

STUDIES ON GAS-PHASE OXIDATION OF NITRIC OXIDE USING OZONE

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STUDIES ON GAS-PHASE OXIDATION OF NITRIC OXIDE USING OZONE

by

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List of Symbols

		Units
	Mean of Error	-
	Standard Deviation	-
T	Temperature	°C @ K
dC_p/dt	Differential of C_p polynomial with respect to t	mg/L.min
r_i	Reaction Rate	mg/L.min
k_i	Rate Constant	$\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$
τ	residence time	s
V	volume	cm^3
v	volumetric flow rate	cm^3/min
C_{ozone}	Concentration of ozone	mol/cm^3
C_{NO}	Concentration of NO	mol/cm^3
q_{ozone}	Flowrate of ozone stream	cm^3/min
q_{NO}	Flowrate of NO stream	cm^3/min
V	flow velocity	m/s

List of Abbreviation

%[NO]	Percentage conversion of NO
ACGIH	American Conference of Governmental Industrial Hygienists
ANOVA	Analysis of variance
CCD	central composite design
CO	Carbon Monoxide
DOE	Design of Experiment
EQA	Environmental Quality Act
FI	factor interaction
H ₂ O	Water
HNO ₂	Nitrous Acid
HNO ₃	Nitric Acid
HC	Hydrocarbon
IDLH	Immediately Dangerous to Life and Health
K	Kelvin
N ₂	Nitrogen
N ₂ O	nitrous oxide
NH ₃	Ammonia
NIOSH	National Institute for Occupational Safety and Health
NO	Nitric Oxide
NO ₂	Nitrogen Dioxide
NO _x	Oxide of Nitrogen
O ₂	Oxygen
O ₃	Ozone

ODE	ordinary differential equation
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Level
PFR	plug flow reactor
PM	Particulate Matter
Ppm	Parts per million
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
SO ₂	Sulphur Dioxide
TIC	temperature indicator controller
TLV	Threshold Limit Value
TWA	time-weighted average
VOC	volatile organic compounds

KAJIAN PENGOKSIDAAN NITRIK OKSIDA DALAM FASA GAS DENGAN MENGGUNAKAN OZON

ABSTRAK

Pembebasan oksida-oksida nitrogen (NO_x) seperti nitrik oksida dan nitrogen dioksida merupakan satu masalah dalam kawalan pencemaran alam sekitar. NO_x adalah sukar untuk disingkirkan di dalam penjerap basah kerana kebanyakannya berada dalam bentuk NO, yang mana kebolehlarutannya sangat rendah. Sekiranya NO boleh ditukarkan kepada keadaan oksida yang lebih tinggi seperti NO₂, HNO₂, dan HNO₃, maka spesies-spesies ini boleh disingkirkan dengan penjerapan basah. Tindak balas pengoksidaan nitrik oksida pada fasa gas dengan menggunakan ozon dikaji dalam kajian ini. Kajian eksperimen dalam satu reaktor aliran palam pada tekanan atmosfera dengan julat suhu tindak balas berbeza-beza daripada 30 hingga 300°C, dengan masa mastautin dari 0 hingga 300s dan nisbah ozon kepada NO adalah 0.5 hingga 1.5 telah dijalankan. Sebagai tambahan, satu kajian dijalankan dengan lembapan dalam salur masuk NO dengan tujuan untuk menentukan sama ada terdapat sebarang kesan penguasaan lembapan terhadap tindak balas pengoksidaan NO dengan ozon.

Sebuah model matematik dibentangkan untuk menghuraikan teori proses pengoksidaan dengan menggunakan pengaturcaraan perisian Matlab. Kesan faktor-faktor seperti masa mastautin, nisbah O₃/NO dan suhu terhadap peratus penukaran NO telah dikaji menggunakan model dengan dua set data. Simulasi model dengan persamaan kadar Atkinson menunjukkan bahawa

penukaran nitrik oksida bertambah dengan masa mastautin. Bagaimanapun nisbah O_3/NO dan suhu optimum adalah masing-masing pada 1.5 dan $200^\circ C$. Hasil-hasil simulasi model menggunakan data daripada Atkinson menunjukkan keserasian data dengan keputusan ujikaji. Satu kajian telah dibuat untuk pengenalpastian nisbah parameter O_3/NO dan suhu untuk pengoptimuman panjang jarak/masa. Kajian ini menunjukkan nisbah O_3/NO pada 1.5 dan suhu pada $200^\circ C$ sangat sesuai untuk optima panjang jarak.

Rekabentuk Ujikaji (DOE) digunakan bagi menilai kesan-kesan suhu, masa mastautin dan nisbah kepekatan O_3/NO terhadap penukaran NO. Hasil nitrogen dioksida dimaksimumkan dengan menentukan keadaan optima menggunakan kaedah permukaan sambutan. Keadaan tindak balas optima adalah pada suhu $224^\circ C$, masa mastautin 158s dan nisbah kepekatan O_3/NO 1.4 yang memberi peratusan penukaran NO pada 98%.

