

# The role of Non-Thermal Plasma Technique in NO<sub>x</sub> treatment: A

## Review

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**Abstract:** Non-thermal plasma (NTP) has been introduced over the past several years as a promising method for nitrogen oxide (NO<sub>x</sub>) removal. The intent when using NTP is to selectively transfer the input electrical energy to the electrons, and to not expend this in heating the entire gas stream, which generates free radicals through collisions, and promotes the desired chemical changes in the exhaust gases. The generated active species react with the pollutant molecules and decompose them. This paper reviews and summarizes relevant literature regarding various aspects of the application of NTP technology on NO<sub>x</sub> removal from exhaust gases. A comprehensive description of available scientific literature on NO<sub>x</sub> removal using NTP technology is presented, including various types of NTP, e.g. dielectric barrier discharge, corona discharge and electron beam. Furthermore, the combination of NTP with catalyst and adsorbent

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for better NO<sub>x</sub> removal efficiency is presented in details. The removal of NO<sub>x</sub> from both simulated gases and real diesel engines is also considered in this review paper. As NTP is a new technique and it is not yet commercialized, there is a need for more studies to be performed in this field.

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

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## 1. Introduction

There is a continuous increase in the number of diesel engines in both stationary and mobile applications, due to their lower operating cost, higher thermal efficiency, longer durability, and their lower hydrocarbon (HC) and carbon monoxide (CO) emissions [1]. Besides HC and CO emissions, they emit 2–20 times more NO<sub>x</sub> and approximately 30-100 times higher particulate matters (PM) than gasoline engines. Moreover, conventional energy sources are close to extinction, and environmental concerns necessitate cleaner fuels being used. Indeed, exhaust emission regulations have become much more stringent in recent times. Alongside these increasingly stringent emissions standards, there is still considerable concern that unregulated pollutants are having a deleterious effect on human health and the environment generally [2-7]. Given the likely health effects associated with gaseous pollutants and ultrafine particles, there is a clear need to monitor the emissions of diesel engines.

Up until now, several technologies have been applied for NO<sub>x</sub> removal from exhaust gases. Selective catalyst reduction (SCR), active lean NO<sub>x</sub> catalysts, lean NO<sub>x</sub> trap catalysis and multiple injection combustion have been considered for NO<sub>x</sub> removal in automobile and stationary engines [8-10]. SCR is used to convert NO<sub>x</sub> into diatomic nitrogen (N<sub>2</sub>), and water (H<sub>2</sub>O) with the aid of a catalyst i.e. a gaseous reductant such as anhydrous ammonia, aqueous ammonia or urea [11, 12]. Zeolite catalysts will be also the mainstay for Japan, US, and Euro VI applications [13]. The advantage of using SCR is that the major byproducts of SCR are harmless nitrogen and water vapour. However, SCR catalysts need high temperatures (around 300°C) for activation. There are some problems in using SCR catalysts, such as the possibility of ammonia leakage, catalyst poisoning, catalyst discharge under the high

temperature conditions or through the influence of sulphur, and the need for the construction of urea solution stations [14, 15]. In addition, diesel exhaust is a highly oxidising environment, and the SCR catalysts used on gasoline engines are not suitable for NO<sub>x</sub> removal in diesel applications [16].

The NTP technique will be considered for emission reduction in diesel engines fuelled by diesel or biodiesel. NTP treatment of exhaust gas is a promising technology for NO<sub>x</sub> removal, which is effective through the introduction of plasma inside the exhaust gases. Plasma is the fourth state of matter consisting of positive and negative charges which have a tendency to remain electrically neutral overall, and over large length scales. It is composed of free electrons, ions, radicals, atoms, and molecules in various states of excitation [17]. Vehicle exhaust gases, both diesel and gasoline, undergo chemical changes when exposed to plasma. Logically, oxidation processes dominate in the presence of oxygen. These reactions include oxidation of hydrocarbons, carbon monoxide, and nitrogen oxides [18].

This review paper provides an overview of the literature concerning NO<sub>x</sub> removal from exhaust gases as conducted by various groups of researchers. The first part of this review is about diesel engine emissions. The second section contains an overview of pulse power technology and its application on plasma treatment of exhaust gases. The final section provides a summary of findings as to how plasma can be effective for NO<sub>x</sub> removal from simulated gases and diesel engines, whilst highlighting the significance of exploring various views concerning plasma emission treatment as held by a number of researchers. The main argument presented in this section suggests that there is a strong correlation between mechanical, chemical and electrical parameters involved in plasma production and exhaust gas treatment, which will



ultimately result in the improvement of diesel engine emission treatment. This review paper seeks to bring together in a systematic way the disparate material on NO<sub>x</sub> removal from exhaust gases.

## **2. Diesel engine emissions**

Diesel engines are used as the power source in a wide variety of industries and their applications are growing rapidly all over the world. Diesel engines have been employed in transportation as the power source for buses, trucks, trains and ships. Moreover, they are used in power plants for power generation, and also in farming, construction and industrial settings. In spite of the large number of diesel engine applications, they continue to produce significant amounts of pollution, particularly NO<sub>x</sub>. Therefore, their increasing numbers in transportation vehicles will cause an increase in global emissions, with nitrogen oxides being the main pollutant from diesel exhaust.

Inside an engine, the complete combustion of the fuels composed exclusively of carbon and hydrogen, would only generate CO<sub>2</sub> and H<sub>2</sub>O, to the exclusion of any other harmful products. However, the very short time is enough for the chemical oxidation processes in combustion chambers, the lack of homogeneity in the carbureted mixtures, and the heterogeneity and rapid variations in the temperature do not allow for the ideal state of thermodynamic equilibrium to be reached [19]. Thus, the incomplete combustion of hydrocarbons results in the formation of a wide range of organic and inorganic compounds distributed among the gaseous, semi-volatile and particulate phases [20] as is schematized in Table 1 [21].

**Table 1**

Typical diesel exhaust composition [21].

	Component	Concentration
Components naturally occurring in air	N <sub>2</sub>	70-75 vol%
	O <sub>2</sub>	5-15 vol%
	CO <sub>2</sub>	2-12 vol%
	H <sub>2</sub> O	2-10 vol%
Regulated harmful components	CO	100-10000 ppm
	HC	50-500 ppm, C1
	NO <sub>x</sub>	30-600 ppm
	SO <sub>x</sub>	Proportional to fuel S content
	PM	20-200mg/m <sup>3</sup>
Unregulated harmful components	Ammonia	2.0 mg/mile
	Cyanides	1.0 mg/mile
	Benzene	6.0 mg/mile
	Toluene	2.0 mg/mile
	PAH	0.3 mg/mile
	Aldehydes	0.0 mg/mile

Diesel exhaust differs from gasoline engine exhaust in two major ways. Firstly, diesel exhaust contains a far higher amount of NO<sub>x</sub>. Secondly, the exhaust is far leaner, that is, it contains far less unburned hydrocarbon and carbon monoxide than a typical exhaust from gasoline engines. Thus, nowadays, the focus of the research on reduction of harmful emissions is mainly focused up on NO<sub>x</sub> [22].

### 3. Health and environmental impacts of NO<sub>x</sub> and emission legislations

Several types of nitrogen oxides exist in the environment: N<sub>2</sub>O, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub>. The abbreviation NO<sub>x</sub> usually relates to nitric oxide (nitrogen monoxide) NO and

nitrogen dioxide  $\text{NO}_2$ , which can be called 'fresh' nitrogen oxides from a photochemical point of view since they reach atmosphere in these forms. Another important nitrogen oxide is  $\text{N}_2\text{O}$  (Nitrous oxide), and it may also be called 'fresh' for the same reasons [15]. Nitrogen oxides form when fuel is burned at high temperatures, as in a combustion process. The primary sources of  $\text{NO}_x$  are motor vehicles (49%), electric utilities (27%), industrial, commercial, and residential sources (19%) and all other sources (5%) that burn fuels [23].

Among the various types of  $\text{NO}_x$ , nitric oxide and nitrogen dioxide are considered toxic. Around 95% of  $\text{NO}_x$  emitted from incineration processes is  $\text{NO}$  and 5%  $\text{NO}_2$  [24]. Nitric oxide is less toxic than nitrogen dioxide. However, as with most radicals,  $\text{NO}$  is unstable and reacts readily with oxygen through photochemical oxidation to form  $\text{NO}_2$  [15].

Studies focused on risk assessment have showed that high outdoor  $\text{NO}_2$  concentrations observed in residential areas contribute to increased respiratory and cardiovascular diseases and mortality [25]. Some of the other negative effects of  $\text{NO}_x$  are acid rain, ground-level ozone (smog), photochemical smog, global warming, nose and eye irritation, visibility impairment, the formation of toxic products and water quality deterioration [26].

