE NO_2/NO_X RATIO IN DIESEL ENGINE EXHAUST GAS FOR IMPROVED DPF REGENERATION

Compared to the conventional active or passive regeneration process, the application of DBD plasma in DPF regeneration is considered a new concept with a high potential for applications in future on-board vehicles (Bromberg *et al.,* 2006). The advantages of DBD plasma are the low operational temperatures which cannot be achieved by catalytic process and without the issue of catalyst degradation.

The most common plasma supported DPF regeneration can be achieved by two different methods, either installing the plasma reactor upstream from the DPF or unifying the plasma reactor with DPF, which is shown in Figures 7.1a and 7.1b respectively. The former arrangement of DPF regeneration has been applied in this study, which for the most part represents the same working principle as the CRT system, replacing the DOC by a DBD plasma reactor.

However, the unified plasma DPF system is more compact, similar to the operating principle of coated DPF. The active oxidant species produced simultaneously incinerate the soot that deposits on the filter at the temperature of 200˚C (Okubo *et al.,* 2003).

The work carried out in this Chapter is separated into two sections; the first part is an extension of the study from Chapter 6 that evaluates the performance of non-thermal plasma in $NO\text{-}NO_2$ oxidation under the actual diesel engine exhaust gas. DPF regeneration is

introduced in the second section to study the effect of NO_2/NO_X ratio obtained under different operating conditions of DBD plasma reactor in filter regeneration.

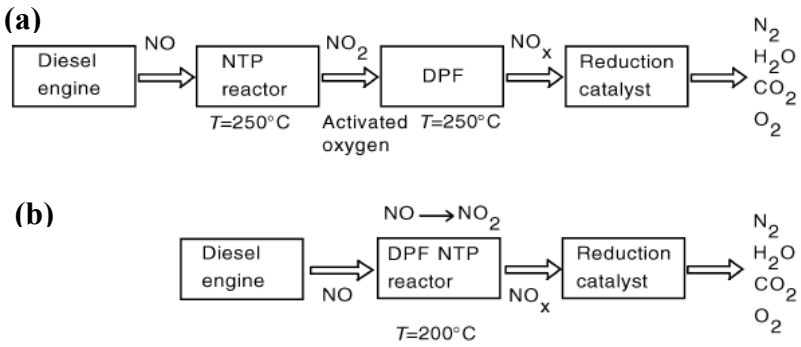


Figure 7.1: Methods of NTP DPF regeneration (Adapted from Okubo *et al.,* 2004).

7.0.1 Test Conditions and Procedure (specific to Chapter 7)

The experimental setup used in this section is illustrated in Figure 7.2, which was similar to that of Chapter 6, in that the same plasma test rig, and analysis systems (electrical and emission) were used, while the bottled gases were replaced by actual diesel exhaust gas. The engine used was described in Chapter 3 and the same DPF arrangement used in Chapter 4 was applied here to study the effect of DBD plasma reactor on DPF regeneration over several engine conditions.

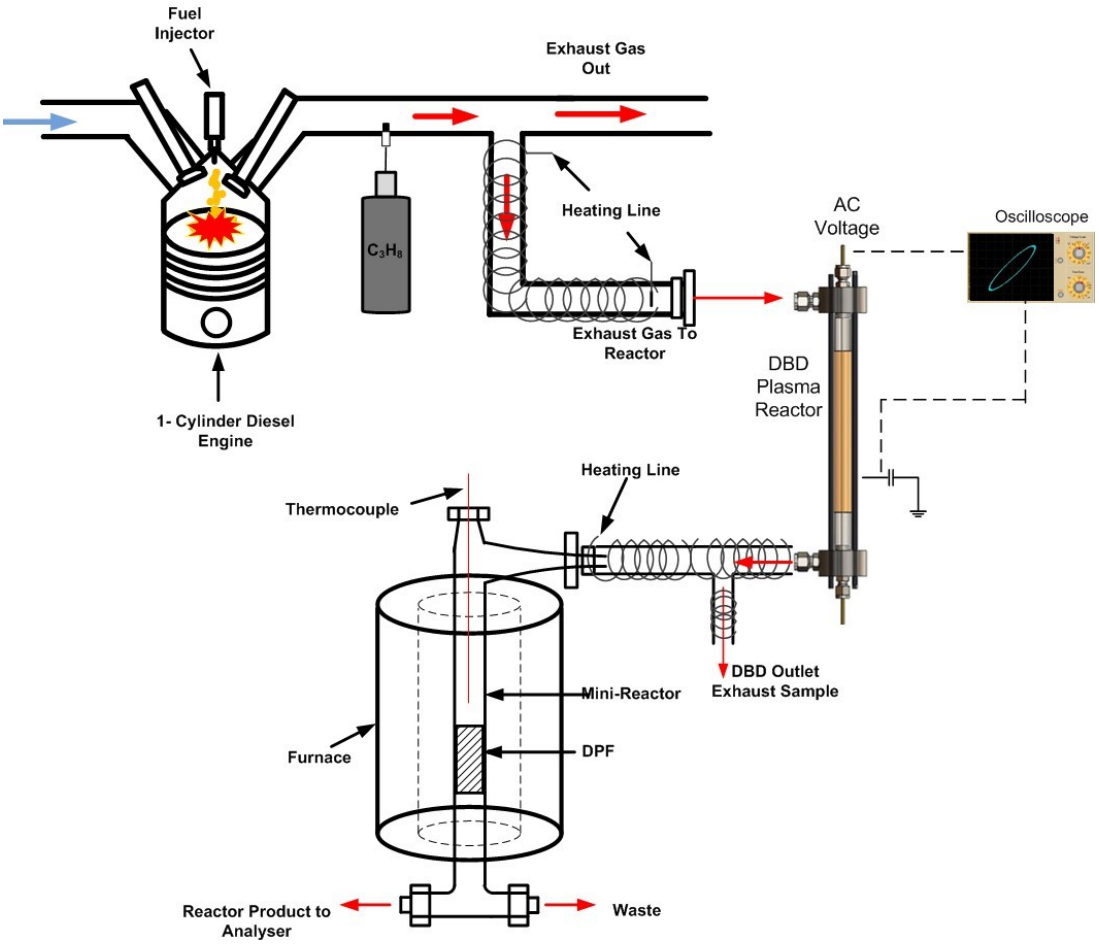


Figure 7.2: The schematic diagram of diesel engine with DBD reactor and DPF system.

Table 7.1: The exhaust gas compositions at 1500rpm engine speed at three different engine conditions.

	Idle	**3bar IMEP (~40%load)**	**5bar IMEP (~70%load)**
O_2 % Vol	18.6	15.55	11.97
CO (ppm)	222	186	137
CO_2 % Vol	1.7	3.76	6.11
NO_X (ppm)	230	560	1020
THC (ppm)	600	350	320
$T_{exhaust}$ (°C)	120	230	350
NO_2/NO_X ratio	0.1	0.1	0.1
Soot (mg/m^3)	2.25	12.53	18.6

7.1 Effects of DBD Plasma Reactor on Different Engine Conditions - Emissions Study

The tests were carried out at the engine speed of 1500rpm for three different engine conditions, idle, 3 and 5 bars IMEP. The exhaust gas composition for each engine condition is shown in Table 7.1, which confirmed that the initial values of NO emissions are within the range of previous studies. The discharge powers of 10, 20, and 30W with four variables of exhaust flow rates 5, 7, 9, 10 l/min were used to feed the DBD reactor to study the effect of specific input power (SIE).