STUDIES ON GAS-PHASE OXIDATION OF NITRIC OXIDE USING OZONE

ABSTRACT

Emission of nitrogen oxides (NO_x) such as nitric oxide and nitrogen dioxide presents a significant problem in environmental pollution control. NO_x is difficult to remove in wet scrubbers because most of it is in the form of NO, which has a very low in solubility properties. If NO could be converted to higher oxidized states such as NO_2 , HNO_2 , and HNO_3 , then these species could be removed by wet scrubbing. Thus, the main aim of this work is to study the gas-phase oxidation reaction of nitric oxide using ozone. Experimental works were carried out in a plug flow reactor at atmospheric pressure with reaction temperatures varying from 30 to 300 °C, residence times ranging from 0 to 300s and ratios of ozone to NO ranging from 0.5 to 1.5 were carried out. In addition, a study is carried out with the presence of moisture in the inlet NO in order to ascertain whether there is any effect of dominance of moisture on oxidation reaction of NO with ozone.

A mathematical model is presented to describe this oxidation process theoretically using Matlab programming software. The effect of factors namely residence time, ratio of O_3/NO and temperature on percentage conversion of NO were studied using the model with the two sets of data. The simulation of the model with rate equation of Atkinson showed that the conversion of NO increased with residence time. However optimum for ratio of O_3/NO and temperature were observed at 1.0 and 200°C respectively. The results of simulations of the model using data from Atkinson showed compatibility of data

with experimental results. A study was made for identification of parameters ratio O_3/NO and temperature for optimization of the traverse length/time. This study showed a ratio of O_3/NO of 1.5 and temperature of $200^\circ C$ suited well for optimum traverse length.

Design of Experiment (DOE) was used to assess the effects of temperature, residence time and concentration ratio of O_3/NO on the conversion of NO. The yield of nitrogen dioxide was maximized by determining the optimum conditions using response surface methodology. The optimum reaction conditions were reaction temperature of $224^\circ C$, residence time of 158s and concentration ratio of O_3/NO of 1.4 which give the percentage conversion of NO of 98%.

CHAPTER ONE

INTRODUCTION

1.1 Nitric Oxide in the Environment

Oxides of Nitrogen (NO_x) consist mainly of nitric oxide (NO) and nitrogen dioxide (NO_2) in the form of gases, which are widely accepted to be harmful entities in the environment. The NO molecule is a free radical, which is known for its high reactivity. It reacts with oxygen (O_2) in air to form NO_2 . From a thermodynamic perspective, NO is unstable with respect to O_2 and nitrogen (N_2) although its conversion to O_2 and N_2 is very slow at ambient temperature in the absence of a catalyst. Since the heat of formation of NO is positive, thus its formation is an endothermic reaction. Therefore the synthesis of NO from molecular N_2 and O_2 requires heat at elevated temperatures ($>1000^\circ\text{C}$). A major natural source of this conversion is lightning. On the other hand, human-related sources are from the use of internal combustion engines that has drastically increased the presence of nitric oxide in the environment (Rafia, 2003). However catalytic converters have been installed in cars to minimize NO formation by catalytic reversion to O_2 and N_2 . NO in the air may be converted to nitric acid causing the acid rain phenomenon. Furthermore, both NO and NO_2 contributes to the depletion of ozone layer.

The National Institute for Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH) have set the permissible maximum exposure level for work place safety standard, based on a typical 10-hour work day (time-weighted average) or TWA, known as Threshold Limit Value (TLV) at 25ppm or 30 mg/m^3 for NO. The

Occupational Safety and Health Administration (OSHA) indicates an 8-hour TWA Permissible Exposure Level (PEL) of also 25ppm for NO (OSHA, 2005). Immediately Dangerous to Life and Health (IDLH) level for adult humans is 100 ppm. At higher concentrations (60-150 ppm), NO can cause immediate irritation to the nose and throat, with coughing and burning in the throat and chest (EPA, 1979). Some 6-24 hours after exposure, a sensation of tightness and burning in the chest develops, followed by shortness of breath, sleeplessness, and restlessness.

Ground-level Ozone (smog) is formed when NO_x and volatile organic compounds (VOCs) react in the presence of sunlight. People with lung diseases such as asthma, and people who work or exercise outside are susceptible to the adverse effects such as damage to lung tissue and reduction in lung function. Ozone (O₃) can be transported by wind currents and can cause health impacts far from the original sources. Other impacts from the ground-level ozone include damaged vegetation and reduced crop yields.

NO reacts with other substances in the air to form acids that fall to earth as rain, fog, snow or dry particles. Some may be carried by wind for hundreds of miles. The damages cause by acid rain included deterioration of cars, buildings and historical monuments; and causes lakes and streams to become acidic and unsuitable for many aquatic lifeforms.