$\text{NO}_x$  is responsible for tropospheric ozone/particulate (urban smog) through photochemical reactions with hydrocarbon [27]. The mixture of  $\text{NO}_x$  and volatile organic compounds (VOC) in the atmosphere when exposed to sunlight can result in the formation of photochemical smog which can cause the infection and encourage the spread of cancer. The yellowish colour of  $\text{NO}_2$  decreases the visibility, contributes to heart and lung problems and can suppress plant growth.  $\text{NO}_2$  can also react with radicals produced from VOCs in a series of reactions to form toxic products such as peroxyacetyl nitrates (PAN) [27, 28].

NO and NO<sub>2</sub> together with sulphur dioxide (SO<sub>2</sub>) are the major contributors to acid rains [27]. When NO<sub>x</sub> and SO<sub>2</sub> exposed to the atmosphere, they react with water to form sulphuric acid and nitric acid which are the main components of acid deposition. Indeed, NO<sub>2</sub> reacts with OH in the atmosphere to form nitric acid (HNO<sub>3</sub>). Nitric acid can also form when nitrogen dioxide (NO<sub>2</sub>) reacts with the nitrate radical (NO<sub>3</sub>) in the presence of atmospheric water or aldehydes. Nitrogen oxides account for approximately 30% of all acid deposition [29]. Nitrous oxide (N<sub>2</sub>O) has some negative effects as well. N<sub>2</sub>O is a greenhouse gas that has a global warming potential more than 300 times higher than that of carbon dioxide [30]. N<sub>2</sub>O can destroyed the stratosphere ozone which increase in UV-B radiation at the earth's surface [31]. Furthermore, animal and human studies indicate that the toxic effects of N<sub>2</sub>O depend on concentration and time. For a time-weighted average of 100 ppm for an 8-hour workday and/or a time weighted average of 400 ppm per anesthetic administration, it would provide adequate protection of dental personnel and be acceptable with existing pollution control methods [32]. However, in patients administered N<sub>2</sub>O for extended periods of time and neurological abnormalities in health care workers who inhaled N<sub>2</sub>O recreationally, it have disproved some effects like anesthetic action and bone marrow depression [32].

The health effects of breathing in diesel exhaust have been shown to be toxic, mutagenic or carcinogenic in animal exposure tests [33]. Also, the exposure of animals to diesel exhaust has produced morphological and biochemical changes in the lung, with an increase in susceptibility to bacterial infection, and the possibility of producing systemic toxic effects. Some human diseases which can be caused from NO<sub>x</sub> are pulmonary edema (swelling), bronchitis, and even pneumonia [34]. Due to the negative effects of NO<sub>x</sub> on health, regulation of exhaust emissions

has recently become increasingly stringent. Government legislation for permissible exhaust emission standards was first introduced for light-duty vehicles only in both Europe and the United States in 1982, and then for heavy-duty engines in 1990 [35]. In Table 2, emission regulations concerning NO<sub>x</sub> are indicated and as shown, with more and more stringent standards being employed day by day [36, 37].

**Table 2**

NO<sub>x</sub> emission standards for diesel vehicles [36, 37].

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

Furthermore, Euro VI regulations will be introduced in 2013 which will enable the harmonization of the European standards with those of the US and Japan [13, 38].

#### **4. Plasma and various power generators**

The term plasma was first introduced by Irving Langmuir (1881-1975) and his colleague Lewi Tonks (1897-1971) in 1929 to describe the inner region of a glowing ionized gas phase produced by means of an electric discharge in a tube [39]. Plasma is the fourth state of matter, that is, an ionized gas into which sufficient energy is provided to free electrons from atoms or molecules

and to allow species, ions and electrons to coexist. Generally, plasma is electrically neutral. The plasma ionization degree is the proportion of atoms that have lost (or gained) electrons [17].

As discussed before, in order to introduce plasma into a gas, the electronic structure of the species (atoms, molecules) should be changed and then excited species and ions will be produced. The required energy for this process can be provided by thermal force, or carried by either an electric current or electromagnetic radiations [40]. Therefore, plasma is divided into thermal or hot plasma and non-thermal or cold plasma. In the thermal variety, molecules dissociate into the atoms at high temperatures around 2000 °C. Gas molecule will be ionised by losing electrons if the temperature goes up to more than 3000 °C. In this state, gas has a liquid-like viscosity at atmospheric pressure and the free electric charges confer relatively high electrical conductivities that can approach those of metals [41]. In thermal plasma, the kinetic energy (temperature) of charged particles and the kinetic energy (temperature) of the background gas are similar. Since all particles are in thermal equilibrium, thermal plasma is also known as equilibrium plasma [42]. In non-thermal plasma (NTP), the electric field transmits energy to the gas electrons and then energy will be transfer to the neutral species by collisions [40]. In NTP, electrons have a kinetic energy higher than the energy corresponding to the random motion of the background gas molecules, generally in the range of between 10,000K and 100,000K (2-3 order of magnitude greater than the background gas) [43]. An example of non-thermal plasma is the gas filling a fluorescent tube. Its temperature is only around 40°C, but the temperature of free electrons in the system exceeds 10,000°C [18]. The intent when using non-thermal plasma is to selectively transfer the input electrical energy to the electrons which then generate free radicals through collisions, and promote the desired chemical changes in the exhaust gas. These reactions

can be accomplished with just a fraction of the energy which is required in the thermal plasma system [43-45].

Generally, three kinds of power generators (namely AC, DC and Pulse) can be used in order to generate plasma. AC and Pulse energisations show a superior NO<sub>x</sub> removal efficiency when compared with DC energisation. However, Pulse energisation is found to be more energy efficient [46].

Pulsed power is generated by instantaneously delivering the energy stored in an energy component, which has been accumulated there gradually to a load. By releasing stored energy over a very short time interval, a huge amount of peak power can be delivered [47]. In other words, the energy, which can be generated with extra low voltage, is released a shorter period of time, which causes higher amplitude [48]. This strategy is called pulsed power. Recently, many studies of industrial applications of pulsed power technology, such as food processing, medical treatment, water treatment, ozone generation, engine ignition, ion implantation, exhaust gas treatment and others resulted from the development of pulsed power generators [48, 49].

Recently, repetitively operated pulsed power generators with a moderate peak power have been developed. These generators are compact, reliable, low maintenance, and have high reproducibility. Using pulsed power technology, non-thermal plasmas have been generated by a pulsed electron beam [50] or a pulsed streamer discharge [51], and can be used to treat nitric oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), particulate matter and volatile organic compounds (VOCs), and also to generate ozone. Non-thermal plasmas have many kinds of chemically activated radicals, such as O (Oxygen radical), O<sub>3</sub> (Ozone), N (Nitrogen radical), N\* (excited Nitrogen radical), N<sub>2</sub><sup>+</sup> (positive ions of nitrogen) and OH, which are generated by

the dissociation and ionization of the ambient gases caused by the impact of energetic electrons [49, 52, 53].

When plasma is introduced inside the exhaust gases, oxidation processes will be started. NO<sub>x</sub>, unburned hydrocarbons, carbon monoxide (CO) and particulate matter (PM) will be oxidized [54]. In spite of NO<sub>x</sub> reduction to N<sub>2</sub> and O<sub>2</sub>, plasma treatment of exhaust gases is more related to NO oxidation to NO<sub>2</sub> [55, 56]. The plasma is believed to show potential to improve catalyst selectivity and removal efficiency.

## **5. Different types of plasma reactors**

NTP can be generated in several ways, such as through electrical corona discharges, radio frequency discharges, microwave discharges [57, 58], dielectric barrier discharges and electron beams. The following NTP technologies are considered for pollution reduction in engine exhaust gases, with each having their advantages for different applications.

### *5.1. Electron beam*

An electron beam is formed in a separate generator, such as a cathode tube, and injected into the exhaust gas. The energy of the electrons is absorbed by the components of the gaseous mixture proportionally to their mass fraction [59]. The energy of electrons can be much higher in the e-beam reactor than in other reactors. Disadvantages of the e-beam reactor include the need for a special reactor for generating the electrons, and poor efficiency in transferring the electrons into the exhaust gas [18, 60].



### *5.2. Corona discharges*

The term corona comes from the crown-like appearance of the plasma discharge when the voltage exceeds a certain value [61]. In a corona discharge reactor, a non-uniform electric field is formed between two concentric electrodes by the sharp edges or points of its electrodes where the radius of the curvature is small. A characteristic of corona discharges is that there is no need to use a dielectric to generate plasma [62, 63]. The electric field must be pulsed in order to prevent the plasma going into the thermal mode and forming an arc [18].

