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Plasma induced catalytic removal of nitric oxide from waste gases

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Removal of Nitric Oxide
from Waste Gases

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Abstract

Plasma catalytic removal of nitric oxide is being studied as a possible solution for environmental pollution of nitric oxide. The method being used is a combination of a catalytic process and a low temperature or non-equilibrium plasma treatment on waste gases. The plasma is brought to existence by a high electric field. The free electrons in the plasma have a much higher temperature than the surrounding gas molecules and can excite the gas molecules in the waste gas. The formed vibrationally excited gas molecules and radicals should enhance removal reactions of the nitric oxide on the catalyst. The advantage of using a low temperature plasma is that one does not need to heat the complete gas mixture.

The experiments are performed in three different reactors. The first reactor is the "fixed bed" reactor and consists of a quartz tube containing a fixed catalytically active bed with in the centre an electrode. This reactor is also used without the fixed bed. The two other reactors do not have catalytic support. The "capillary" reactor consists of two electrodes in a quartz capillary, with the discharge axial to the gas flow. The third reactor is the "gliding arc" reactor and consists of two diverging electrodes in the gas flow direction. The effects of different important parameters for the nitric oxide removal reaction are determined: the energy input, temperature effects, catalyst type and particle size. The influences of some important gases are determined: nitrogen, oxygen, water vapour. Also, the effect of some reductants is determined: hydrogen, methane, hexane and iso-octane.

From the experiments great importance of radicals is learned. In combination with a catalytic bed nitrogen radicals are important for the reaction. In the empty "fixed bed" reactor •OH and •O radicals appear to be necessary for a reaction to occur. No evidence was found for the importance of vibrationally excited molecules.

A 90% removal of nitric oxide can be obtained in dry nitrogen with 1000 ppm nitric oxide with silica as a catalyst for energy costs of 120 eV/NO. The reaction products are nitrogen and oxygen. Water vapour and oxygen have a bad influence on the reaction: 2 to 3 times higher energy costs for a 2 to 3 times lower conversion. In the empty "fixed bed" reactor at least 5% water vapour and 3% oxygen are needed for the oxidation of nitric oxide to nitrogen dioxide. Here a conversion of 90% can be reached for 50 eV/NO in nitrogen with 1000 ppm nitric oxide. When γ-alumina is used as a catalyst a plasma induced adsorption is observed. For 50 eV/NO nitric oxide can be completely reaction adsorbed as nitrates on the γ-alumina surface until it is saturated. Desorption of nitric oxide and nitrogen dioxide occurs at 400 °C. The capillary reactors produce nitric oxide in presence of oxygen. In pure nitrogen with 1000 ppm nitric oxide a complete conversion can be obtained for 500 to 1000 eV/NO.
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Preface

In front of you, you find my graduation work, done at the Eindhoven University of Technology from February 1994 to February 1995. At the end of my education I wanted to do something different than pure chemistry. At the department of inorganic chemistry my eye fell on a subject with contact persons at the faculty of electrotechnical engineering. I did not understand the terms of the subject yet, but I thought it would be a perfect way to graduate on this multi disciplinary subject of plasma induced catalysis and it sure was. Now, a year later, I learned a lot like: most people at the faculty of electrotechnical engineering are physicists, waterskiing, physicists make calculations for each molecule where chemists only start at $6 \cdot 10^{23}$ molecules, Belgians do drink a lot, both car and motor driving, a lot about creativity with electrotechnical equipment, everything about computer graphic formats (I used CGM), and of course all I wrote in this report.

I could not have done all the work alone. Among all the people who helped me to survive the quest of my graduation like Huub, Ad, Loek, Herman, Annemiek, Vadim, Frank, Yves, Eddy, professor Rutgers, professor van Santen, my housemates all my other friends and my parents. I would like to thank a few people especially: Ruud van Hardeveld for his enormous knowledge about the subject and forcing me to finish the project, Marnix Tas, my direct coach, with his enormous fascination to work, his even more enormous creativity to perform experiments with his "Marnix reactors" and his endless stream of perfect recommendations and finally Barend Franco, my roommate for a year with which I joined the good times I had at the faculty. During the year I had different conquests with him, unfortunately for him I won the last.

The work done is a part to the promotion of Marnix Tas and is made financially possible by DSM. I wish Marnix good luck with his promotion.
Chapter 1

Introduction

In today's world, environmental problems are considered very important. Billions of dollars are being invested, to solve these problems. The decrease of the ozone layer, the greenhouse effect and acid rain are important problems of today.