The NO_X emission from diesel exhaust gas contained NO and NO_2. As the NO conversion after the plasma process included NO reduction and NO oxidation process. Therefore the NO_X distribution and the comparison of NO and NO_X conversion were undertaken and illustrated in Figures 7.3 and 7.4 respectively.

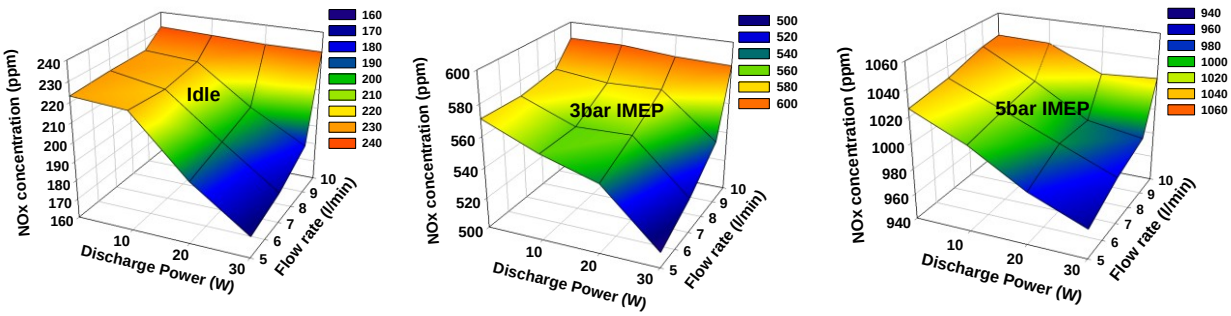


Figure 7.3: NO_X emission for different flow rates and discharge power.

The results show that, the highest NO and NO_X conversion can be achieved by a combination of the highest discharge power (30W > 20W > 10W) and low exhaust gas feeding flow rate (5 l/min >7 l/min > 9 l/min > 10 l/min) to the plasma reactor. This is because under such conditions the reactor is receiving the largest SIE which generates more

energetic electrons to react with the exhaust gas. Similar results have been reported by other researchers (Ravi *et al.,* 2003; Takaki *et al.,* 2004). In brief, NTP demonstrates minimal benefit by directly applying it to the exhaust emission treatment (NO_X or PM reduction), however, it is effective in selective oxidation of NO to NO_2, which is suitable to be used as a pre-oxidiser.

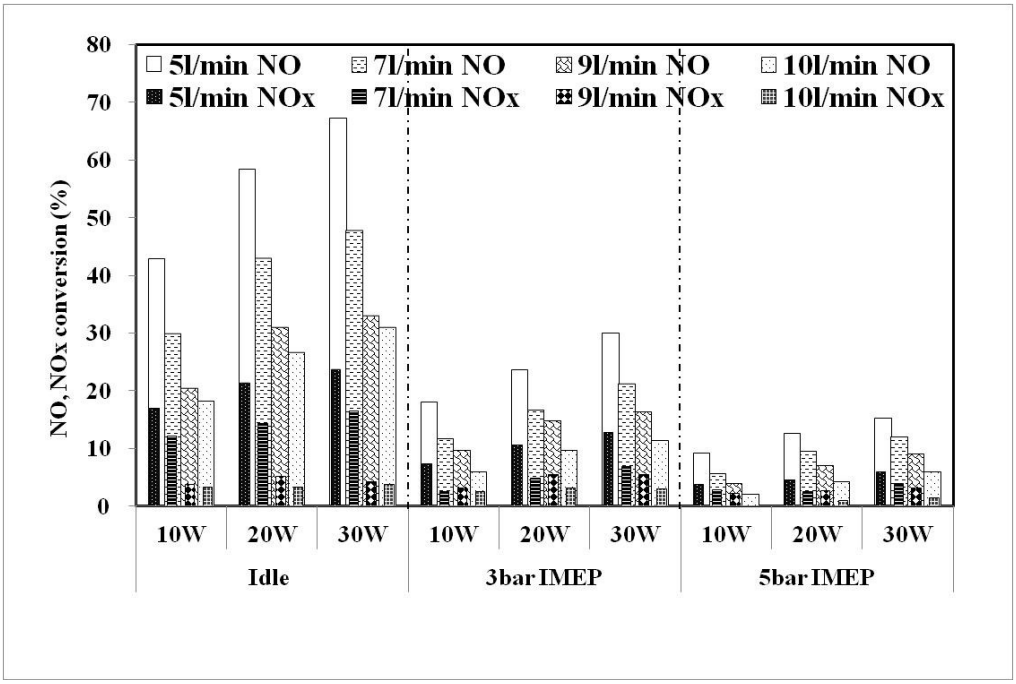


Figure 7.4: NO, NO_X conversion after the DBD plasma reactor.

Secondly, the NO and NO_X conversion were depleted by the increased engine load to 5bar IMEP conditions. Based on the findings from Chapter 6, several reasons can be used to support this observation:

(1) The effect of initial NO emission.

At an idle engine condition, the initial NO in the exhaust gas is relatively low (around 180ppm), compared to 3bar and 5bar IMEP, the NO level is about 530ppm and 980ppm respectively.

(2) The effect of oxygen concentration.

The oxygen content in the exhaust gas is increased in the order of idle > 3bar > 5bar IMEP. As the O_2 concentration increased, O_2 molecules have a higher opportunity to react with electrons for producing oxidative radicals, which is useful for the NO to NO_2 oxidation.

(3) The effect of temperature.

The temperature in the exhaust gas was increased under the high engine load condition. Penentrate *et al.* (1997b) have confirmed that under the high temperature conditions, NO oxidation was diminished. The O radicals consume the NO_2 and convert it back to NO (McLarnon and Penetrante, 1998).

(4) The effect of soot emission.

The soot emission also has a close relation with the engine operating conditions. At the high engine load condition, the soot emission is several magnitudes higher than the low load or idle condition. The heavy mass of the soot has a negative effect on electron collision and decreased the probability of the impact of electrons with the background gas under the same processing volume.

From the comparison of NO_X and NO conversion mentioned above, NO has a higher conversion rate compared to NO_X. It is concluded that, most of the NO was converted into NO_2, instead of reduced to form N_2. Therefore only the energy efficiency of NO conversion is presented, which is shown in Figures 7.5 representing the idle, 3bar and 5bar engine conditions respectively. The symbols in black, green and red represent the discharge power of 10, 20 and 30W, respectively.