One member of the NO_x gases, nitrous oxide or N₂O, is a greenhouse gas. It accumulates in the atmosphere with other greenhouse gasses, causing a

gradual rise in the earth's temperature. This will lead to increased risks to human health, a rise in the sea level, and other adverse changes to plant and animal habitat.

1.2 Formation Process of Nitric Oxide.

Three processes have been identified for the formation of nitric oxide: fuel nitric oxide, prompt nitric oxide, and thermal nitric oxide (Alexander, 2001) which are explained below.

a) Fuel nitric oxide is formed as a result from the nitrogen content in the fuel. Many fossil fuels consist of a number of elements, which may include N_2 . Once this fuel is burnt, the nitrogen in the fuel reacts with oxygen at high temperatures to form NO_x .

b) Prompt nitric oxide is formed directly at the flame front. As fuel is burned in internal combustion engines (e.g., it is injected into the burning chamber of the diesel engine), a flame front travels through the combustion chamber. As air is present at the flame front which is also the location of the highest temperature (close to the adiabatic flame temperature), N_2 in air reacts with oxygen and thus NO_x is formed.

c) Thermal nitric oxide is formed as a result of high temperatures in the non-reacting zone. As the formation of NO_x is an exponential function of temperature, the local temperature plays an important role in the production of nitric oxides. During or after a combustion reaction, nitrogen is present in all

parts of the combustion chamber (as it is a major part of air). As the temperature rises, this nitrogen reacts with excess air to form NO. As an example, NO formation in Diesel engines is a significant problem.

Thermal nitric oxide contributes the largest portion to the total NO_x formed, while prompt nitric oxide is of minor magnitude. On the other hand fuel nitric oxide can vary significantly as nitrogen might not be present in all types of fuels. However, regardless of the types of NO, an emission of NO is definitely an environmental problem. Based on the facts presented above, there is a strong need to reduce NO emission using appropriate technology.

1.3 Sources of NO Gases Released to the Environment

In Malaysia, the NO gas comes mostly from energy use (Rafia *et. al.*, 2003). The main contributors to increasing atmospheric NO concentration are mobile sources, stationary sources, and open burning sources. For the past 5 years, emissions of NO from mobile sources (i.e., motor vehicles) have been the major source of air pollution, contributing to at least 70.75% of the total air pollution. Emissions from stationary sources generally have contributed 20.25% to the air pollution, while open burning and forest fires have contributed approximately 3.5% (DOE, 2001). According to the Department of the Statistics (Goh, 2006), Malaysia, in 2004, the percentages, of the NO emission load by type were motor vehicles, 83%; power plant, 6%; industrial, 7%; and other sources, 4%; (Figure 1.1).

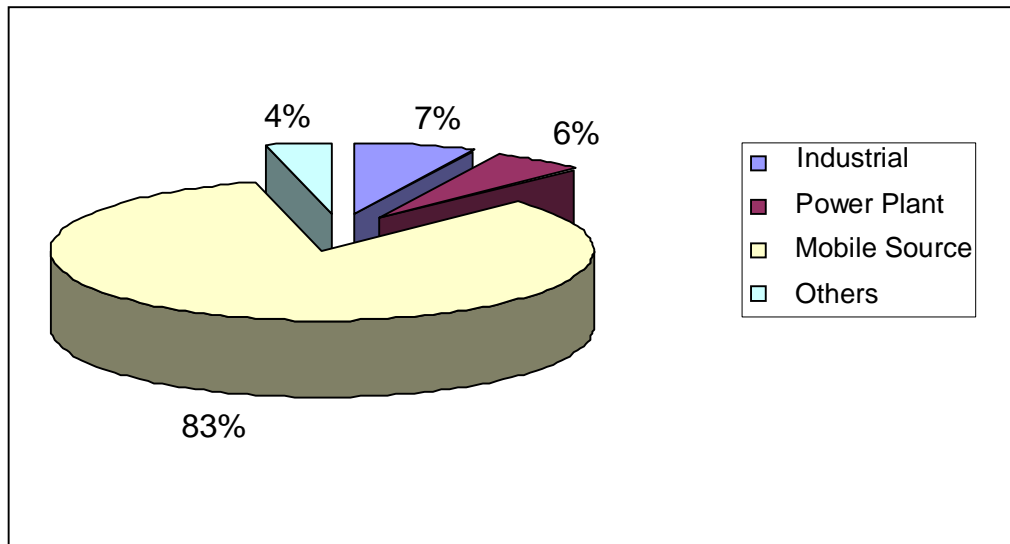


Figure 1.1: Sources of nitric oxide in Malaysia. (Goh, 2006)

Mobile sources, which include motor vehicles such as personal cars, commercial vehicles, and motorcycles, are the main contributor to air pollutions. New environmental regulation amendments to the Environmental Quality Act (EQA) and the phase-out of leaded gasoline sales could reduce the emission. Significant first steps toward implementing Malaysia's Clean Air Plan was achieved in 1996 with the approval of two regulations that were designed to reduce emissions from mobile sources. The Environmental Quality (Control of Emissions from Diesel Engines) Regulations 1996 and the Environmental Quality (Control of Emissions from Petrol Engines) Regulations 1996 focus on prevention by controlling vehicular emissions at the manufacturing or assembly stage (DOE, 2001). The emissions standards in the new regulations have been based on the European Economic Commission on Standards.