The nitrogen oxides are one of the malefactors in air pollution. Eight different nitrogen oxides are known, but only three are normally detected in the atmosphere. Nitrous oxide (N₂O) is a colourless, non-flammable, non-toxic gas with a slightly sweet taste and odour. Nitric oxide (NO) is also colourless and non-flammable, but it is odourless and harmful for the lungs. Nitric oxide can be oxidised to nitrogen dioxide (NO₂). Nitrogen dioxide is a reddish-brown, non-flammable, very toxic gas and characterized by a strong choking odour [1]. Nitric oxide and nitrogen dioxide are generally grouped together and called NOₓ. Both nitrogen dioxide and nitric oxide are stable in the atmosphere.

Nitric oxide is produced in air enriched combustion processes. Nitric oxide is formed from nitrogen and oxygen at high temperatures (> 800 °C). It is also formed from nitrogen containing compounds in coal and fuels. Flue gases contain besides typically 200 to 1500 ppm nitric oxide, also nitrogen, 0 to 6% oxygen, 10 to 15% carbon dioxide, 7 to 10% water vapour and, depending on the fuel, sometimes more than 1000 ppm sulphur dioxide.

Combustion processes are not the only sources of air pollution by nitric oxide. Chemical plants, that manufacture nitric acid, are another [2]. In the nitric acid manufacturing, problems arise where one nitric oxide molecule is regenerated from three reacted nitric oxide molecules (eq. 1.1 and 1.2).

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]  \hspace{1cm} (1.1)  
\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \] \hspace{1cm} (1.2)
The rate of reaction 1.1 decreases quickly at low nitric oxide concentrations, because it is second order in nitric oxide. Exhaust gas of a modern nitric acid plant consists of about 100 ppm nitric oxide, 70 ppm nitrogen dioxide, 3% oxygen, nitrogen and only 0.4% water.

The reaction 1.1 in a heterogeneous reaction in water aerosol also causes acid rain. In the atmosphere nitric oxide oxidises to nitrogen dioxide which reacts further to nitric acid. The reaction of nitric oxide with -OH radicals to HNO₂ is important in atmospheric chemistry [3]. The last reactions occur higher in the troposphere.

A principal source of manmade nitrogen oxides results from the combustion of fossil fuels in power plants, heating equipment and combustion engines. Unburned hydrocarbons and nitrogen oxides are responsible for series of photochemical reactions in the atmosphere, which under certain conditions can cause smog. Nitric oxide oxidises the formed carbonic acids to aldehydes, which cause the harmful compound of smog. The nitric oxide is recovered from the nitrogen dioxide by sunlight higher in the troposphere [4] [5].

Nitric oxide also attacks the ozone layer. The main part of the ozone layer is in the stratosphere, at a height between 15 and 50 km. After a reaction with ozone (eq. 1.3), nitric oxide is regenerated in a chain reaction (eq. 1.4) and is therefore very noxious [6] [7].

\[
\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2 \\
NO_2 + O & \rightarrow NO + O_2
\end{align*}
\]

New research suggests that besides nitric oxide, nitrous oxide causes even more damage to the ozone layer [3]. The concentration nitric oxide is higher in the stratosphere than in the troposphere. Diffusion of nitric oxide to the ozone layer in the stratosphere is not possible. Nitrous oxide is destroyed by ozone in the stratosphere and forms 50% nitric oxide, and 50% nitrogen and oxygen (reaction 1.5 and 1.6).

\[
\begin{align*}
O_3 &= O_2 + O \left(^1D\right) \\
N_2O + O \left(^1D\right) &\rightarrow 2NO \text{ or } N_2 + O_2
\end{align*}
\]

To reduce the NOₓ emission, two routes can be followed. The first method is the development of cleaner combustion processes that give cleaner waste gases. The second possibility is the removal of the NOₓ from the waste gas. Thermodynamically nitric oxide would react to nitrogen and oxygen in the atmosphere at lower temperatures, but the activation energy barrier is too high for the reaction to occur. The second possibility, the removal of nitric oxide from waste gases, has been studied in the present project. The process that is going to be used is a combination of two known pollution control techniques.