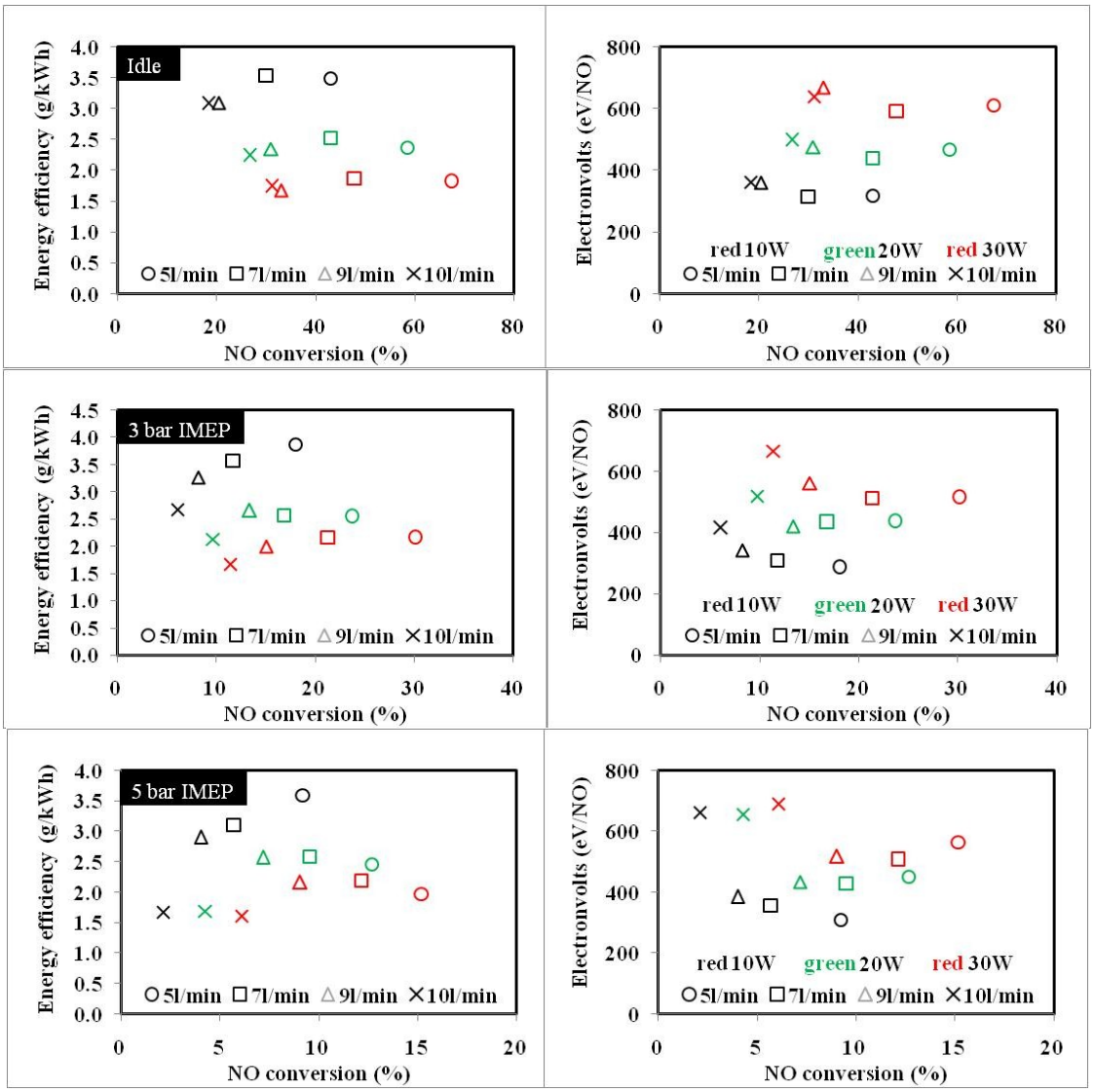


Figure 7.5: Energy efficiency of NO conversion for idle, 3bar IMEP and 5bar IMEP engine conditions.

At the idle engine condition, the energy efficiency of NO conversion obtained is relatively constant, and was not affected by changing the flow rates under a specific discharge power condition. In contrast, for the engine conditions of 3 and 5 bar IMEP, the NO conversion energy efficiency is more sensitive to the variable of flow rate, which is decreased by increasing the flow rates from 5 to 10 l/min. For all the cases, the energy efficiency of NO conversion is depleted over the high discharge power condition.

In summary, the energy efficiency of converted NO into NO_2 is closely related to SIE, and vice-versa to the relation of discharge power and flow rate. The maximum NO conversion efficiency obtained was similar for the SIE of 120J/L, around 3.58g(NO)/kWh, 3.89g(NO)/kWh, and 3.6g(NO)/kWh corresponding to idle, 3 bar and 5bar IMEP engine conditions respectively.

The NO conversion does not maintain a good energy efficiency level when the rate of conversion is increased, which means, further improvements (geometry, power supply, system) are required to increase the feasibility of applications in aftertreatment systems.

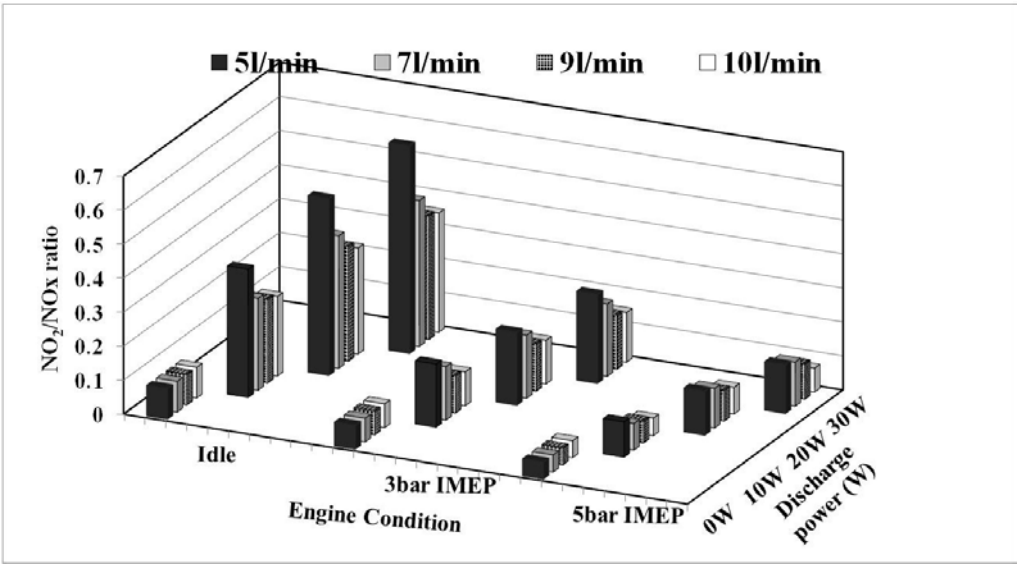


Figure 7.6: NO_2/NO_X ratio of each engine conditions after DBD plasma reactor.

Figure 7.6 shows the NO_2/NO_X ratio before and after the DBD plasma reactor. The NO_2/NO_X ratio coincides with the performance of NO conversion efficiency obtained; the highest NO_2/NO_X ratio of 0.54 was found at idle engine condition under the SIE of 360J/L, which is the largest point of NO conversion achieved. For the 3bar and 5bar IMEP, the trends of NO_2/NO_X ratio are similar, averaging lower than the levels suggested for DPF regeneration (NO_2/NO_X ratio = 0.3 ~ 0.6).

7.2 Effects of DBD Plasma Reactor and Propane Addition at Moderate Load Engine Condition - Emissions Study

In this section, the effect of propane was carried out at the engine speed of 1500rpm, 3 bar IMEP. The propane was added to the exhaust gas before entering the DBD reactor over the molar ratio of C_3H_8/NO_X 0.5, 1.0, and 2.0. Part of the engine exhaust was fed into the DBD reactor under the flow rates of 5, 7, and 10 l/min with the discharge power of 10, 20, and 30W. The NO_X emission and the conversion of NO and NO_X after the DBD reactor are collated in Figures 7.7 and Figure 7.8 respectively.