### *5.3. Dielectric barrier discharge*

The basic design of a dielectric barrier discharge (DBD) reactor consists of a set of electrodes with at least one dielectric barrier between them. As a result of the presence of the dielectric barrier, the discharges require higher voltage for their operation. In other words, the electric field must be high enough to cause breakdown in the gas [64]. The gas is passed through the dielectric surfaces, while the electrodes produce the sufficient electrical field between them to cause plasma to form. A common feature of both DBD and corona discharge is that small scale electron streamers are formed [62]. However, a DBD produces a homogenous discharge with low energy consumption and this discharge process is also the mechanism through which charges are transported [65]. Whealton et al. [62] explained that after applying the electric field perpendicular to the dielectric, electron streamers are formed. Space charge then builds up on the dielectric surface, locally terminating the external applied electric field, and then finally extinguishing the discharge. The material used for dielectric barriers is usually quartz glass,

silica glass or alumina; however, they can also be made from ceramic materials, and thin enamel or polymer layers in special cases [18, 64].

#### *5.4. Dielectric packed bed reactor*

The dielectric packed bed reactor is similar to the DBD, but with a different configuration of dielectrics. Pellets of dielectric material are placed in the gap between the barrier and the electrode. One advantage of this system is that relatively low applied voltages can be used to form a plasma over a relatively large separation of the electrodes [63]. Another advantage of this system is that it is possible to use catalyst pellets, which makes this type of reactor a possible choice for plasma-catalyst systems. However, the high pressure drop and attrition of the pellets are disadvantages of this system [18].

#### *5.5. Surface plasma discharge*

In this system, the dielectric barrier completely fills the gap between the two electrodes. One of the electrodes covers one side of the dielectric barrier completely; however, the other electrode only partially covers it, making it distinct from the surface discharges and DBD. The plasma is generated next to this dielectric surface which is in contact with the gas. When the electric field is applied, the surface plasma covers the entire dielectric surface [62]. A feature of this discharge is that after a few nanoseconds, charge begins to build up at the dielectric surface, which has the effect of reducing the electric fields outside the dielectric, eventually extinguishing the discharge [18].

## 6. Plasma NOx removal

NOx storage reduction (NSR), selective NOx recirculation (SNR) and non-thermal plasma have been considered increasingly in recent times, with a view to developing techniques to reduce NOx emissions in diesel engines[55, 66-68].

Non-thermal plasma (NTP) technology has been introduced as a promising method for NOx removal from simulated gases as well as real diesel engine exhaust. In an NTP reactor, NOx concentration is reduced by a set of reactions between free electrons, ions, radicals, atoms, and molecules which are formed in plasma. The NOx reduction reactions generally can be divided in two groups:

NOx removal reactions, and

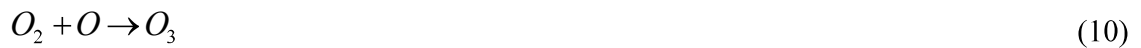
NO – NO2 conversion reactions.

In the first group, some of the primary and main NOx removal reactions could be summarized as the following [55, 69-73]:

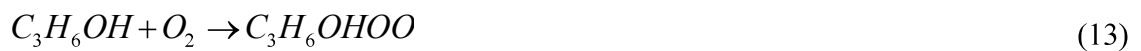


where  $N_2(A)$  represents  $N_2$  metastable state.

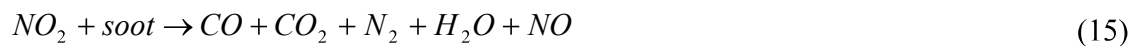
The second group of reactions (which involves the reactions of oxidizing NO to NO<sub>2</sub>) could be summarized as the following [55, 72-74]:



Hydrocarbons are attributed an important role in NO<sub>x</sub> removal by using plasma discharge. The reaction paths for NO<sub>x</sub> removal change significantly from that without hydrocarbon additives. In the presence of hydrocarbons, the efficiency of NO<sub>x</sub> reduction and NO – NO<sub>2</sub> conversion is greatly increased due to the reactions between the hydrocarbons and NO<sub>x</sub> such as [18]:



Furthermore, the NO-NO<sub>2</sub> conversion due to the oxidation by O/OH radicals or by hydrocarbons is less probable since the O/OH radicals decrease in the presence of soot inside the diesel engine exhaust. Moreover, some NO<sub>2</sub> can react with soot by the following reaction [75]:



In addition, in the presence of water, some other reactions are also involved, which are as follows [76]:

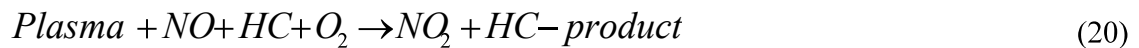


and

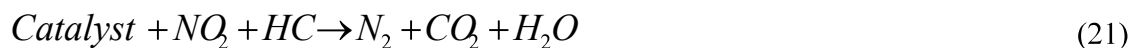


Therefore, the reactions taking place during the treatment of actual diesel exhaust vary largely from that of the simulated gas mixtures, due to the presence of various hydrocarbons, aldehydes and water in the diesel exhaust.

On the other hand, many studies suggest that the conversion of NO to NO<sub>2</sub> is an important intermediate step in the reduction of NO to N<sub>2</sub> [77], and that the most efficient way to do this is to use a plasma reactor along with an additional catalyst reactor. In the first step, the plasma oxidises NO to NO<sub>2</sub> in the presence of HC [78]:



In the second stage, the catalyst reduces NO<sub>2</sub> to N<sub>2</sub> by selective reduction using hydrocarbons [78]:



In general, some researchers employed NTP using different combinations of gases to simulate real exhaust gases from engines in order to examine the ways that different parameters affected the system [76, 79-95], and others study real engines to enhance the efficiency of the NTP [46, 74, 75, 78, 88, 96-111].

Various kinds of NTP reactors were studied by the researchers. The earlier kind of NTP reactors were electron beam reactors, which were mostly employed from 1980 to 2000 [112-

115]. The majority of researchers applied dielectric barrier discharge (DBD) reactors [74, 75, 79, 93-95, 98-106, 109-111]. Some used packed bed DBD reactors [46, 80, 83, 98, 99, 103, 106, 116] and others used DBD assisted reactors along with another catalyst or adsorbent reactor [74, 80, 84, 86, 100, 101, 104-106, 109, 110]. However, some researchers studied corona reactors [78, 81, 82, 85, 87, 88, 96, 97, 107, 108]. In addition, some researchers examined surface plasma discharge reactors [76, 91, 117]. Note that in some studies, the packed bed DBD reactor is called a single stage plasma-catalytic system, with the catalyst or adsorber placed in the discharge zone. The DBD assisted reactor (used with another catalyst or adsorbent reactor) is also called a two stage system, with the catalyst or adsorbent placed downstream of the plasma. The advantage of single-stage reactors is that the active species react on the catalyst surface in the discharge zone. However, in the two-stage systems, the oxidation of NO to NO<sub>2</sub> in the plasma increases the catalyst performance, since the NO<sub>2</sub> removal is better than the NO removal near the catalyst [118].

## *6.1. NO<sub>x</sub> removal from simulated gases*

### *6.1.1. DBD reactor*

Mizuno et al. [79] in 1998 investigated NTP at very low temperatures, below 100°C. Different simulated gases (NO+O<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O gas cylinders) were examined to simulate the exhaust of a thermal power plant. A straight wire DBD reactor was used for all simulations. The concentration of NO and NO<sub>2</sub> was measured at three different temperatures: room temperature, liquid nitrogen temperature and solid ethanol temperature. The voltage source for

this study was pulse DC voltage, and the maximum supplied voltage and pulse frequency was 30 kV and 60 Hz respectively. At low temperature, it was claimed that the plasma process is effective to remove gaseous pollutants, as well as to promote plasma chemical reactions. To cite one particular case, the removal efficiency of nitrogen (DeNO) at room temperature was 20%, at liquid nitrogen temperature (-196°C) it was 60% and at solid ethanol temperature (-114°C) it was 98%. Note that the removal efficiency or removal ratio was defined as follows:

$$NO_R = \frac{(NO_i - NO_e) \times 100}{NO_i} \quad (22)$$

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

Wang et al. [92] conducted a complete investigation on the effects of electrode connection, diameter, material, shape of the inner electrode, and dielectric material on NO removal in order to improve the performance of dielectric barrier discharge reactors. The simulated gas examined in this paper is the combination of NO and N<sub>2</sub>. An AC power supply with a peak voltage of 30kV and peak frequency of 10 kHz was employed. The specific energy density (SED) parameter which is defined as the ratio of discharge power to the gas flow rate is considered to compare different case studies. For the same removal efficiency, it is better to have a lower specific

energy density regarding the energy consumption. If the SED parameter of 10 J/L (for a 3-L-class diesel engine) can be achieved, which is around 3% of automotive diesel engine power output over the United State Federal Test Procedure (US FTP) test cycle, it will come to a practical level [119].