The first process is the catalytic reduction of nitric oxide by reductants, like ammonia or hydrogen. The catalyst lowers the activation energy for the exothermic process of reducing nitric oxide. The catalytic reaction only occurs above 350 °C and is the most used method at the moment. It is a very energy intensive method when applied to the exhaust gas of the nitric acid plant. The temperature of
the waste gas from a nitric acid plant is only 0 °C and has to be heated. However, the catalytic cleaning of the exhaust gases from automotives is successful. The exhaust gas has a higher temperature and also contains reducing components like carbon monoxide. Only initially, with a cold start, the catalyst does not work because of the low temperature.

The second technique, an electrical technique, is a pulsed corona discharge treatment of the flue gas. This new technique generates radicals in the flue gas, which can react with nitric oxide. The reactions are mainly chain reactions with ·OH radicals [8]. This method converts NOx into nitrates, which are separated from the flue gas as solid salts. The pulsed corona technique can also be used for simultaneous conversion of SOx to solid sulfates. The advantage of this technique is, that it can be executed at low temperatures. The disadvantage is the energy consumption in the high voltage power supply. For industrial purposes, the high voltage pulse circuits with a larger power are, as yet, not very efficient, reliable and payable.

The present research aims the removal of nitric oxide by a combination of a corona discharge and a catalyst. A corona discharge produces different excited species. Two possible reaction can occur: Either the excited species activate the nitric oxide, which can adsorb at the catalyst, or a homogeneous radical mechanism that is faster than the catalyst reaction leads to nitric oxide removal. The advantages of a plasma catalytic removal of nitric oxide are the use of low temperature waste gases and the lower activation energy of the catalytic reaction. More on the hypothesis of the plasma induced catalytic reaction can be found in chapter 2.

In chapter 3 a model is treated that describes the relation between the energy input and the nitric oxide conversion. The model is used to compare measurements with different energy inputs. The equipment used for the experiments is described in chapter 4. Also the three reactors used are described.

The research started with a schematic determination of important parameters. The influences of the catalyst bed type, nitrogen, oxygen and water vapour concentrations are very important to know. Also the total energy input and the temperature dependence are determined. Reductants, like hydrogen or methane can be added to reduce the nitric oxide. The experimental results of the variation of parameters are described in chapter 5. Finally, the experimental results are combined in chapter 6, the conclusion of the research. The chapter ends with recommendations for further research.
Chapter 2

Hypothesis of Plasma Induced Catalytic Reactions

In this chapter the hypothesis of the present study on nitric oxide removal is introduced. The hypothesis is based on the combination of catalysis on one side and plasma induced reactions in the gas phase on the other side.

A catalyst lowers the total activation energy for a reaction. It offers an alternative reaction route, which consists of several elementary reactions with relatively low activation energies. In heterogeneous catalysis, gas molecules are adsorbed at a surface. At the catalytic surface the molecules react. After the reaction they desorb from the surface. The different reaction steps have their own activation energies. The activation energies are low compared to the activation energy of the homogeneous reaction. As a consequence, the desired reactions occur at lower temperatures. More about catalysis is written in section 2.1.

Sometimes one desires a reaction at a very low temperature ( < 10 °C). The activation barriers of catalytic reactions can be even too high for that low temperatures. Other ways have to be found to get over the reaction activation energy barriers. Also the desorption must be enhanced to keep a clean reaction surface. The use of a low temperature plasma is a possibility to enhance catalytic reaction at low temperatures. A plasma is an ionised gas containing all kinds of excited species, ions and free electrons. The plasma may also be used to get over the activation energy barriers of one or more of the different reactions steps of a catalytic reaction. More about the low temperature plasma can be found in section 2.2.

Our aim is to let excited gas molecules react at the catalytic surface. This reaction has to remove nitric oxide from waste gases. Nitrogen molecules will be vibrationally excited by a non-equilibrium plasma. The waste gases contain only ppm's of nitric oxide. Vibrationally excited nitrogen excites the nitric oxide vibrationally. Vibrationally excited nitric oxide should increase its reactivity towards adsorption on the catalyst and react at the surface to nitrogen and oxygen. The problem may be that the relaxation time for the vibrationally excited molecules is too short. They can be quenched by
collisions, but not very easily. The question is if enough excited nitric oxide molecules can reach the surface.