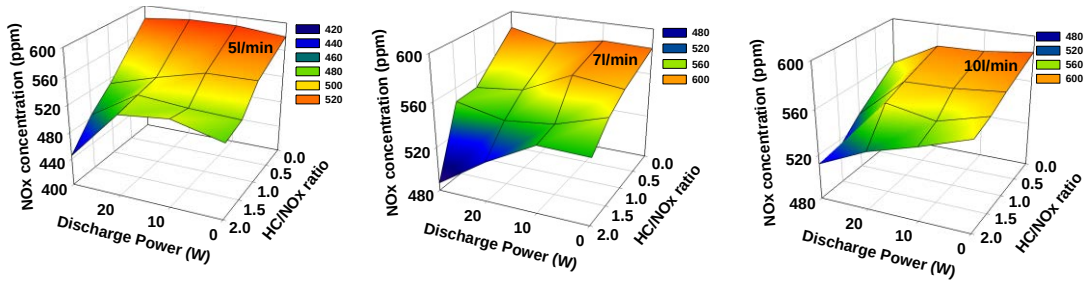


Figure 7.7: Effect of C_3H_8/NO_X ratio (Engine condition: 1500rpm, 3bar IMEP).

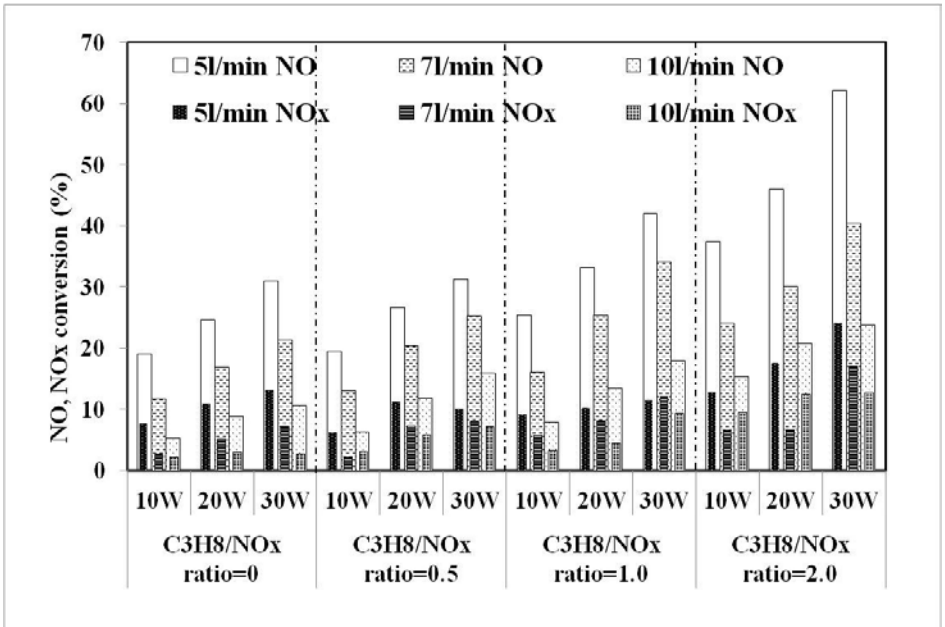


Figure 7.8: NO and NO_X conversion at different molar ratio of C_3H_8/NO_X, at the engine speed of 1500rpm and 3bar IMEP.

Under the low C_3H_8/NO_X ratio, the effect of C_3H_8 on NO_X and NO conversion is not clear, while the contribution was slightly increased at the C_3H_8/NO_X ratio of 0.5. Approximately 65% of NO conversion was found at high C_3H_8/NO_X ratio (2.0) for the 30W discharge power, which is the largest improvement achieved in the present study.

It is apparent that, C_3H_8 addition is more promising in promoting the NO conversion instead of the NO_X conversion. Although the reaction mechanism of C_3H_8 promoted NO to NO_2, oxidation has already been presented in the previous Chapter. The general reactions (7.1-7.3) are discussed herein that can be adopted with any types of hydrocarbons, or possible reactions with the HC that are present in exhaust gas (Mok and Nam, 1998).

$$RO + O_2 \leftrightarrows HCHO + HO_2 \quad (7.1)$$

$$R + O_2 \rightarrow RO_2 \quad (7.2)$$

$$RO_2 + NO \rightarrow CH_3O + NO_2 \quad (7.3)$$

The HC is initially decomposed by free radicals (e.g. O, OH, O_3) generated from the plasma reaction to produce useful radicals such as, alkyl (R), alkoxy (RO) and acyl (RCO) radicals. These species are active oxidation agents which can react with NO to convert them into NO_2. It is notable that, the HO_2 radical from equation (7.1) also represents another important radical operationalised in the NO oxidation process.

The energy efficiency of the NO conversion for the C_3H_8/NO_X ratio of 0.5, 1.0 and 2.0 are presented in Figures 7.9a, 7.9b and 7.9c respectively. The symbols in black, green and red represent the discharge power of 10, 20 and 30W respectively.

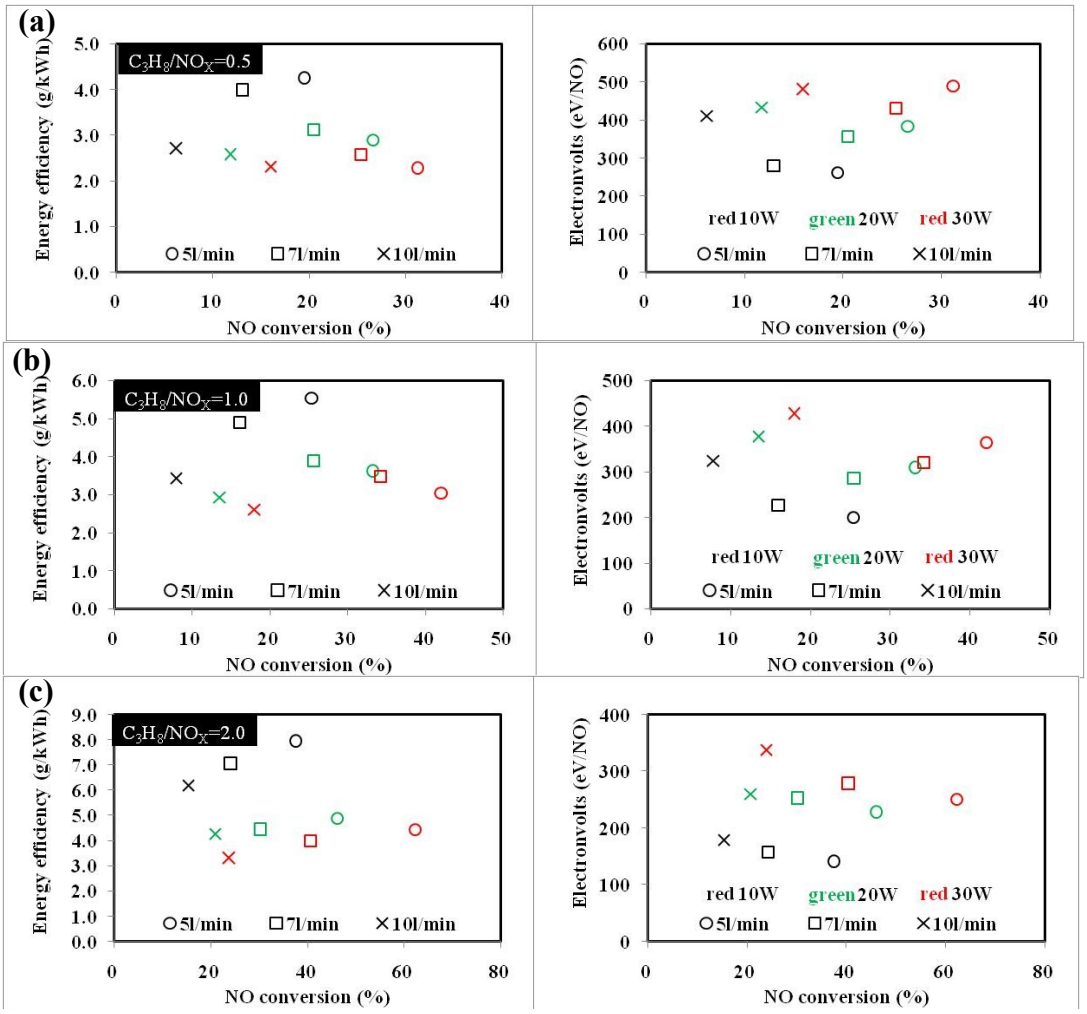


Figure 7.9: Energy efficiency of NO conversion for (a) 0.5, (b) 1.0 and (c) 2.0 of C_3H_8/NO_X ratios.