It was shown that when a high voltage was applied to the outer electrode and when a smaller discharge gap was selected in the coaxial reactor, a smaller breakdown voltage was required, and therefore better NO removal could be achieved with the same high voltage. Furthermore, increasing the inner electrode diameter increased the NO removal efficiency due to the decrease in the discharge gap. Three different materials were tested for the inner electrode, and showed that tungsten had a higher NO removal efficiency than copper or stainless steel, due to a larger secondary electron emission. Copper proved more effective than stainless steel [120]. The use of a screw electrode as an inner electrode was also tested in comparison with a rod electrode, and this showed that the NO removal efficiency was higher with the screw electrode than the rod electrode, as the equivalent gap capacitance of the reactor with the screw electrode was lower. The screw electrode generates a large number of micro discharges with a small energy deposition per micro discharge [121], and the discharge is more intense in the screw electrode reactor, due to the higher input power when compared with the rod electrode reactor under the same applied voltage. In addition, the accidental surface of the screw electrode makes the moving gases become turbulent, increasing the probability of particle collisions and intensifying the plasma reaction. Finally, they examined various dielectric materials and showed that the NO removal efficiency was higher when using corundum when compared with ceramic and quartz materials,



since the relative permittivity of corundum is higher than ceramic materials. Quartz was the least effective material to be used.

In 2012, Vinh et al. [93, 94] investigated the effects of different PM compositions and oxygen fraction on NO<sub>x</sub> removal efficiency in simulated exhaust gas by a dielectric barrier discharge needle-to-cylinder reactor at room temperature. They also studied the combination between a dielectric barrier discharge reactor and a wall-flow type diesel particulate filter (DPF)[122]. A diffusion flame formation system was used to produce PM [123]. The simulated gas was the combination of NO, N<sub>2</sub>, O<sub>2</sub> and PM. A 50 Hz alternative high voltage supply in the range of 5kV to 15kV was used. It was shown that PM could increase the NO<sub>x</sub> removal efficiency intensely; however, PM was more effective when they introduced fresh PM in to the reactor. For example, by using 100mg fresh PM in a special case, the NO<sub>x</sub> removal efficiency was 28%; however, it was around 12% without using PM. They claimed that the existence of PM inside the reactor incurs O radicals react with HC or soot besides other reactions. Therefore, the NO<sub>2</sub> formation process is slower and consequently, the NO<sub>x</sub> removal efficiency is higher. Accordingly, PM has worked as a reactive agent in the reactor [93]. Furthermore, the NO removal efficiency is much higher in the presence of oxygen than the case without oxygen; however, the NO<sub>x</sub> removal efficiency is not different.

#### *6.1.2. Packed bed DBD reactor*

In 1999, Yamamoto et al. [80] compared two types of plasma reactors, studying reaction by-products and NO<sub>x</sub> removal efficiency. One was an ordinary packed-bed reactor without any barrier, and the other was a barrier type packed-bed plasma reactor. In addition, the effect of

using  $\text{Na}_2\text{O}_3$  after the plasma reactor to reduce the amount of produced  $\text{NO}_2$  was studied. The  $\text{NO}_2$  will react with sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) to form a non-toxic water-soluble  $\text{Na}_2\text{SO}_4$  as a final product. Mok and Lee [124] in 2006 were also used  $\text{Na}_2\text{SO}_3$  as a reducing agent to remove sulfur dioxide and nitrogen oxides simultaneously. Ferroelectric  $\text{BaTiO}_3$  pellets were used inside the reactors, with a 15kV and 60Hz AC power supply. A mixture of NO balanced with  $\text{N}_2$  in a gas cylinder, and dry air supplied by a compressor was employed to simulate the exhaust gas. The concentration of NO,  $\text{NO}_2$ ,  $\text{NO}_x$ , CO,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{HNO}_2$  and  $\text{HNO}_3$  (aqueous solution) were measured. It was shown that the hybrid system using the barrier type packed-bed plasma reactor, followed by the chemical reactor with  $\text{Na}_2\text{SO}_3$ , provided nearly 100%  $\text{NO}_x$  removal efficiency with negligible reaction by-products of  $\text{N}_2\text{O}$ , CO,  $\text{HNO}_2$  and  $\text{HNO}_3$ . It was claimed that the cost of this system was approximately 15 times more economical than the conventional selective catalyst reduction (SCR) process. The effect of reactor diameter and the optimum diameter of pellets for hybrid systems was also investigated. It was found that the  $\text{NO}_2$  conversion was higher and  $\text{NO}_x$  reduction was smaller for 1.5 mm diameter electrodes (the smallest size of electrode diameter considered), when compared with 5.0 mm diameter electrodes. Furthermore, 1.5mm diameter electrodes produced less reaction by-products, such as  $\text{N}_2\text{O}$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$  and CO, thus making this electrode most suitable for the hybrid system. In addition, the  $\text{BaTiO}_3$  pellets with a diameter of 3.0 mm (the largest size considered) provided the best results on the hybrid  $\text{NO}_x$  control system. The decomposition of the air alone for both different reactors was also studied, along with the effects of power supply voltage. However, the power supply frequency was not considered.

In 2011, Rajanikanth and Rout[83] studied the dielectric packed bed reactor for the removal of NO<sub>x</sub> from simulated gas, and compared this with a conventional DBD. Gas cylinders of NO in N<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and O<sub>2</sub> were used to simulate the vehicle exhaust gas at room temperature, and changes in the concentration of NO, CO, CO<sub>2</sub> and O<sub>2</sub> were also considered. Three types of catalyst were used as dielectric pellets: alumina (Al<sub>2</sub>O<sub>3</sub>), Alumina coated with palladium as catalyst (Al<sub>2</sub>O<sub>3</sub>-Pd), and barium titanate (BiTiO<sub>3</sub>). The voltage source for this study was a single-phase AC supply, and the range of voltage and pulse frequency of the supplier was 15-28.6 kV and 50-125Hz, respectively. The pulse rise time was 34ns. It was shown that the presence of a packed dielectric bed increased the discharge power. Therefore, for a given reactor size and set of operating conditions, higher NO removal efficiencies at lower voltages could be achieved. Barium titanate pellets showed better removal efficiency than the other proposed pellets. For example, DeNO was 76% for DBD alone. It was 84%, 72% and 100% for DBD with alumina, alumina coated with palladium, and barium titanate pellets, respectively. The major contribution of this paper was its comparability with conventional catalytic converters which operate at an exhaust gas temperature around 300°C or above. In addition, the effects of pulse frequency and pulse voltage were also studied. It was shown that the NO removal ratio increased with an increase in the pulse repetition ratio, and an increase in the peak of applied voltage. This effect was due to the higher discharge power resulting from the higher pulse repetition rate and higher peak voltage.

In 2003, Ravi et al. [116] considered the effect of temperature on NO conversion using simulated gases consisting of NO, O<sub>2</sub>, and N<sub>2</sub> in the presence of various hydrocarbons: ethylene, acetylene and n-hexane. They also studied acetylene with the presence of H<sub>2</sub>O in the simulated

gas. A packed bed DBD reactor with glass beads as pellets was used. The concentration of NO and NO<sub>2</sub> was measured at different temperatures, from room temperature up to 200°C. 60 Hz AC high voltage was applied, ranging from 8kV to 16kV. It was found that the discharge power increased with increasing the temperature. NO conversion in the presence of ethylene and n-hexane was better than that of acetylene at all temperatures. The adding of acetylene at room temperature showed no better conversion of NO than when there were no additives. At higher temperatures, the conversion of NO was enhanced. A little enhancement in NO and NO<sub>x</sub> removal was observed in the presence of water vapor, due to the effect of OH and O radicals for NO removal.

### *6.1.3. Combined DBD reactor with catalyst or absorber*

In 2003, Ravi et al. [84] investigated the conventional DBD reactor when combined with a catalytic reactor at different temperatures. Three different reactors were studied: DBD alone, catalyst alone, and a cascaded plasma catalyst reactor. The catalyst used was a commercially available SCR catalyst (V<sub>2</sub>O<sub>5</sub> – WO<sub>3</sub> / TiO<sub>2</sub>). The simulated gas was the composition of NO, O<sub>2</sub>, and N<sub>2</sub> in the presence of ethylene and ammonia only for the cascaded reactor. A 60Hz AC 14kV high voltage power supply was used. It was shown that the rate of oxidation of NO to NO<sub>2</sub> decreased with temperature. In addition, it was shown that by using cascaded plasma catalyst reactors, the NO<sub>x</sub> removal efficiency was more pronounced, especially at low temperatures, and this was labeled as a “synergy effect”. However, clear reasons for this synergy effect were not given. Also it was also claimed that this behavior may not be common to all types of catalysts at

various temperature, and one must choose the optimal operating energy density, depending on the characteristics of the individual catalyst.