The exhaust gases, which are discharged from the diesel engine, contain several constituents that are harmful to human health and to the environment.

Table 1.1 lists the typical toxic compounds and its range of concentration in diesel fumes. The values at the lower end are for new, clean diesel engines, while the values at the higher end are characteristic for older equipment. The emission of NO_x, which consist of nitric oxide and nitrogen dioxide range from 50 to 2500 ppm.

Table 1.1: Emissions from Diesel Engine (Dieselnet, 2006)

Component	CO	HC	PM	NO _x	SO ₂
Units	Ppm	Ppm	g/m ³	ppm	ppm
Range	5-1,500	20-400	0.1-0.25	50-2,500	10-150

Meanwhile, the major harmful emissions from LPG engines, similar to those from other internal combustion engines are carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x). Unlike diesel engines, there are practically no particulate emissions from LPG engines. The ranges of concentration for particular emissions are listed in Table 1.2.

Table 1.2: Emissions from LPG Engine (Dieselnet, 2006)

Components	CO	HC	NO _x
Units	vol. %	Ppm	ppm
Range	0.2 . 2	50-750	250 - 2,000

Out of the above, approximately 80% of NO_x is reported to be nitric oxide (Barber *et. al*, 2001). Table 1.3 presents the typical NO emissions for other combustion system using fossil fuels.

Table 1.3: Typical NO emissions for other combustion system using fossil fuels.

Plant type	Fuel	Typical NO emission (ppm)
Atmosphere Fluidized Bed Combustor (shallow bed) ¹	Coal	300 . 700
Atmosphere Fluidized Bed Combustor (deep bed) ¹	Coal	200 . 400
Chaingrate Stoker ¹	Coal	150 . 250
Underfeed Stoker ¹	Coal	150 . 250
Spreader Stoker ¹	Coal	300 . 400
Pulverised Fuel Burner ¹	Coal	350 . 1000
Pressurised Fluidized Bed Combustor ¹	Coal	150 . 250
Not specified ²	Coal	500 . 1000
Not specified ²	Oil	100 . 500
Not specified ²	Gas	100 . 1000

Emission of NO is therefore a significant problem in Malaysia. NO is formed by many combustion processes, and they are the key ingredient of photochemical smog and acid deposition. Low NO_x burners and other combustion control strategies have achieved a limited reduction of NO_x emissions. In some cases, post-combustion NO_x control is necessary. However, such technology is expensive, being primarily selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR). In addition to high capital cost for SCR, both systems require injection of ammonia (or urea) into the

combustion flue gases. Typically, these processes achieve removal efficiencies of only 80. 90% with SCR and 25. 40% with SNCR (Sexton 2004).

1.4 Problem Statement.

The main component of NO_x (NO and NO_2) in most practical exhaust and flue gases is NO. NO have low solubility, while NO_2 is highly soluble in water. Thus, if NO can be converted into NO_2 , it can then be treated using a wet method and eventually could be removed simultaneously with SO_2 by wet scrubbing.

On if the promising alternative method easily available to convert NO into NO_2 may be the injection of ozone into the exhaust gas. Ozone can be efficiently produced by dielectric barrier discharge (Kogelschatz U., 2003). It has been found that the ozone injected into the exhaust gas reacts fast with NO without producing any harmful by-products in a wide range of temperature before it itself get decomposed into O_2 and O (Mok, 2006b). Furthermore, the oxidation of NO by ozone is more energy efficient than that by the non-thermal plasma process since the reduction of NO_2 back to NO does not occur (Mok, 2004). The ozone treatment of NO to NO_2 is therefore very a promising technology.

1.5 Research Overview

Until now, only limited research works are published on oxidation of nitric oxide using Ozone (Atkinson *et. al.*, 2000; Ishwar, 1995; Mok *et. al.*, 2004; Tomio *et. al.*, 2000). Even though ozone could be used in the oxidation of nitric

oxide, formation of ozone itself is energy consuming and the process needs to be optimized. So far theoretical and subsequent optimization studies have not been satisfactorily carried out. The present study attempts to model using mathematical methods as well as statistical method (DOE), the reaction of ozone with nitric oxide which usually disposed through an exhaust gas pipe or in a chimney. The model thereafter is used to estimate optimized conditions for conversion as well as overall reaction rate. The models are compared with experimental data.