In general, the average energy efficiency of NO conversion by C_3H_8 addition is increased, especially for the condition of C_3H_8/NO_X ratio = 2.0; the highest energy efficiency reached double the level of the initial value (without the addition of C_3H_8), about 8.0g/kWh, corresponding to 140eV/NO. The result obtained illustrates that this plasma system not only works well for the synthetic gas studied, but is also suitable for the actual exhaust gas treatment under reasonable energy conditions. This is confirmed with a comparison to the work carried out by the research group of Mohapatro (2010), that studied the NO_X treatment on a cross flow reactor (which is built up by nine tubular reactors connected in parallel).

206eV is required for converting one NO molecule under the idle engine with a filter exhaust gas condition.

However, further energy improvements have been made by the support of catalyst under the DBD plasma reactor that is referred to as the cascaded plasma-alumina adsorbent process (Mohapatro and Rajanikanth, 2010), in which the energy requirement is only 27eV/NO that corresponds to the NO conversion efficiency of 89%. From this point of view, DBD plasma reactor can work within more energy saving conditions under the plasma-catalyst system.

7.3 Plasma DPF Regeneration

It is apparent that under the plasma condition the NO_2/NO_X ratios are increased with an intensification of C_3H_8/NO_X ratios (Figure 7.10). This is due to the high level of NO that was oxidised into NO_2 under the effect of C_3H_8.

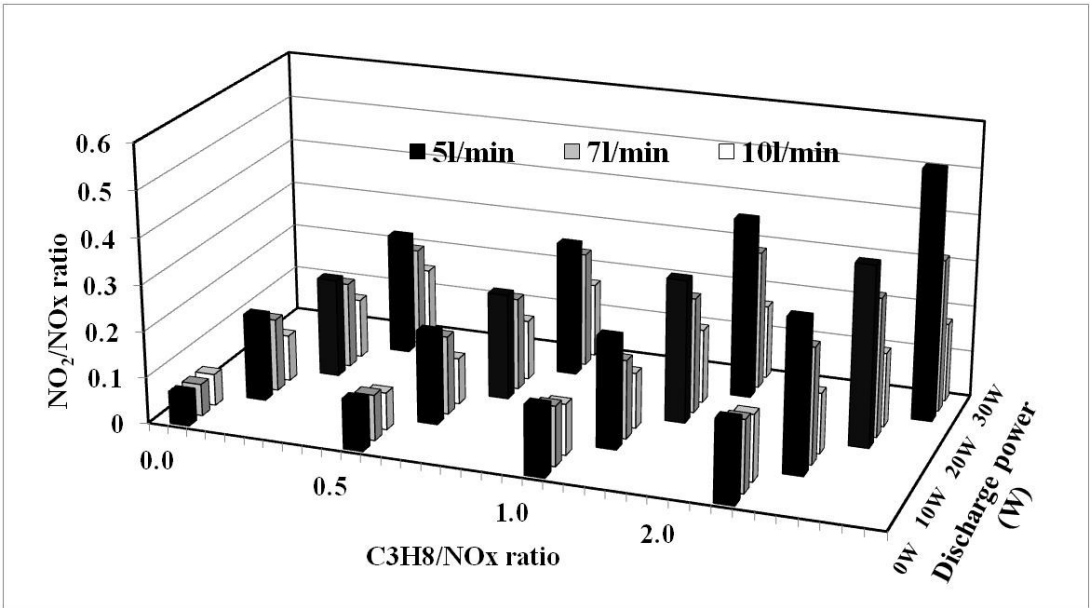


Figure 7.10: NO_2/NO ratios of different C_3H_8/NO_X ratios before and after DBD plasma reactor at the engine speed of 1500rpm 3bar IMEP.

DPF loading was investigated using a) raw engine exhaust gas (serving as a baseline filter loading profile), b) DBD plasma reactor, and c) DBD plasma reactor with C_3H_8 addition (C_3H_8/NO_X ratio = 1.0). The plasma reactor was operated at the flow rate of 5l/min and 30W of discharge power (SIE = 360J/L). Based on the information and discussion of DPF regeneration at the suitable range of NO_2/NO_X in Chapter 4, the plasma working at the condition of C_3H_8/NO_X ratio = 1.0 was selected, having a NO_2/NO_X ratio of 0.39, instead of the condition in which the largest ratio of NO_2/NO_X (0.54) was recorded at the C_3H_8/NO_X ratio = 2.0.

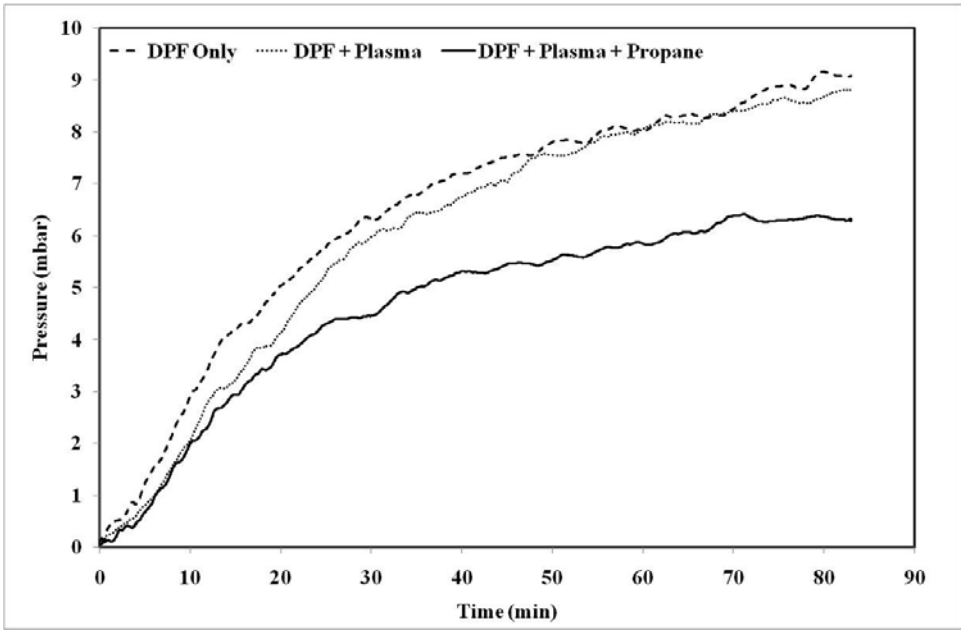


Figure 7.11: Pressure drop across the DPF.