In 2004, Mok et al. [86] studied NO<sub>x</sub> removal by using a packed bed plasma reactor assisted with monolith V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst using AC and pulse voltage. Various effective parameters such as initial NO<sub>x</sub> concentration, gas flow rate, gas humidity and reaction temperature were studied. The simulated gas was the composition of N<sub>2</sub>, O<sub>2</sub>, NO balanced with N<sub>2</sub> and ethylene. It was claimed that ethylene helped NO oxidation to NO<sub>2</sub>. It was shown that increasing the initial concentration of NO<sub>x</sub>, decreases the removal efficiency for the same energy density; however, if the NO<sub>2</sub> fraction keeps constant, the NO<sub>x</sub> removal efficiency is similar for different initial concentrations of NO<sub>x</sub>. This was an important finding in this paper which is rare in other studies. Furthermore, from their paper, increasing the gas flow rate decreases the efficiency of NO<sub>x</sub> removal. According to the effect of water vapor, it was shown that for the plasma-catalyst system, by increasing the humidity from 0 to 3%, the NO<sub>x</sub> removal efficiency was decreased almost 10% and further increase in humidity did not have a significant effect on NO<sub>x</sub> removal efficiency. It was also shown that for the catalyst alone reactor, increase in the reaction temperature enhances the NO<sub>x</sub> removal efficiency; however, the reaction temperature is hardly influenced by the NO<sub>x</sub> removal efficiency.

#### *6.1.4. Corona reactor*

In 2000 and 2001, Namihira et al. [81, 82] studied the effects of pulse-width in improving NO<sub>x</sub> removal efficiency. They designed a new DC voltage generator in the order of 10 nanoseconds pulse-width. A corona discharge reactor and gas cylinders of N<sub>2</sub>, NO and H<sub>2</sub>O were

used, and the concentration of NO and NO<sub>2</sub> was measured at ambient temperature. They studied low pulse frequencies range from 1-13 pps (pulses per second) and various pulse widths from 40-120ns. It was shown that the removal ratio of NO decreased with an increasing pulse repetition rate and an increasing pulse-width. However, the removal energy efficiency increased with a decreasing pulse-width. In other words, the removal energy efficiency was higher for shorter pulse-widths at a fixed NO removal ratio. The authors claim that their results are clearly in coincidence with another study which used electron beam irradiation without any additive [125, 126]. The removal energy efficiency for the comparison was calculated as follows:

$$NO_E = \frac{\frac{G}{22.4[l/min]} \times (NO_i - NO_e) \times 60[min/h] \times 10^{-3}}{f \times E} \quad [mol/kWh] \quad (23)$$

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

In 2004, NO<sub>x</sub> removal mechanism by a DC corona discharge has been considered by Arai et al. [85]. A mixture of N<sub>2</sub>, O<sub>2</sub>, and NO was used as the test gas. In their experiments, oxygen concentration was changed between 0 and 20%. The initial concentration of NO was kept at 100ppm and the residence time inside the reactor was 17sec. It was shown that the NO<sub>x</sub> removal mechanism depends on oxygen content. In the case of NO+N<sub>2</sub> mixture, NO reduction process has been controlled by exited N<sub>2</sub> radicals. However, in the case of NO/N<sub>2</sub>/O<sub>2</sub> mixture, NO mainly was converted to NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> by ozone generated from corona discharge.

In 2006, Saito et al. [87] studied the effect of H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> on NO removal by using a DC corona discharge. The base gas in their experiments was a mixture of N<sub>2</sub>/O<sub>2</sub> (20%)/NO (100ppm) and the coexisting gases was added to the base gas. They considered both

positive and negative discharge in their tests. When moisture was added to the base gas,  $\text{NO}_x$  removal was 30% at energy density of 50J/L in the case of positive corona discharge and 90% at 250J/L for negative discharge. It was found that the existence of  $\text{CO}_2$  in the base gas was not desirable. When  $\text{CO}_2$  was added to the base gas, the  $\text{NO}_x$  concentration increased up to twice at 920 J/L compared to the case of  $\text{CO}_2$  free for positive discharge. In the case of negative discharge, about 200 J/L more energy was needed to get 90%  $\text{NO}_x$  reduction compared to the base case. In the case of  $\text{C}_2\text{H}_4$  addition,  $\text{NO}$  was oxidized to  $\text{NO}_2$  for positive discharge and  $\text{NO}_x$  was hardly removed. However,  $\text{NO}_x$  was decreased with a lower energy density in the case of negative discharge. In the case of simulated gas ( $\text{N}_2/\text{O}_2/\text{NO}/\text{H}_2\text{O}/\text{CO}_2/\text{C}_2\text{H}_4$  mixture), the  $\text{NO}_x$  removal efficiency was more than 90% and the energy density was lower compared with the base gas. However, some byproducts such as  $\text{CO}$ ,  $\text{O}_3$ ,  $\text{NO}_3$ , and  $\text{NO}_2$  have been increased in the case of simulated gas.

#### *6.1.5. Surface plasma discharge reactor*

In 2011 and 2012, Jolibois et al. [76, 91] studied a wet-type reactor featuring a surface discharge. This system was studied, with a coil inserted in the electrical circuit during the treatment process, and also with a catalyst ( $\gamma\text{-Al}_2\text{O}_3$ ). The simulated gas examined was a mixture of  $\text{NO}$  and air. Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) was used to obtain the wet condition required. With wet conditions, the  $\text{NO}_x$  removal efficiency is improved by dissolving  $\text{NO}_2$  into the liquid as  $\text{NO}_2^-$  and  $\text{NO}_3^-$  ions [127]. However, the continuous absorption of nitrogen oxides causes saturation and acidification of the liquid, and results in the inhibition of further absorption. By adding  $\text{Na}_2\text{SO}_3$ , the nitrite and nitrate ions reduce to  $\text{N}_2$ , and therefore gas

absorption is facilitated [128]. A comprehensive study was made of variations in voltage and frequency, and it was shown that the NO<sub>x</sub> removal efficiency was higher in relation to the signal frequency variations, rather than voltage variations. Furthermore, they showed that the removal efficiency was improved by inserting a coil between the power supply and the surface, and was also improved by using a catalyst. It was claimed that the inductance influenced the power consumed by the plasma.

#### *6.1.6. Complex unique types of reactors*

In 2009 and 2010, Matsumoto et al. [89, 90] developed a new pulse generator: the nanosecond pulsed generator. This can produce 80kV high voltage, with 2ns rise and fall time, 5ns pulse width and a pulse frequency of 0-100pps. The authors claimed that this generator can achieve 100% removal efficiency. The simulated gas examined was a mixture of N<sub>2</sub> and NO. The nanosecond pulsed discharge was shown to have a distinct advantage in energy efficiency for NO removal when compared with sub-micro-second pulse discharge and other discharge methods. The effects of repetition ratio and applied voltage were studied, and it was shown that the NO removal ratio increased with an increase in the pulse repetition ratio and by increasing the peak of applied voltage due to the more discharge energy. In addition, it was shown that the positive pulse voltage gave a higher NO removal ratio than the negative pulse voltage when delivered at the same repetition rate in the case of lower applied peak voltage. On the other hand, there were no changes between the NO removal via positive and negative pulse voltage in the case of the higher applied peak voltage. Unlike previously mentioned studies, in this case, the authors studied the effects of reactor geometry. They showed that the NO removal ratio was



increased by using a smaller reactor internal diameter. In addition, the NO removal ratio was increased by using a longer reactor, since the gas residence time in the reactor was also increased. Another important result of this study was that the NO removal ratio was increased considerably with the presence of O<sub>2</sub> and water fed by bubbling into the gas stream. This result demonstrated that the introduction of O<sub>2</sub> and water in this way is more effective for NO removal due to the effectiveness of the OH radicals or O radicals. In the 2010 study[90], it was shown that the nanosecond pulse discharge had more advantages than DBD and corona discharge as regards NO energy efficiency and the NO removal ratio.

In Table 3 is an overview of the papers studied, considering NTP for NO<sub>x</sub> removal from simulated gases.