In experimental studies, a NO stream is mixed with ozone together in a tubular reactor. The rate of oxidation of NO is investigated with different operating parameters such as temperature, ratio O_3/NO and moisture content. The effect of temperatures of NO oxidation was studied by varying the temperature from 30°C - 300°C. The effect of residence time was also studied where the residence time was varied between zero to 300 seconds. The effect of ratio O_3/NO is carried out by adjusting the ratio of O_3/NO between 0.5-2.0.

The current modeling work also included the mathematical modeling of the oxidation reaction of NO with ozone. The models were simulated varying the same parameters used in the experiment. Then experimental data were compared with mathematical modeling data that was developed using Matlab R2006b.

The optimization studies were carried out to get the optimum conditions for oxidizing of NO using ozone. The software used for the optimization studies

was Design of Expert (DOE). The model was further used in order to evaluate condition for optimized overall conversion rate which could lead to shorter treatment (exhaust) length.

1.6 Research Objectives

The main purpose of this research is to study the effect of ozone treatment to reduce NO for typical engine exhaust gases. The research was carried out according to the following objectives:

1. To setup an experimental rig for oxidizing NO using ozone treatment.
2. To carry out the experimental studies of the gas-phase oxidation of NO by investigating conversion of NO with different operating parameters such as temperature, ratio concentration O_3/NO , residence time and presence of moisture.
3. To model gas-phase oxidation reactions of NO using ozone and compare with experimental data.
4. To optimize the process parameter of NO oxidation using Design of Experiment (DOE).
5. To evaluate the condition for optimization of overall conversion rate in an exhaust.

1.7 Organization of Thesis.

There are five chapters in this thesis including the current chapter and each chapter gives important information of the thesis.

The next chapter presents, the literature reviews. This chapter presents a review of literature on methods employed for removal of NO. The properties of O₃ and manufactured was also presented. Studies related to ozonation of nitric oxide were also discussed. General methods available and later employed for optimization of experimental data were presented.

Chapter 3 covers the materials and methods used throughout the current study. The first and second sections presented information about materials and chemicals used and a general description about the equipments used respectively. The third section describes the experimental rig. Later the experimental measurements and procedures are described. The Details of mathematical modeling method and the optimization method using DOE and other methods are presented.

Chapter 4 presents the experimental results together with the discussion. The first section presents the experimental results for effects of NO oxidation with ozone. Section two presents the discussion on application using DOE and optimization studies thereof. The third section discusses the results of mathematical modeling for the effect of parameters on NO oxidation using ozone. The mathematical model experimental result, which is finally used to evaluate parameters for optimizing the overall conversion is presented at the end.

Finally, Chapter 5 presents the conclusions and recommendations related to the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Methods of Removal of Oxides of Nitrogen.

As seen from previous chapter, mobile sources emit about 83% of NO in Malaysia. The emission requirement necessitates the use of exhaust treatment devices consisting of a catalytic system for oxides of Nitrogen removal. Various catalytic technologies such as lean oxides of Nitrogen catalyst (Tonkyn *et.al.*, 2003), oxides of Nitrogen trap (Asanuma *et. al.*, 1999), selective catalytic reaction (SCR) (Koebel *et. al.*, 2000) and plasmacatalyst (Brøer *et. al.*, 2000) have been tried to reduce the NO_x emission level. Among the oxides of Nitrogen removal technologies, the SCR is well established, and is considered as the most promising way to reduce oxides of Nitrogen (Koebel *et. al.*, 2000; Hug *et. al.*, 1993).

Methods of control oxides of Nitrogen can be categorized as pre- and post-combustion methods. In applications involving internal combustion engines, oxides of Nitrogen control is achieved by a number of techniques such as modification of the compression ratio, equivalence ratio and the use of Exhaust Gas Recirculation (Koebel *et. al.*, 2000). These methods try to keep the combustion temperature low and are classified as pre-combustion techniques. The amount of NO_x reduction achieved through these methods is extremely limited and is insufficient for compliance with the stringent regulations (Eastwood P., 2000). Post-combustion methods (also known as after-treatment

methods) are more effective in this regard and are therefore relatively more popular and are discussed in the following sections.

2.1.1 Post Combustion Methods of Removal of Oxides of Nitrogen.

2.1.1.1 Removal by Reduction of Oxide of Nitrogen.

In several methods, the excessively produced oxides of Nitrogen gases are converted into water and nitrogen via a catalytic converter. In order for the conversion step to function liquid/gaseous ammonium substances are injected into the exhaust gas stream which reacts with NO_x gases inside the ceramic catalytic converter. Nitrogen oxides (NO₂ and NO) react with Ammonia (NH₃) to form water (H₂O) and nitrogen (N₂) (ACEA, 2003).