The results of DPF regeneration are shown in Figure 7.11. The soot loading profiles are similar for the base line and plasma only tests as can be seen by the pressure drop profiles over the DPF. The use of plasma with C_3H_8 addition promotes the soot oxidation in the DPF due to increased NO_2 and O_3 availability.

This allows the soot oxidation process at the lower temperature conditions compared to the conventional methods (DOC, burner) used. The plasma chemical reactions with soot are shown in the following:

$$C + 2NO_2 \rightarrow CO_2 + 2NO \quad (7.4)$$

$$C + NO_2 \rightarrow CO + NO \quad (7.5)$$

$$C + 2O_3 \rightarrow CO_2 + 2O_2 \quad (7.6)$$

$$C + O_3 \rightarrow CO + O_2 \quad (7.7)$$

Therefore it is believed that, for the regeneration process of the plasma only test (NO_2/NO_X ratio = 0.26), the initial pressure drop is due to the effect of O_3 and minimal contribution of NO_2. The pressure across the DPF increases quickly, as the soot accumulation process is faster than the soot oxidation process under the limited number of NO_2 present in the system. In the case of plasma with the C_3H_8 addition (NO_2/NO_X ratio = 0.39), more NO_2 can be supplied to oxidise the soot that accumulates within the filter.

7.4 Conclusion

Actual diesel exhaust gas was used to study the performance of DBD plasma reactor on the NO-NO_2 oxidation and DPF regeneration process.

Compared to the preliminary study on synthetic mixtures, the NO-NO_2 oxidation process presented here is slightly low. This is due to the complex compositions that exist in

the actual exhaust gas and the hot exhaust temperature that is not favorable for the NO oxidation process. However, the propane addition successfully overcome the low NO-NO_2 conversion activity at higher exhaust temperatures; and increase the NO_2/NO_X to higher ratio which is adaptable in DPF regeneration process.

The advantages of low exhaust gas treatment and similarity NO-NO_2 oxidation performance as commercialize DOC, demonstrated that non-thermal plasma can be potential alternative devices applied in DPF regeneration. The initial assessment of this device has proved to be successful over different engine conditions. For future practical application, other important parameters such as cost effectiveness, durability and safety have to be taking into account.

CHAPTER 8

CONCLUSION

An improved NO-NO_2 oxidation process can contribute to fulfilling the future emission standards in diesel engines for both NO_X and PM. However, this process is kinetically limited at low temperatures and thermodynamically limited at high temperatures, restricting the downstream aftertreatment (e.g. SCR, DPF) performance which relies on NO_2.

The main focus for the investigation in this thesis has been on enhancing the NO_2/NO_X ratio in the diesel exhaust at a wider temperature window through several possible oxidation methods which can potentially be applied on-board the vehicles. These methods include processes that apply to the in-cylinder combustion and engine exhaust gas treatment.

The NO_2 produced in the engine cylinder or in the exhaust can then be facilitated in the low temperature DPF regeneration. The following summaries the conclusions drawn from the main findings of this thesis and proposes some suggestions for future research in this field.

8.1 Concluding Remarks

8.1.1 In-Cylinder NO-NO_2 Oxidation Method

The study of the in-cylinder NO-NO_2 oxidation was carried out by using H_2 and reformate as REGR (e.g. gas that contains H_2, CO, and EGR) as a supplement to diesel fuel.

The results suggested that, the application of EGR contributed to the NO_X reduction, and aided the consumption of the NO_2 emissions at high engine load conditions. This is because the EGR addition reduced the global in-cylinder air/fuel ratio (λ) and increased the

fuel concentration influence of the in-cylinder temperate and combustion efficiencies leading to an inhibition of NO oxidation to NO_2.

Conversely, the application of REGR with H_2 and CO in the combustion chamber was found to improve the combustion process reducing the formation of C-containing species. It therefore, not only suppressed the total NO_X concentration but also raised the NO_2 proportion in the engine exhaust. The REGR used also allowed some of the un-combusted H_2 to enhance the HC-SCR process in reducing NO_X and to further promote NO_2 production.

8.1.2 Exhaust Gas NO-NO_2 Oxidation Methods

8.1.2.1 Thermal Oxidation

A thermal reactor was designed to help and support the knowledge of thermal oxidation of the NO-NO_2 oxidation process under actual diesel exhaust gas condition.

Under untreated exhaust gas conditions (without additives or catalysts), the NO oxidation process is limited to a narrow temperature window. The NO_2 concentration of about 40ppm started to increase from 600˚C and reached the peak value of approximately 70ppm at 700˚C. The NO_2 later declined to the initial value when the temperature was further increased to 900˚C.

Under the condition of propane addition, the thermal oxidation process had a double benefit. The NO_2 level for each temperature is increased and the NO_2 production peak (approximately 180ppm) is shifted towards lower temperatures (550˚C). Although, the results shows that thermal oxidation under propane addition promotes NO-NO_2 oxidation, the temperature for NO_2 production peak occurred at a point higher than the range of typical exhaust temperatures.

Therefore, the advantages of this oxidation method are only present when applied in conjunction with DPF regeneration to achieve the accumulative effect of soot oxidation with both oxidant (O_2 and NO_2) under high temperature conditions. This provides the lowest pressure drop (highest regeneration efficiency) across the DPF when the thermal reactor is operated at 500˚C with 1.5 the C_3H_8/NO_X ratio = 1.5; compared to other regeneration processes that rely on one oxidant.

8.1.2.2 Catalytic Oxidation

DOC

An industry prototype DOC was used to study the catalyst effect on NO-NO_2 oxidation process. This provided a reference to access the level of NO_2 produced and the final NO_2/NO_X obtained by the other oxidation methods applied.

The DOC allows the NO oxidation to start at a relatively low temperature condition. The NO_2 level starts to increase just after CO reached the maximum point of its conversion (90%) at about 200˚C. The NO_2 concentration reached the highest level (around 125ppm, doubling the initial NO_2 concentration) when the DOC temperature was increased up to 370˚C.

A small pressure drop across the DPF was observed at the regeneration temperature of 350˚C when the DOC (NO_2/NO_X=0.3) was installed upstream from the DPF.

HC-SCR

The performance (reduction of NO_X) of silver-alumina (Ag/Al_2O_3) HC-SCR only exists when operated with additives (e.g. HC, H_2). Due to the remaining H_2 in the exhaust gas after the combustion of REGR, the HC-SCR was applied together with REGR combustion to study the NO-NO_2 oxidation process in the actual exhaust gas. The presence of H_2 in the exhaust

helps with the catalyst activity for NO_X reduction, whereas the NO_2 availability supports the soot oxidation over the DPF. As a whole, the system (REGR + HC-SCR + DPF) is able to simultaneously improve both NO_X and reduce PM emissions.

8.1.2.3 Advanced Oxidation (NTP)

DBD non-thermal plasma systems were designed to study the effect of NTP on the NO-NO_2 oxidation process over the actual diesel exhaust gas condition.

A preliminary test was carried out using three different synthetic gas mixtures to investigate the NO to NO_2 oxidation. In the mixture of N_2/NO, the main reaction found was the chemical reduction of NO into N_2 by the $N(^4S)$ species. In the mixture of N_2/NO/O_2, the effectiveness of the emitted N-atom or O-atom from the reactor provides different roles in the NO_X conversion process (e.g. NO oxidation/ NO reduction). In the mixture of N_2/NO/O_2/C_3H_8, the positive effect of C_3H_8 on NO oxidation was stronger than the presence of O_2 and had a better energy efficiency of NO conversion.