A reductant can be added to help the reaction. This can work in two ways. Normally oxygen atoms are difficult to remove from the catalyst surface at low temperatures. Hydrogen or hydrocarbons enhance the removal of oxygen atoms by formation of water and/or carbon dioxide. On the other hand reductants can burn the oxygen from the gas mixture. All waste gases contain oxygen. It is difficult to reduce nitric oxide in an oxygen environment. A solution must be found for this problem.

In new pollution control techniques using coronas, it is known that radicals are very important. Especially ·OH is relevant for the removal of NOx and SOx. It is of interest if and how radicals combined with a catalytic reaction are relevant for the nitric oxide removal.

2.1 Catalysis

A catalyst is used to lower the total activation energy of a reaction. Normally three main reaction steps can be distinguished in heterogeneous catalytic reactions. Firstly, the reactants have to adsorb at the catalytic surface. At the surface the reaction takes place. After the reaction the products desorb. These three steps are shown in figure 2.1 [9].

![Figure 2.1: Schematic representation of a heterogeneous catalytic reaction.](image)

The first step, the dissociative adsorption, usually has the highest activation energy. The adsorption step is rate limiting for the reaction in this case. Catalytic reactions only occur above a certain temperature to get over the first activation energy barrier. Another problem can be the desorption rate. This rate must also be fast enough to keep enough free catalytic sites.

The surface area of the catalyst is very important, because that is the place where the reaction has to take place. Support materials with a high surface area/volume ratio are used for this reason. Well-known support materials are highly porous silica (SiO2) and γ-alumina (Al2O3). Catalytic materials can be dispersed on these support materials. In this way the surface area/volume ratio is optimized for the expensive catalytic materials.
Transition metals like iron, copper, or platinum are a very important group of catalysts. The transition metals are characterized by a valence electron distribution of which the d-band is very important. When an atom or molecule is adsorbed, a bond is created between a metal atom or cluster at the surface and the adsorbate. Interaction occurs when the bonding orbitals are filled. More valence electrons will lead to filling of the anti-bonding orbitals, which causes repulsion [10]. Moving to the right in the periodic system, the bond strength between the adsorbed molecule and the transition metal surfaces decreases, due to the increasing occupation of the d-band. Transition metals can also be dispersed on support material (see section 4.2.1). In section 5.1.5 the use the oxidative form of this type of catalyst is described.

2.2 The Low Temperature Plasma

A plasma is an ionized gas. It contains, besides ions and free electrons, all kinds of excited species. Two types of atmospheric plasmas are the thermal plasma and the non-thermal plasma. The gas temperature of the thermal plasma is many thousands degrees C (\(> 8000\) °C). A non-thermal plasma or non-equilibrium plasma is a low temperature plasma where the free electrons have a much higher temperature than the gas molecules. The advantage of using a non-equilibrium plasma is that one does not heat the complete gas mixture.

The low temperature plasma is generated by a high electric field. The electric field accelerates electrons, which ionizes the gas and excite the gas molecules. With respect to the desired excitation of a molecule the mean electron energy of the plasma is important. The mean electron energy depends on the gas mixture, the electric field and the pressure. The mean electron energy can be written as:

\[
\bar{e} = e \frac{E_{\text{loc}} \lambda_e}{e}
\] (2.1)

In equation 2.1 \(e\) is the elementary charge, \(E_{\text{loc}}\) is the local electric field strength and \(\lambda_e\) is the mean free path of the electron. A high local electric field is necessary for a high electron energy.

A high electric field can give breakdown. This is not desirable because the plasma-arc of an electrical breakdown is thermal. To prevent breakdown, two possibilities can be chosen: Short voltage pulses with a fast voltage decrease or a dielectric barrier (see section 4.2.1). A high density of electric field lines around a point or thin wire of the non-uniform field gap refers to a high local electric field. A discharge can easily start at the point. The intensity of the field strength is much lower at the plane (see fig. 2.2).

The electrons move to the anode and will collide with molecules on their way. In such a collision energy is transferred to the molecule which will be excited or ionized. These collisions are inelastic, because a part of the electron energy is used to excite the gas molecule. The kinetic energy of the electron is transferred to potential energy of the gas molecule. The total charge of the system must be zero. When an electron moves to the anode, it leaves behind a positive ion. The positive ion moves to the cathode, where it collides and can emit a secondary electron. The secondary electrons move to the grounded electrode through the conductive channel formed by the previous ionisation wave and
causes breakdown. When a dielectric barrier is used, the space charge decreases the electric field and no secondary electrons can be formed. Breakdown is prevented. Another possibility is use of high voltage pulses with a short duration time. The discharge starts immediately after the voltage rise but cannot develop to a thermal plasma because of the rapidly decreasing applied voltage. The advantage of these solutions to prevent breakdown is that a higher electric field can be used which gives a higher mean electron energy (eq. 2.1) [8][11].