Vanadium pentaoxide, platinum, iron/chromium oxides and zeolites are among the catalysts that can be used (Giriraj, 2004). The usage of ammonia is critical since it is a very aggressive and poisonous substance. The handling of ammonia is also critical. As a result urea is used for selective catalytic reduction engines. Instead of ammonia, it is slightly less effective but far less hazardous.

2.1.1.2 Removal by Oxidation of Oxide of Nitrogen.

Various processes, including combustion modifications, dry processes and wet processes have been developed to remove NO from flue gas (Adewuyi *et. al.*, 2003; Miessner *et.al.*, 2002; Chen *et. al.*, 2002; Barman *et. al.*, 2006).

Various oxidation methods that are commonly used in the removal of oxides of Nitrogen are discussed below.

(a) Methods using Oxygen.

Hirokazu *et. al.* (1999) studied the chemical kinetics and rate constant of gas-phase oxidation of nitric oxide with oxygen in studies related to inhalation therapy. The studies have been carried out because of the potential toxicity of nitric oxide (NO) and its oxidizing product nitrogen dioxide (NO₂), any system for the delivery of inhaled NO must aim at predictable and reproducible levels of NO and at as low concentrations of NO₂ as possible.

Miessner *et. al.* (2002) have carried out research on the removal of NO_x by plasma-enhanced selective catalytic reduction. In the off-gases of an internal combustion engine running with excess oxygen, non-thermal plasmas (NTPs) have an oxidative potential, which results in an effective conversion of NO to NO₂.

Laurent *et al.* (2003) developed a modelling of the phenomena involving oxygen in the process which was clearly demonstrated as well as promoting conversions during the adsorption of NO_x on trap catalysts. The mechanism of the process is adsorption of NO, O₂ on the platinum sites followed by the reaction between NO₂ and BaO to form Ba(NO₃)₂ on the surface of the catalyst. This formation of barium nitrate is limited by the thermal decomposition reaction which liberates NO in the gas phase

The reaction kinetics of NO oxidation with oxygen and the deactivation behaviour for two Pt/Al₂O₃ catalysts having different dispersions has been investigated by Mulla *et al.* (2006). The reaction was shown to be nearly first order with respect to NO and O₂ and nearly negative first order with respect to NO₂, and the apparent activation energy (E_a) was 81.8±5 kJmol⁻¹. With respect to the fresh catalyst, the sintered catalyst showed a similar E_a (80.9 ± 5 kJmol⁻¹) and apparent reaction orders for NO and NO₂, with a lower O₂ order (0.7 ± 0.04). After the NO oxidation reaction attained steady state, both fresh and sintered catalysts showed an average oxygen uptake of about 1.5 times the number of Pt surface atoms. When the oxygen uptake was increased to the equivalent of two oxygen atoms per surface Pt by a different pre-treatment, the NO oxidation turnover rate decreased by 85% with respect to the original steady-state level.

Cobalt-based catalysts supported on TiO₂ and ZrO₂ were studied for the oxidation of NO to NO₂ in excess oxygen. This research was studied by Matthew *et al.* (2007). NO oxidation was studied as the first step in a two-step catalytic scheme where NO is oxidized to NO₂ and in turn NO₂ is reduced with CH₄ to N₂ under lean conditions. Catalysts were prepared by sol. gel (SG) and incipient-wetness impregnation (IWI) techniques and characterized by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), laser Raman spectroscopy (LRS), and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS).

Gas-phase photo-catalytic oxidation (PCO) of nitric oxide (NO) with immobilized TiO₂ films was studied by Zhongbiao *et. al.* (2007). It was found that the PCO efficiency of the catalyst was mainly dependent on the hydrothermal conditions. The optimal values of hydrothermal temperature and hydrothermal time were 200°C and 24h, respectively. Furthermore, it was also known that the photocatalytic efficiency would decrease remarkably when the calcinations temperature was over than 450°C. Under the optimal conditions (hydrothermal condition: 200°C for 24h; calcinations temperature: 450°C), the photocatalytic efficiency of catalyst could reach 60% higher than that of Degussa P25.

A study of the adsorption and reaction of NO in the presence of oxygen and water vapour on an activated carbon obtained from oil palm shells is presented by Wolfgang *et. al.* (2007). The study is based on the measurement of breakthrough curves, at temperatures between 100 and 150°C, and on the subsequent thermal desorption in a fix bed reactor. The concentration of the gas components, NO, O₂ and H₂O, corresponds to a simulation of a flue gas in a coal fired power plant. The experimental results show that the reactions on this system include the simultaneously adsorption, reduction and catalytic oxidation of NO together with the adsorption of created NO₂. During desorption NO₂ reacts to NO through a reductive desorption process. An acceleration of the NO oxidation occurs when the saturation level of the adsorbed NO is reached, resulting in a maximum on the breakthrough curve. Different adsorbed NO species are formed during the process: one thermal unstable NO, and three thermal stable NO species, NO₂, NO and (NO)₂ dimers, respectively

(b) Methods using Chlorine Dioxide

Chlorine dioxide has been extensively used for oxidation, disinfection, and bleaching of oxides of nitrogen. It was proved promising by Dong-Seop *et. al.* (2006) for the simultaneous removal of SO₂ and NO. It exhibited almost 100% SO₂ removal and 70% NO oxidation.