Under actual diesel exhaust gas conditions, the overall performance of DBD plasma reactor on the NO-NO_2 oxidation was decreased. This is due to the complex compositions that existed in the actual exhaust gas and the hot exhaust temperature that was not favourable for the NO oxidation process. This trend of reduced NO_2/NO_X ratio was also observed when the engine load was increased from idle to 3bar and 5bar IMEP under the constant SIE of plasma as a results of the increased exhaust gas temperatures and a greater density of combustion by-products.

In the low exhaust temperature (250˚C) of the DPF regeneration study, the plasma-alone regeneration process is not beneficial. This is due to an insufficient NO_2 level (NO_2/NO_X

ratio=0.26) produced from this plasma system and as a result soot the accumulation rate is higher than the soot oxidation. Conversely, when 'plasma + propane' was used the higher amount of NO_2 (NO_2/NO_X ratio=0.39) is facilitated in the soot oxidation process, this allows the DPF to continuously regenerate at low temperatures.

8.2 General Closing Remark

The use of DPF is currently the most promising solution for PM emission reduction from diesel engines. Modern diesel engines operate at low temperatures leading to DPFs systems malfunctioning. Furthermore diesel engine exhaust gas temperatures are expected to be further reduced, a trends that is expected to make DPF regeneration even more challenging. Therefore, several technologies have been proposed in order to reduce soot oxidation temperatures. For example, NO_2 oxidises the accumulated soot on the DPF at low temperature conditions.

In this study, several possible methods have been proposed and studied that can be used to promote the NO-NO_2 oxidation in the engine exhaust gas. These NO-NO_2 oxidation processes are operated at the exhaust gas temperature which ranges from room temperature to the maximum temperature of 900°C over different oxidation methods; this provides the information for designing the DPF regeneration at different engine operating conditions.

Further, the advantages of facilitated hydrogen in the aftertreatment systems have also been examined. The present study has confirmed the effect of hydrogen that significantly promotes the HC-SCR performance, and allowed the system simultaneously to remove the NO_X and PM with an increased NO_2/NO_X ratio. Alternatively, NTPs constitute a further method for low temperature DPF regeneration implications, in which it is considered as one

of the most promising solutions for cold start emission treatment, which is still difficult to achieve by catalyst technologies (due to the problem of catalyst light-off temperature).

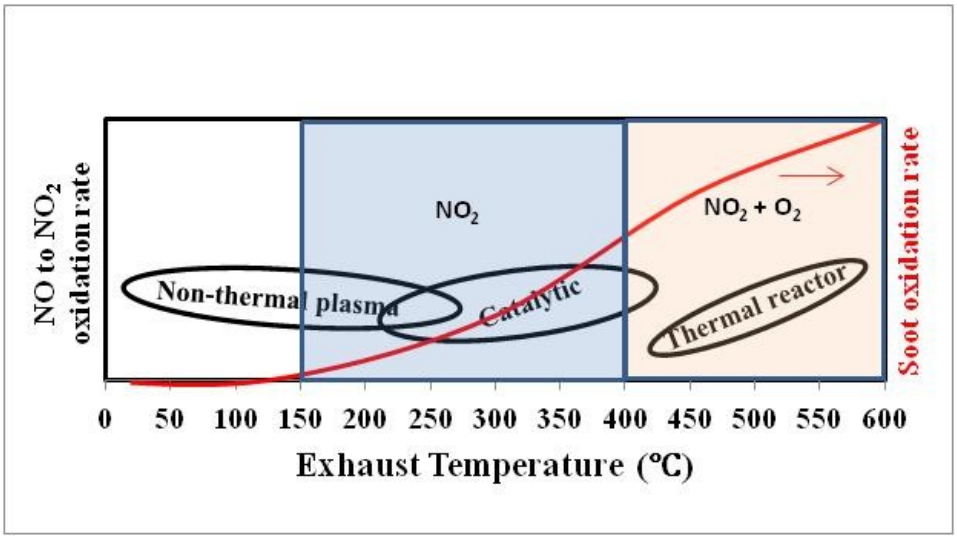


Figure 8.1: Pre-oxidiser methods on NO-NO_2 oxidation and the contribution of oxidation agents in DPF regeneration process.

In general, based on the results found in this thesis, Figure 8.1 summarises the effect of pre-oxidiser methods on NO-NO_2 oxidation and the contribution of oxidation agents in DPF regeneration process. This provides the information for designing the DPF regeneration at different exhaust temperature conditions which listed in following:

- At low exhaust temperatures, the NO-NO_2 oxidation was initially activated by non-thermal plasma and the soot oxidation slowly starts at 150˚C. This system successfully provides the solution for cold start emission treatment.

- At moderate exhaust temperatures, the catalytic NO-NO_2 oxidation activity is located at typical diesel exhaust operating temperatures. The NO_2 produced from the catalyst was continuously supplied to regenerate the soot accumulated on the DPF. This system required exhaust gas reached the catalyst light-off temperature to obtain the highest performance of DPF regeneration.

- At high exhaust temperatures, the thermal oxidation method accumulates the benefit of both oxidisers (NO_2 and O_2 oxidation agent). Therefore soot was more effectively removed from the DPF compare to the former conditions. This system successfully reduces the soot loading in the DPF and represents the alternative to traditional active regeneration. It is suggested that this approach minimizes the thermal stress over the DPF as well as the fuel penalty associated to traditional DPF active regeneration.

8.3 Future Work

I. The thermal oxidation process shows a good increment of NO_2/NO_X under the effect of C_3H_8, and is associated with a high efficiency of DPF regeneration. Therefore, it is suggested to test different types of HCs in order to investigate $NO\text{-}NO_2$ oxidation at even lower temperatures.

II. The REGR + HC-SCR + DPF established a potential solution for NO_X and PM emissions. It is suggested that integrating the present system with DOC will achieve a potential '4-way catalyst' performances. This system allows the removal of NO_X, PM, CO and HC from the diesel emissions which, it is believed will provide the most promising aftertreatment device in the future.

III. The application of NTPs in exhaust gas treatment has several advantages which cannot be achieved by conventional treatment methods; it is believed that these technologies will represent the next alternative aftertreatment device model to meet the forthcoming emission regulations. Therefore the future study should focus on the following experimental research:

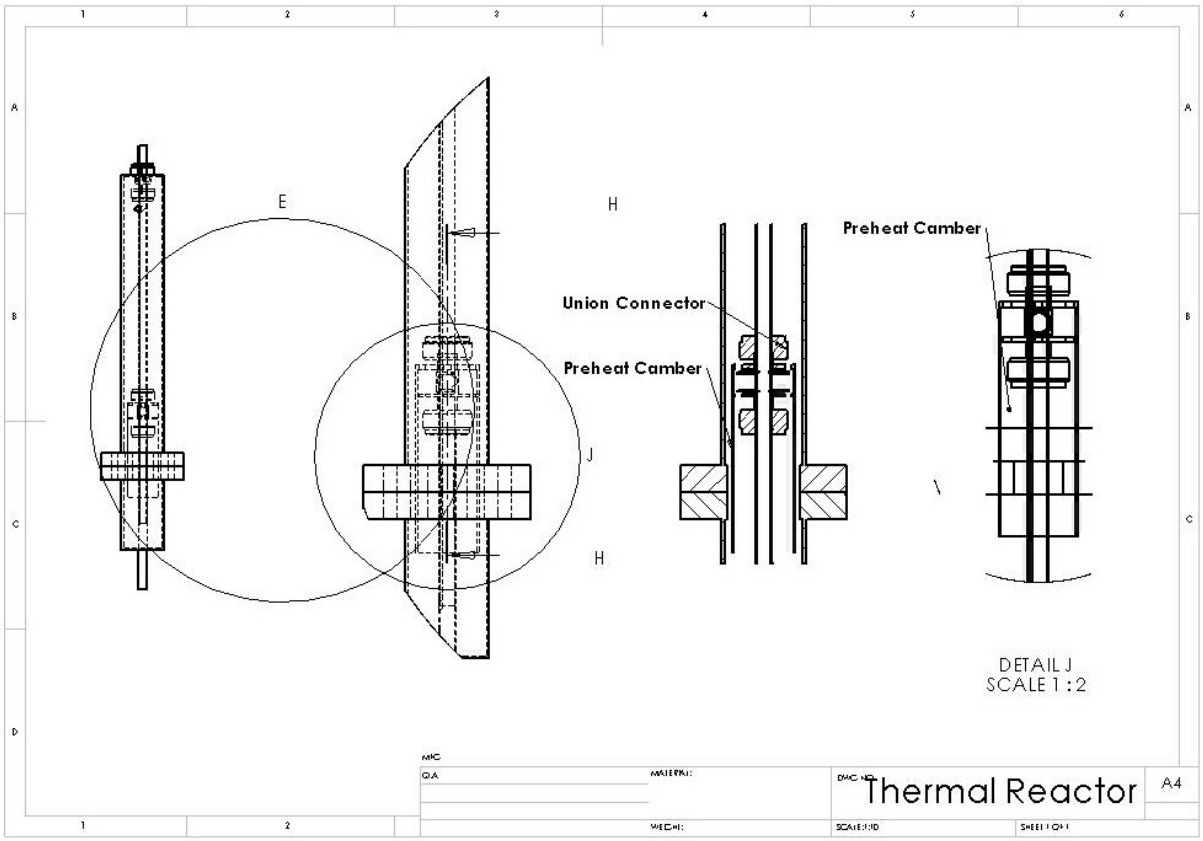
- Comparing the capacitance value of filtered and non filtered exhaust gas, to

understand the effect of soot on electrical discharge behaviors; this can be done by studying the Lissajous Diagram.

- Improving the energy efficiency of NO-NO_2 oxidation by examining different HC additives, and through the modification of electrode designs.
- Designing a new reactor which can unify the plasma and DPF to study the new 'Plasma + DPF' integral system and demonstrate successful DPF regeneration at 200˚C.

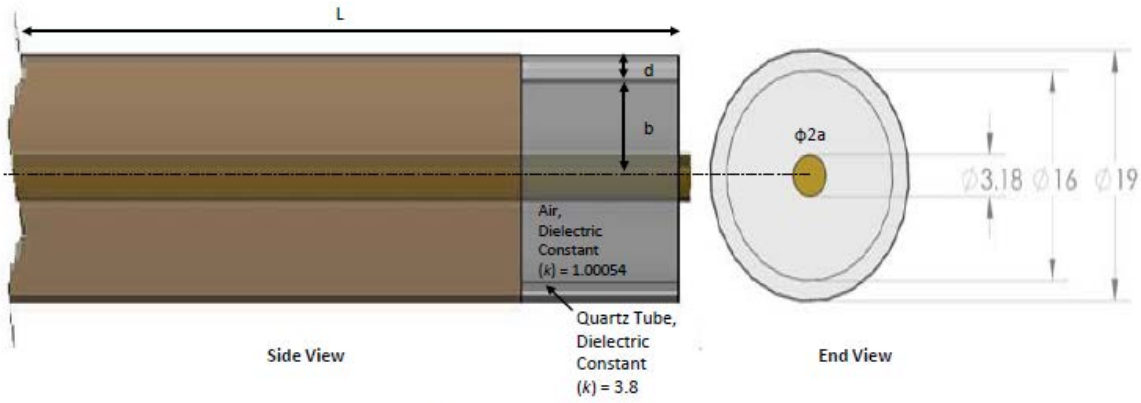
APPENDIX A

THERMAL REACTOR DRAWING



APPENDIX B

ELECTRIC FIELD CALCULATION



$$E = \frac{V_{pk-pk}}{d \ln\frac{d+b}{d}}\left(\frac{C_d}{C_d + C_a}\right)\sin(\omega t)$$

$$C_a = \frac{2\pi\varepsilon_0 L}{\ln\left(\frac{b}{a}\right)}$$

$$C_d = \frac{2\pi\varepsilon_0 L(b+d)}{\frac{(b-a)}{k_a} + \frac{d}{k_d}}$$

E	Electric field (kV/cm)
V_{pk-pk}	Applied voltage peak to peak (kV)
d	Discharge gap (cm)
b	Radius of dielectric (cm)
C_a	Capacitance of discharge zone (μF)
C_d	Capacitance of dielectric (μF)
a	Radius of inner electrode (cm)
L	Discharge length (cm)
k_a	Relative permittivities of air
k_d	Relative permittivities of dielectric
ε_0	Permittivities of vacuum (F/m)

APPENDIX C

LIST OF AUTHOR'S REFEREED CONFERENCE, JOURNAL PUBLICATIONS, PATENTS AND AWARDS

E.1 Journal papers Published/Accepted for Publication

1. ***J.J. Chong***, A. Tsolakis, S.S. Gill, K. Theinnoi, S.E. Golunski. Enhancing the NO_2/NO_X ratio in Compression Ignition Engines by Hydrogen and Reformate Combustion, for Improved Aftertreatment Performance. **Journal of Hydrogen**, 35 (2010) 8723 – 8732.

2. ***J.J. Chong***, A. Tsolakis, J.M. Herreros. The effect of diesel oxidation catalyst (DOC) and thermal oxidation for enhancing the NO_2/NO_X ratio in diesel engine exhaust gas. **Applied Thermal Engineering** (2012). (Manuscript submitted)

3. ***J.J. Chong***, A. Tsolakis, J.M. Herreros, W.C. Chang. Non-thermal plasma enhancing NO_2/NO_X ratio in the diesel engine for regenerate the particulate filter at low temperature. (In preparation)

E.2 Conference Papers Published/ Accepted for Publication

1. ***J.J. Chong***, A. Tsolakis, W.C. Chang. The review of on-board hydrogen production and CO purification for transportation fuel cells. B1301 (June 28 - July 1, 2011 – Lucerne, Switzerland) **European Fuel Cell Forum** 2011.

2. ***J.J. Chong***, A. Tsolakis, W.C. Chang, J.M. Herreros. On-board hydrogen storage and fuel reforming processes for transportation fuel cell. (March 30, 2011 – NEC, Birmingham UK) **7th Annual International Conference Partnering & Exhibition**.

3. W.C. Chang, ***J.J. Chong***, Y. C. Li, H. S. Su. A tri-metal catalyst made for the unitized regenerative fuel cell. March 30, 2011 – NEC, Birmingham UK) **7th Annual International Conference Partnering & Exhibition**.

E.3 Patents Application

1. ***Jun Jie Chong***, "Dual Plasma Devices for Onboard Hydrogen Production and Exhaust Gas Emissions Control" **UK Patent application 2011**, submitted.

2. ***Jun Jie Chong***, "Plasma Flow Channel for PEM-Fuel Cell" **UK Patent application 2012**, submitted.

E.4 Awards

1. Finalist in the 'Competitions and Exhibitions' at House of Commons – UK Parliament by **SET for BRITAIN** (2011)

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