**Table 3**Overview of published papers featuring NTP for NO<sub>x</sub> removal from simulated gases.

Authors	Year	Reactor type	Gas type	Catalyst/ adsorbent type	Reactor inlet temperature	Flow rate	Power generator	Peak voltage	Peak pulse frequency	The range of studied energy density
Mizuno et al. [79]	1999	DBD reactor	Simulated gas (N <sub>2</sub> O/ O <sub>2</sub> /N <sub>2</sub> /CO <sub>2</sub> /H <sub>2</sub> O)	-	20, -196°C, -114°C	1-8 L/min	Pulses generated by DC voltage supply	30kV	60Hz	-
Yamamoto et al. [80]	1999	Packed-bed DBD reactor	Simulated gas (N <sub>2</sub> /NO)	BaTiO <sub>3</sub>	Room temp.	1-2 L/min	AC high voltage supply	15kV	60Hz	-
Namihira et al. [81, 82]	2000 2001	Corona reactor	Simulated gas (NO/N <sub>2</sub> /O <sub>2</sub> /H <sub>2</sub> O)	-	29.2C	2-12 L/min	Pulses generated by DC voltage supply	49.2kV	13pps	-
Rajamikanth and Rout[83]	2001	Packed-bed DBD reactor	Simulated gas (NO/N <sub>2</sub> /CO <sub>2</sub> /O <sub>2</sub> )	Al <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> - Pd, BiTiO <sub>3</sub>	Room temp.	2 L/min	Pulses generated by DC voltage supply	50kV	12.5pps	10 – 60 J/L
Ravi et al. [116]	2003	DBD reactor	Simulated gas (NO/N <sub>2</sub> /O <sub>2</sub> /H <sub>2</sub> O)	-	Room temp. and 200°C	2 L/min	AC high voltage supply	16kV	60Hz	0 – 160 J/L
Ravi et al. [84]	2003	Combined DBD reactor with catalyst	Simulated gas (NO/NO <sub>2</sub> /O <sub>2</sub> /N <sub>2</sub> / ethylene, ammonia)	V <sub>2</sub> O <sub>5</sub> - WO <sub>3</sub> /TiO <sub>2</sub>	100, 150 and 200°C	2 L/min	AC high voltage supply	14kV	60Hz	0 – 160 J/L
Arai et al. [85]	2004	Corona reactor	Simulated gas (N <sub>2</sub> /O <sub>2</sub> /NO)	-	-	1 L/min	DC high voltage power supply	15kV	-	0-1500 J/L
Saito et al. [87]	2006	Corona reactor	Simulated gas (N <sub>2</sub> /O <sub>2</sub> /NO/H <sub>2</sub> O/CO <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> )	-	-	1 L/min	DC high voltage power supply	15kV	-	0-2500 J/L
Matsumoto et al. [89, 90]	2009 2010	Pulsed streamer discharge reactor	Simulated gas (N <sub>2</sub> /NO)	-	-	2 L/min	Nanosecond pulsed generator	80kV	50pps	-
Jolibois et al. [76]	2012	DBD / Surface plasma reactor	Simulated gas (N <sub>2</sub> /NO)	γ-Al <sub>2</sub> O <sub>3</sub>	Room temp.	1 L/min	AC high voltage supply	20kV	5kHz	0 – 190 J/L
Wang et al. [92]	2012	DBD reactor	Simulated gas (N <sub>2</sub> /NO)	-	-	10 L/min	AC high voltage supply	30kV	1kHz	100 – 800 J/L
Vinh et al. [93, 94]	2012	DBD reactor	Simulated gas (N <sub>2</sub> /NO/O <sub>2</sub> /PM)	-	Room temp.	0.5, 1 and 2 L/min	Alternative high voltage supply	15kV	50Hz	0 – 300 J/L

## 6.2. *NO<sub>x</sub> removal from diesel engines exhaust gas*

### 6.2.1. DBD reactor

In 2008, Rajanikanth et al. [75] studied two different types of dielectric barrier discharge reactors (wire-cylinder and pipe-cylinder) using simulated gas and real diesel engine exhaust. It was shown that, due to a shorter discharge gap, the pipe-cylinder reactor had more NO<sub>x</sub> removal efficiency than the wire-cylinder reactor. The reason is the consumed power of the plasma discharge in the discharge gap which depended inversely on the gap length. They claimed that the average electric field in their pipe-cylinder reactor with 1.625mm discharge gap is about 140 kV/cm and the corresponding electron energy is about 13eV, which is higher than the chemical bond energy of NO (6.50eV), NO<sub>2</sub>(3.11eV), and CO(11.12eV) molecules. They showed that for an energy density of higher than 30 J/L, NO removal efficiency for the pipe-cylinder is about 20-25% greater than that of the wire-cylinder reactor. However, for the NO<sub>x</sub> removal efficiency, it is almost the same after the energy density of 120J/L. In this year, in another paper [109], they performed this experiment on cascaded plasma adsorbent and achieved the same results - the pipe-cylinder reactor had superior NO<sub>x</sub> removal efficiency when compared with the wire-cylinder reactor.

In 2011, Mohapatro et al. [111] studied a crossed flow dielectric barrier discharge reactor on the removal of NO<sub>x</sub> from a 3.75kW diesel engine. This reactor consisted of 9 electrodes with the gas flowing radially rather than axially toward the electrodes. This unique feature of this new DBD reactor improved the performance of NO<sub>x</sub> removal from diesel engine exhaust due to the higher discharge and longer residence time. Since their results were obtained without using any

catalysts/adsorbents, the authors claimed that by using a cross flow DBD reactor they could remove a significant amount of NO<sub>x</sub> from diesel engine exhaust with less energy. For example in one case, with nine electrodes, the DeNO was 100% and DeNO<sub>x</sub> was 95% with an energy efficiency of almost 3.5 g/kWh NO. However, with one electrode, the DeNO was 74% and DeNO<sub>x</sub> was 45% with an energy efficiency of almost 23.1 g/kWh NO. The voltage source in this study was a pulse generator with a peak voltage of 25kV and frequency of 75pps. The pulse rise time was 20ns and the pulse duration was 13ms.

#### 6.2.2. Packed bed DBD reactor

In 2002, Rajanukanth et al.[98] compared the results for filtered real diesel engine exhaust and simulated gas. They used a DBD reactor alone, plus a packed bed DBD reactor (a hybrid adsorber plasma reactor-HAPR) with three different molecular sieves as adsorbent beads: MS-3A, MS-4A and MS-13X. Their experiments were conducted at the room temperature and also 200°C (the average exhaust temperature in urban driving cycles). A 6kW diesel engine was used to study the effect different NTP reactors on filtered real diesel engine exhaust and the concentration of NO, NO<sub>2</sub>, CO, CO<sub>2</sub> and aldehydes was considered during all the experiments. A single-phase AC supply with a high voltage range from 15kV to 25kV and a frequency of 100pps was employed. It was claimed that the hybrid adsorber plasma reactor (HAPR) successfully demonstrated NO<sub>x</sub> removal from diesel engine exhaust. It was shown that the NO<sub>x</sub> removal efficiency when using a plasma reactor alone is 36%. This efficiency increased with the HAPR to 73% at room temperature and 78% at 200°C. It was also determined that MS13X was the superior adsorbent for NO<sub>x</sub> removal.

In 2003, Yamamoto et al. [16] investigated the effect of non-thermal plasma on a filtered 2kW diesel engine exhaust at different loads. Three different plasma reactors were evaluated: pulse driven DBD reactor, pulse driven dielectric packed bed reactor and AC driven dielectric packed bed reactor. BaTiO<sub>3</sub> ferroelectric pellets were used for the packed bed DBD reactor. The characteristics of the power supply were: a peak voltage of 25kV, 1.2ms pulse width, with 13.7ns pulse rise time for the packed bed DBD reactor and 6.1ns for the DBD reactor. The frequency of the AC supply was 60Hz and pulse supply was 210Hz. It was found that the AC packed-bed reactor and pelletless pulsed reactor showed better performance in terms of the discharge power and NO<sub>x</sub> removal efficiency, with minimum reaction products for a given power at no load engine. When the engine load exceeded 50%, there was only a limited decrease in NO reduction and all the reactors performed more or less equally. It is claimed that the total operating cost of the plasma-chemical hybrid system can be one-third to one-fifth of the conventional selective catalytic process. The key finding of this study is the amount of power consumption required for various configurations. Power consumption for the pulsed corona reactor without pellets is less than the pulsed corona with BaTiO<sub>3</sub> pellets, and both are less than the 60Hz AC packed bed plasma reactor.

In 2006, Rajanikanth et al. [41] studied the injection of nitrogen radicals into the real diesel engine exhaust for the technique of NO<sub>x</sub> removal by plasma. N<sub>2</sub> gas was passed through a separate plasma reactor in order to produce N radicals which were then injected into the treatment zone. Both the NTP reactor and the reactor which produced N radicals are DBD reactor. The removal efficiency without injecting of N radicals has been compared with considering the injection of N radicals. The pulse generator was used in this study as a high

voltage generator in the range of 14kV to 25kV, and the pulse frequency was 130pps. It was shown that by injecting N radicals, there was quite significant improvement in NO<sub>x</sub> removal efficiency. However, the specific energy density, which is defined as the division of power to flow rate, increased considerably. It is claimed that this increment in removal efficiency without the use of catalysts or adsorbents is an important step toward NO removal by a plasma reactor alone.