Another study has attempted to clean up nitric oxide from the simulated flue gas using aqueous chlorine-dioxide solution in the bubbling reactor (Bal-Raj *et. al.*, 2007). Experiments have been carried out to examine the effect of various operating variables like input NO concentration, presence of SO₂, pH of the solution and NaCl feeding rate on the removal efficiency of oxides of nitrogen at 45°C. Complete oxidation of nitric oxide into nitrogen dioxide has occurred on passing sufficient ClO₂ gas into the scrubbing solution.

(c) Methods using Hydrogen Peroxide

Many studies have been carried out for the use of H₂O₂ to oxidize pollutants in flue gas. The oxidation of low concentration volatile organic compounds (VOCs) using H₂O₂ has been reported to be effective in a non-flamable environment (Cooper *et. al.* 1991). Laboratory work of Kasper *et. al.* (1995) has shown that injecting H₂O₂ into heated air spiked with NO oxidized most of the NO to NO₂ and subsequently to HNO₃. Collins *et. al.* (2001) demonstrated 90% conversion of NO (in combustion flue gas) at mole ratios of H₂O₂:NO_x of about 1.0. Kinetic mechanisms of H₂O₂ have enhanced NO oxidation at moderate temperatures were investigated by Chao (1994) based on a mechanism

developed by Miller *et. al.* (1989). Other reaction mechanisms were also proposed to investigate the H₂O₂ enhancement of the oxidation of NO experienced in a pilot plant. A kinetic modelling of the use of hydrogen peroxide to enhance the oxidation of nitric oxide under post flame conditions in the presence or absence of sulphur dioxide has been presented by Piyavadee *et. al* (2005)

Zamansky *et al.* (1996) published results from a comprehensive pilot plant study simulating a large-scale boiler, showing that more than 90% of the NO was converted to NO₂ at a molar ratio of 1.5 of H₂O₂/NO. His work also confirmed that the optimum temperature for the reactions was about 500°C. Several researchers have observed a 97% conversion of NO to oxidation products at 500°C using an H₂O₂: NO molar ratio of 2.6:1, and a 75% conversion with a H₂O₂: NO ratio of 1.6:1 (Kasper *et. al.* 1996). Haywood and Cooper *et. al.* (1998) showed that the peroxide usage ratio could be reduced to less than 1.3:1 while still achieving 90% conversion of NO.

2.2 Ozone

Ozone is formed naturally in the atmosphere, as a colorless gas having a very pungent odor. Ozone, chemically, is the triatomic, allotropic form of oxygen having the chemical symbol O₃ and a molecular weight of 48. Ozone, under standard atmospheric temperature and pressure, is an unstable gas that decomposes readily into molecular oxygen. Ozone has many commercial and industrial applications. It is used commercially in potable and non-potable water treatment, and as an industrial oxidant. Ozone has several significant

advantages over its chemical alternatives (Nutech O₃, Inc, 2006). Among them are:

- Ozone can be generated on-site.
- Ozone is one of the most active, readily available oxidizing agents.
- Ozone rapidly decomposes to oxygen leaving no traces.
- Reactions do not produce toxic halogenated compounds.
- Ozone acts more rapidly, and more completely than other common disinfecting agents do.

Ozone is a very reactive species, which allows for catalytic oxidation reactions to occur close to room temperatures. Ozone rapidly decomposes to oxygen leaving no traces. Ozone has an oxidizing power higher than hydrogen peroxide, chlorine dioxide, oxygen and many other oxidants (Wojtowicz, 1996). Ozone has been chosen as chemical oxidant for NO oxidation (Mok, 2006a). Table 2.1 presents the oxidizing potential of ozone compared with of various oxidants.

Table 2.1: Oxidizing potential of various reagents (Ullmann, 1991).

Oxidizing Reagent	Oxidizing potential (eV*)
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate	1.67
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine gas	1.36
Hypobromous acid	1.33
Oxygen	1.23
Bromine	1.09

*eV = Electronvolt.

2.2.1 Ozone Generation.

Ozone has a half-life of 12 hours or less in the atmosphere and degrades into simple diatomic oxygen as its decomposition product. Because of its relatively short half-life, it is necessary to generate ozone on-site prior to application. The two main methods used in ozone generation are by using UV-light and by corona-discharge (Rice, 1996).