In the inhomogeneous electric field, streamer coronas and glow discharges can occur. Electronegative molecules have a positive effect on the streamer corona in our case. These molecules miss one or two electrons in the outer shell and form stable negative ions. This formation of negative ions by electron capture is called attachment. Attachment causes a lower charged ion particle velocity which prevents breakdown.

When a dielectric barrier is used, the discharge is called a silent or dielectric discharge. The mean electron energy in dry air at the head of a corona streamer is 10 eV and about 1 eV in the tail. A silent discharge has a mean electron energy in dry air of 4 eV and a glow discharge of about 1 eV. At increasing electron energy, different excited species can be formed (see table 2.1).

<table>
<thead>
<tr>
<th>electron energy</th>
<th>temperature of gas</th>
<th>temperature of gas</th>
<th>lowest excited state</th>
<th>highest excited state</th>
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<tr>
<td>momentum</td>
<td>&gt; 0 eV</td>
<td>&gt; 0 eV</td>
<td>0.1-0.2/ν eV</td>
<td>&gt; 13 eV</td>
</tr>
<tr>
<td>rotation</td>
<td>&gt; 0 eV</td>
<td>&gt; 0 eV</td>
<td>0.1-0.2/ν eV</td>
<td>&gt; 13 eV</td>
</tr>
<tr>
<td>vibration</td>
<td>0.1-0.2/ν eV</td>
<td>0.1-0.2/ν eV</td>
<td>lowest excited state</td>
<td>highest excited state</td>
</tr>
<tr>
<td>electronic</td>
<td>&gt; 1 eV</td>
<td>&gt; 1 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissociation</td>
<td>&gt; 5 eV</td>
<td>&gt; 5 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ionisation</td>
<td>&gt; 13 eV</td>
<td>&gt; 13 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: typical electron energy values for different excitation states
The momentum and rotational energy of molecules is the temperature of the gas. This type of excitation has a too low energy to be important for plasma induced reactions. It is ineffective to use a plasma as an oven in case of nitric oxide removal.

Vibrationally excited molecules are more important. The relaxation time of for instance vibrationally excited nitrogen, is relatively long (50 μs). Resonant energy exchange is also possible between excited and non-excited molecules. Highly vibrationally excited molecules are formed in the streamer channel. Unfortunately the vibrational energy of highly excited molecules is transferred to ground state molecules around the channel by collisions. Very quickly only lower vibrationally states occur which are less reactive.

Electronically excited molecules have a too short relaxation time (< 1 ns) and are not considered important for surface reactions or even gas phase reactions.

Dissociation can give ions, but normally gives radicals. Radicals have long life times and are also very reactive. Radicals can initiate chain reactions. In flue gas cleaning and also in our case, great importance is proven for ·OH radicals [Bibliography].

Ionisation only occurs at the highest electron energies. The ion recombination rate is too high because of the long range coulomb interaction. At low temperatures ions have a very life time in the gas phase and are not considered important for plasma induced reactions [11]. Ions are important for the corona discharge.
Chapter 3

The Conversion as a Function of the Energy Input

A theoretical model is developed, to learn more about the influence of the energy input on the conversion. We calculated the nitric oxide conversion as a function of the energy input. The model is based on the simple geometry of a plug flow reactor with a simple kinetic system of reactions under steady state conditions.

We assume that first the nitric oxide conversion will rise linearly with the energy input. However, it will be very difficult to remove the last molecules. Full conversion will be reached asymptotically. With the model experiments with different energy inputs can be compared, but with the same gas composition.