In 2009, Srinivasan et al. [46] studied three different voltage energisations (AC/DC/pulse) on the removal of NO<sub>x</sub> from both filtered and unfiltered diesel engine exhaust. A packed bed DBD reactor was used, with dielectric beads. It was claimed that the performance of pulse power was better than AC and both were better than the DC energisation. The average electric field in the AC case is not as high as that observed in the pulse energised reactor or for the DC case; the average energy gained by the electrons under DC is insufficient to generate any radicals. In other words, the same removal efficiency could be achieved with less specific energy density in the pulse power than with AC power or with DC power.

### 6.2.3. Combined DBD reactor with catalyst or absorber

In 2003, Rajanikanth et al. [100] investigated a cascaded system of plasma and adsorption process for NO<sub>x</sub> and total hydrocarbon (THC) removal from a 6kW real diesel engine's exhaust. A part of the exhaust gas was passed through a particulate filter first to filter out solid particulates and then fed to the reactors. Three different systems were evaluated: a DBD reactor, an adsorbent reactor and a cascade system. The cascade system consisted of a DBD reactor

upstream of an adsorbent reactor. Three different adsorbent beads were used: activated alumina, MS-13X and activated charcoal. The concentration of NO, NO<sub>2</sub>, NO<sub>x</sub>, CO, THC and aldehydes were measured at different temperatures. A high voltage AC system with a peak voltage of 25kV and frequency of 100pps was used in this study. It was shown that the NO<sub>x</sub> removal efficiency was higher with the plasma-associated adsorption (cascaded) process when compared with the individual processes, and the removal efficiency was found to be almost invariant in time. For example, in one special case, DeNO<sub>x</sub> was 10% for SED 52J/L, however, for an adsorbent reactor alone, it was 14% and for a cascaded system, it was 25% for SED 52 J/L. In addition, activated charcoal and MS-13X were more effective for NO<sub>x</sub> and THC removal, respectively. It was also shown that NO<sub>x</sub> removal efficiency decreases with an increase in temperature for all the three adsorbents. However, the temperature was more effective for MS-13X and it proved less effective for the two other adsorbents. For example, with MS-13X, the NO<sub>x</sub> removal efficiency was almost 65% at 25°C and 45% for 140°C.

In 2004, Rajanikanth et al. [101] again studied the cascaded plasma catalyst; however, they used a filtered diesel engine exhaust at a different load and also used SCR (V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>) as a catalyst. It was shown that the NO removal efficiency decreased with an increase in exhaust temperature. In addition, the DeNO decreased when increasing the engine load, due to an increase in the initial concentration of NO. They showed that with the catalyst alone under 200°C, NO<sub>x</sub> removal was not affected. However, the plasma-assisted catalytic reactor was successfully employed to remove NO<sub>x</sub> from diesel engine exhaust at different loads of the engine. In one particular instance, the NO<sub>x</sub> removal efficiency were 33%, 27% and 87% respectively for a plasma reactor, a catalyst reactor and a plasma-assisted catalyst reactor.

In 2007, Rajanikanth et al. [104] performed the same experiment as [74] (cited previously), but this time in a more detailed fashion. The researchers examined a plasma reactor with an adsorbent and then a catalyst reactor, while using different kinds of adsorbent and catalyst materials. They showed that between three different adsorbent materials (activated charcoal, MS-13X, activated alumina), the activated charcoal cascaded with plasma exhibited superior adsorption properties. Furthermore, MS-13X cascaded with plasma gave higher NO<sub>x</sub> removal efficiency when compared to activated alumina cascaded with plasma. It was shown that the performance of the cascaded process at high temperatures was poorer than that at room temperature, due to the poor performance of plasma and adsorbent processes at higher temperatures. Examined four-stage cascaded plasma catalyst was also examined. When comparing the four-stage cascaded plasma catalyst with the two-stage model, the four-stage catalyst showed superior performance. It was expressly claimed that the cascaded plasma-adsorbent reactor could be a viable option for low temperature (<200 °C) stationary diesel exhaust NO<sub>x</sub> treatment. However, the cascaded plasma-activated catalytic reactor could also be a better option for non-stationary diesel exhaust NO<sub>x</sub> treatment, since it is not significantly affected by the plasma reactor temperature.

In 2009, Rajanikanth et al. [110] presented a novel way for generating high voltage for the plasma reactor in diesel engine exhaust. A solar powered high frequency electric discharge was developed to improve the size and specific energy density required in comparison with the traditional repetitive pulse or AC energisation. This generator can produce up to 16kV high voltage with a high frequency of 12.2 kHz and a pulse rise time of 24ns. This new high voltage generator was employed with DBD reactors, and different systems were examined, such as



cascaded plasma-adsorbent and cascaded plasma-catalyst reactors. It was shown that under this solar-powered high-frequency AC application, there was a considerable improvement in the NO<sub>x</sub> removal, when compared with other generators. For example, in the DBD reactor, NO<sub>x</sub> removal efficiency was 22%, 27% and 46% respectively for the 50Hz ordinary AC power supply, repetitive pulse power supply and 12.2 kHz AC power supply energised by solar powered battery. In addition, the cascaded system of solar-powered generator with adsorbent had superior performance when compared with other systems. It was claimed that this solar-powered high voltage power supply could be designed for a possible retrofit in vehicles. It could be used on top of a vehicle with appropriate mechanical fixtures. However, it would need modification to the reactor and the plasma in order to accommodate the actual exhaust flow-rate and temperature.

#### 6.2.4. Corona reactor

In 1998 and 1999, Puchkarev et al. [78, 96, 97] investigated the effect a transient, non-equilibrium plasma on NO<sub>x</sub> removal. They developed a pulsed corona discharge with a peak voltage of 49kV, a frequency of 1 kHz, a pulse rise time of 20ns and a pulse duration between 50 and 100ns. They studied the effects of diameters of inner and outer electrodes, reactor length, annular dielectric inserts to prevent arcing, flow rates, pulse repetition rates, plasma volume, and pulsed and mean energy deposition into the gas on NO removal. These parameters were studied in order to determine the optimum conditions for cost effective NO/NO<sub>x</sub> removal. They showed that short pulses are more effective for efficient energy usage rather than longer pulses. In addition, the energy cost using positive corona is 1.5-2 times higher than that for negative corona

for the same NO<sub>x</sub> removal. Note that the energy cost defined in this study was calculated as follows:

$$\varepsilon = \frac{250 \cdot E \cdot f}{F \cdot \Delta NO_x} \quad (eV / molecule) \quad (24)$$

where  $\varepsilon$  is the energy cost,  $E$  is the energy deposition into the gas,  $f$  is the frequency and  $F$  is the flow rate.  $\Delta NO_x$  is the NO<sub>x</sub> removal in ppm.

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

Koga et al. [88] compared the effect of corona discharge for NO<sub>x</sub> removal in engine exhaust gas and simulated gas. They considered a mixture of N<sub>2</sub>/O<sub>2</sub>/NO/NO<sub>2</sub>/H<sub>2</sub>O/CO<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> as the test gas. It was shown that the NO<sub>x</sub> removal characteristics in real exhaust and simulated gas were similar if the composition were same. Effect of flow rate and residence time has been studied as well. The flow rate was changed in the range of 0.5 to 20 L/min. By increasing the residence time, NO<sub>x</sub> removal has been increased. Furthermore, the energy density for NO<sub>x</sub> removal depends on initial NO<sub>x</sub> concentration. When initial concentrations were 160 ppm and 24 ppm, the required energy densities for 90% NO<sub>x</sub> removal were 200J/L and 700J/L, respectively.

In 2007, Vinogradov et al. [107] investigated on the DC corona discharge technology for NO<sub>x</sub> removal from diesel engine exhaust. Various geometrical parameters of a rectangular corona reactor were studied in order to find the optimum parameters for the best reactor performance. A

high voltage DC system with a peak voltage of 50kV was used in this study. Comprehensive research was performed on a polarity of the corona discharge, and this showed that as regards both cleanness (mass of NO<sub>x</sub> removed relative to its initial mass), and efficiency, negative polarity is preferable. It was shown that the cleanness was almost independent of the engine load; in other words, it did not depend on the initial NO<sub>x</sub> concentration. However, the efficiency is relatively low for 0kW and twice as high for 2.5, 4.5, and 7.5 kW diesel engines. Therefore, it was concluded that this type of corona reactor is more suitable for higher engine loads. In addition, a comprehensive study was presented of the effective parameters of the reactor which influenced the residence time. In 2008 [108], they studied the same corona reactor, but with a pulsed discharge. It was shown in this case, that the cleanness and efficiency are independent of the polarity of the electrodes; however, the positive polarity provided a more stable discharge, and a lower concentration of ozone than negative polarity.