Two types of ultraviolet lamps have been marketed commercially; one mostly providing 254 nanometer (nm) UV lamp and the other one providing mostly 185 nm UV light (Ted Rich, 1994). Air (usually ambient) is passed over an ultraviolet lamp, which splits oxygen (O_2) molecules in the gas. The resulting oxygen atoms (O_1), seeking stability, attach to other oxygen molecules, forming ozone (O_3) (Ozone Solution, 2004).

Ozone generation by corona-discharge is most common nowadays and has many advantages. It is also known as silent electrical discharge. It makes use of oxygen-containing gas passing through two electrodes separated by a dielectric and a discharge gap. High voltage is applied to the electrodes, causing an electron flow through across the discharge gap. These electrons provide the energy to form ozone. To control and maintain the electrical discharge, a dielectric made out in ceramic or glass is used. The excessive heat of the electrodes is often cooled by cooling water or by air (Lenntech, 2004). Figure 2.1 shows a basic ozone generator using corona discharge method.

The general reaction of conversion of oxygen to ozone is as shown in equation 2.4 below.



This reaction is endothermic and requires a considerable input of energy. Advantages of the corona-discharge method are greater sustainability of the unit, higher ozone production and higher cost affectivity.

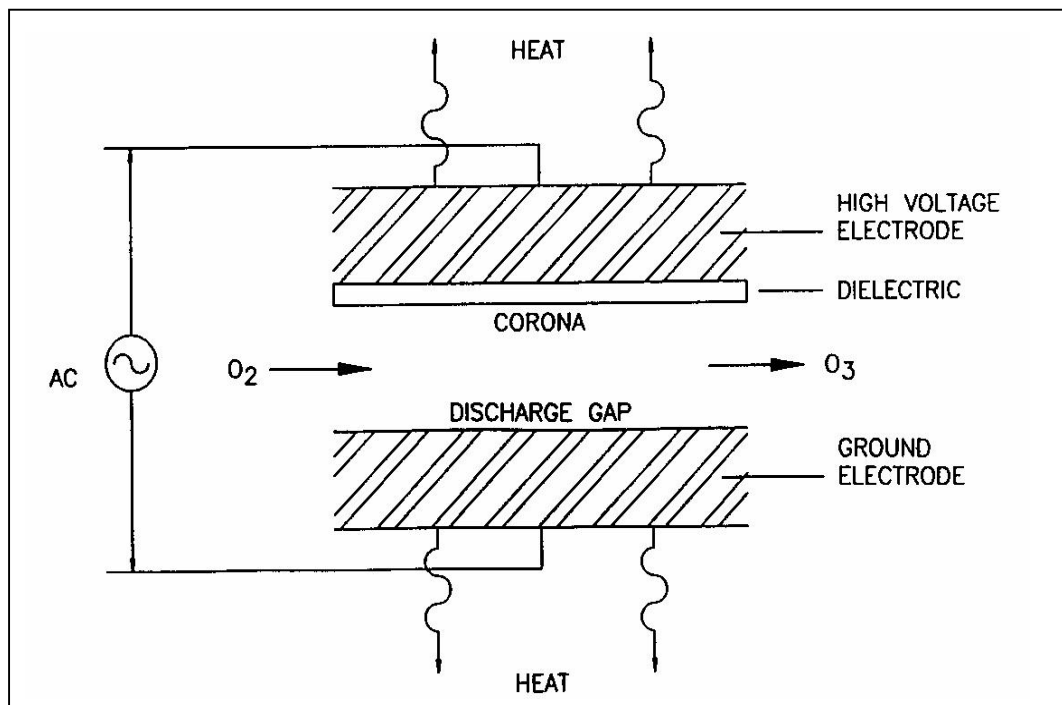


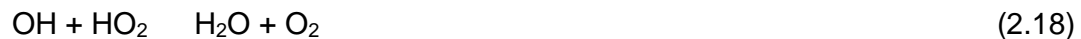
Figure 2.1: Basic Ozone Generators using corona discharge method.

2.3 Ozonation of Nitric Oxide.

The overall reaction of NO with ozone can be presented by the sample reaction given below.



However, Ishwar (1995) has independently examined the features of a process reaction of NO at low temperatures by ozone. A stream representative of NO_x-laden flue gas is introduced into a 1000 cm³ volume of perfectly stirred reactor (PSR) at 1 atm and 300 K. Different amounts of ozone were added to the flue gas in order to conduct a parametric investigation. The process is modeled employing the reactions set and simulated in a PSR. The related reactions considered in his investigation are presented below.





Ishwar (1995) reported that the above low-temperature reaction set involving NO_x is different from that at pertinent at high temperatures, since different temperature regimes lead to separate pathways during chemical processes. He concluded that removal of NO due to ozone oxidation occurs largely through the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, The oxidation of NO to NO_2