#### 6.2.5. Effect of carbonaceous soot oxidation on NO<sub>x</sub> removal

Rajanikanth et al. [74, 75, 102, 105, 106] studied the effect of carbonaceous soot oxidation on NO<sub>x</sub> removal. They used unfiltered diesel engine exhaust which contains carbonaceous soot, and measured the concentration of CO<sub>2</sub>, CO, NO, NO<sub>2</sub>, THC and aldehydes. They were compared using six different reduction systems: a DBD alone, an adsorbent alone, a cascaded plasma-adsorbent reactor (PRAR), a pellet bed catalyst reactor, a honeycomb catalyst reactor and a cascaded plasma-catalytic reactor (PRCR). A high voltage AC system with a peak voltage of 25kV and a frequency of 130pps was employed on a 4.4kW diesel engine exhaust at no load condition. Three different temperatures were examined: 24°C, 100°C and 150°C.

It was shown that the NO<sub>x</sub> removal efficiency using the plasma technique was improved with the presence of carbonaceous soot in the diesel engine raw exhaust gas due to the reactions with NO<sub>2</sub>. Taking as an example one case, for a specific energy of 50J/L, NO<sub>x</sub> removal efficiency was 45% for an unfiltered diesel engine; however, DeNO<sub>x</sub> was 30% for filtered diesel exhaust gas [74]. In Table 4, the initial concentration of the main substances in a diesel engine exhaust that participate in plasma NO<sub>x</sub> removal for a 2.6kW diesel engine at 40% load have been tabulated [75, 109].

**Table 4**

Initial concentrations of the main substances in diesel engine exhaust.

Substance	Concentration (ppm) or volume fraction (%)
O <sub>2</sub>	12.5%
CO <sub>2</sub>	4.9%
CO	1770 ppm
NO	600 ppm
NO <sub>2</sub>	66 ppm
NO <sub>x</sub> (NO+NO <sub>2</sub> )	666 ppm

In addition, different adsorbent beads were tested, such as activated charcoal, molecular sieves, MS-13X and activated alumina. Adsorbent reactor alone and PRAR approved to show good performance in NO<sub>x</sub> removal; however, they did not exhibit efficient CO removal. They used various catalysts, such as conventional two-way and three-way catalysts, but only studied CO removal with the catalyst reactor. It was shown that generally, catalysts have a positive effect

on CO removal. Although the two-way catalyst exhibits a more effective CO removal than the three-way catalyst, the problem is that the catalyst did not show effective results on NO<sub>x</sub> removal due to a high oxidising environment in the diesel engine exhaust.

In Table 5, an overview of the studies considering NTP for NO<sub>x</sub> removal from diesel engine exhaust is schematized.

**Table 5**

Overview of the published papers considering NTP for NO<sub>x</sub> removal from diesel engine exhaust.

Authors	Year	Reactor type	Gas type	Catalyst/adsorbent type	Reactor temperature	Flow rate	Power generator	Peak voltage	Peak pulse frequency	The range of studied energy density
Puchkarev et al. [78, 96, 97]	1998 1999	Corona reactor	Diesel exhaust gas	-	-	1-10 L/min	Pulse supply	49kV	1kHz	-
Rajamikanth and Ravi[98]	2002	DBD reactor / Combined DBD reactor with adsorbent	Simulated gas (NO in N <sub>2</sub> , O <sub>2</sub> , CO) / Diesel engine exhaust at no load	MS-3A, MS-4A, MS-13X	Room temp. and 200°C	2 L/min	AC high voltage supply	25kV	100pps	-
Yamamoto et al. [99]	2003	DBD reactor / Packed bed DBD reactor	Diesel engine exhaust at various loads	BaTiO <sub>3</sub>	Room temp.	3 L/min	AC high voltage supply / pulse supply	25kV	60Hz for AC / 210Hz for pulse	-
Rajamikanth et al. [100]	2003	DBD reactor / Combined DBD reactor with adsorbent	Diesel engine exhaust at no load and load 50%	Activated alumina, MS-13X, activated charcoal	Room temp.	2 L/min	AC high voltage supply	25kV	100pps	0 – 100 J/L
Rajamikanth and Ravi[101]	2004	DBD reactor / Combined DBD reactor with catalyst	Diesel engine exhaust at various loads	SCR (V205/TiO2)	100, 150 and 200°C	2 L/min	Pulse supply	-	80pps	0 – 100 J/L
Rajamikanth et al. [74, 102, 105, 106]	2004 2005 2007	DBD reactor / Combined DBD reactor with catalyst and adsorbent	Diesel engine exhaust at various loads	Adsorbent: activated charcoal, molecular sieves MS-13X, activated alumina / catalyst: conventional 2-way and 3-way catalyst, non-conventional activated Alumina(Al <sub>2</sub> O <sub>3</sub> )	24, 100, 150°C	4 L/min	AC high voltage supply	25kV	130pps	0 – 100 J/L

Rajamikanth and Sushma[103]	2006	DBD reactor / Combined DBD reactor with adsorbent	Diesel engine exhaust at various loads	BaTiO <sub>3</sub>	Room temp.	4 L/min	Pulse generator	25kV	130pps	-
Koga et al. [88]	2006	Corona reactor	engine exhaust gas and Simulated gas (N <sub>2</sub> /O <sub>2</sub> /NO/NO <sub>2</sub> /H <sub>2</sub> O /CO <sub>2</sub> /C <sub>3</sub> H <sub>4</sub> )	-	-	0.5-20 L/min	DC high voltage power supply	15kV	-	0-2500 J/L
Rajamikanth and Srinivasan[104]	2007	DBD reactor / Combined DBD reactor with catalyst and adsorbent	Diesel engine exhaust at various loads	Adsorbent: activated charcoal, molecular sieves MS-13X, activated alumina / catalyst: alumina	24, 100, 150°C	4 L/min	AC high voltage supply	25kV	130pps	0 – 100 J/L
Vinogradov et al. [107, 108]	2007 2008	Corona reactor	Diesel engine exhaust	-	25°C	8 L/min	DC high voltage supply / pulse supply	50kV	1000Hz	0 – 140 J/L
Rajamikanth and Sinha [75, 109]	2008	DBD reactor / Combined DBD reactor with adsorbent	diesel engine exhaust at various loads and Simulated gas (NO/N <sub>2</sub> /O <sub>2</sub> ), Diesel engine exhaust at various loads	MS-13X/carbon molecular sieves(CMS)/activated charcoal	Room temp.	2 L/min	Pulse supply	25kV	130pps	0 – 190 J/L
Srinivasan et al. [46]	2009	Packed bed DBD reactor	Diesel engine exhaust at various loads	-	Room temp.	2 L/min	DC/ AC high voltage supply /pulse supply	25kV	130pps	0 – 190 J/L
Rajamikanth et al. [110]	2009	DBD reactor / Combined DBD reactor with catalyst	Diesel engine exhaust at various loads	Commercially available catalytic converter	Room temp.	2-4 L/min	AC high voltage supply /AC high voltage supply (solar powered battery) / pulse supply	16kV for AC, 25kV for pulse	50Hz for AC, 12.2kHz for AC (solar), 87pps for pulse	90 J/L
Mohapatro et al. [111]	2011	Cross-flow DBD reactor	Diesel engine exhaust at load 27%	-	-	2-25 L/min	Pulse supply	20kV	75pps	0 – 550 J/L

## **7. Conclusion**

As presented in this review, non-thermal plasma has been shown to have promising potential for the removal of NO<sub>x</sub> from exhaust gases. Many studies have been conducted in order to improve the existing technologies and to develop new ways to increase the performance of NTP. Various combinations of NTP with catalyst and adsorbent have also been initiated in order to increase the NO<sub>x</sub> removal efficiency. Study of the published papers indicates that pulse power technology is more efficient for generating the plasma, and has increasingly been applied in recent years. Furthermore, combining NTP with a catalyst or adsorber while using a packed bed reactor can be more effective than NTP alone. The NO<sub>x</sub> removal efficiency from the exhaust gas in diesel engine is higher than simulated gases due to the presence of carbonaceous soot in the emission gas. Most of the presented studies are not beyond a laboratory scale. There are also some contradictions in some aspects of NTP, such as what polarity is optimum for NO<sub>x</sub> removal. Regarding the existing publications, energy consumption is the main challenge of using this technology. More comprehensive researches should be considered to improve the electrical aspects and also reactor design. Additionally, even fewer studies investigated the economics of NTP technology. In the view of global health and environmental concerns and increasingly stringent emission regulation restrictions, NTP technology is predicted to become commercially viable in the future, and therefore, more research is a necessity in order to make this technology widely available.

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