We suppose the reaction takes place in a gas mixture of pure nitrogen containing a low concentration nitric oxide. Only two relevant reactions are considered in the kinetic part of the model: first the reaction of a nitrogen radical with nitric oxide (eq. 3.1) and second the recombination of nitrogen radicals (eq. 3.2) in a three particle collision. The formed oxygen radicals are assumed to combine to molecular oxygen without influencing the nitric oxide conversion. Other reactions with mono-oxygen radicals are considered too slow to contribute significantly because of their low concentration.

\[ \text{NO} + N\cdot \rightarrow N_2 + O\cdot \quad (3.1) \]
\[ 2N\cdot + M \rightarrow N_2 + M \quad (3.2) \]

Equation 3.3 and 3.4 show the reaction rates of reactions 3.1 and 3.2. \( k_1 \) and \( k_2 \) are the reaction rate constants. \([M]\) is the concentration of the bulk gas molecules. The removal rate of nitric oxide is a radical reaction with nitrogen radicals (eq. 3.3). In equation 3.3 the nitrogen radical concentration is the unknown parameter.
The model supposes a plug flow in the reactor. Two gases are added: nitrogen and nitric oxide. The conversion of nitric oxide \((X)\) (or \(X_{NO}\)) can be determined by the mass balance of the reactor. Equation 3.5 denotes the mass balance of a plug flow reactor \([12]\). The nitric oxide removal rate, \(r_{NO}\), is a function of the nitric oxide conversion in equation 3.5. \(V_t\) is the reactor volume, \(F_{NO}\) is the nitric oxide flow. \(V_t/F_{NO}\) is the contact time of nitric oxide in the reactor \([\text{m}^3\text{s/mol}]\).

\[
\frac{dX}{r_{NO}(X)} = \frac{V_t}{F_{NO}}
\]

(3.5)

The nitrogen radical concentration is unknown in the reaction rate of nitric oxide removal. This concentration can be determined by assuming steady state conditions. Under the steady state conditions, the concentration of nitrogen radicals is constant at every position and moment in the reactor. This means that the production rate of nitrogen radicals \(P_{N^*}\) must be equal to the disappearance reaction rate \(D_{N^*}\), (eq. 3.6).

\[
\frac{d[N\mathbf{^*}_t]}{dt} = \frac{P_{N^*} - D_{N^*}}{V_t} = 0
\]

(3.6)

To determine the nitrogen radical production rate a linear relation is assumed with the energy input. By collisions of electrons with a nitrogen molecule, the molecule is split into two nitrogen radicals at an energy threshold \(E_{el}\) equal to the dissociation energy, \(E_{diss}\) [J/mol]. The production term of nitrogen radicals is proportional to the energy input, \(W_{in}\) [W], for every part of energy equal to the dissociation energy (see eq. 3.7). Electrons with a lower energy than the dissociation energy will not dissociate a nitrogen molecule, so the electron energy will be lost. Also a part of the electron energy higher than the dissociation energy will be lost. An efficiency factor \((f_{eff})\) is introduced to compensate for this energy loss.

\[
P_{N^*} = 2 \cdot \frac{W_{in}}{E_{diss}} \cdot \frac{1}{f_{eff}}
\]

(3.7)

The disappearance rate \((D_{N^*})\) of nitrogen radicals is the sum of the disappearance reaction rates of reactions 3.3 and 3.4 (eq. 3.8).

\[
D_{N^*} = k_1 [NO]_t [N]_t + k_2 [M] [N]_t^2
\]

(3.8)

The nitrogen radical concentration is now determined by combining equation 3.8 with the steady state assumption (eq. 3.6). Considering only positive radical concentrations and using the root of an equation of second degree, equation 3.9 is found for the nitrogen radical concentration.
\[
[N_t] = \frac{-k_1 [NO]_t + \sqrt{k_1^2 [NO]_t^2 + 4 k_2 [M] P_N}}{2 k_2 [M]}
\]  

(3.9)

The nitric oxide concentration at time \( t \) depends on the inlet concentration and the conversion in nitric oxide at time \( t \) (eq. 3.10).

\[
[NO]_t = (1 - X_t) [NO]_0
\]

(3.10)

When equations 3.9 and 3.10 are combined with equation 3.4, the disappearance rate of nitric oxide can be expressed in terms of conversion, energy input and rate constants. This expression can be combined with equation 3.5 which gives the final expression for the conversion of nitric oxide as a function of the energy input (eq. 3.11).

\[
\int_{0}^{x_{NO}} \frac{d X_t}{(1 - X_t)^2 \left( -1 + \frac{8 k_2 [M] * W_{in}}{k_1^2 [NO]_0^2 (1 - X_t)^2 V_r E_{dis}/f_{eff}} \right)} = \frac{V_r^2 k_1^2 [NO]_0}{2 F_{tot} k_2 [M]}
\]

(3.11)

In equation 3.11 is \( F_{tot} \) the total flow through the reactor [m\(^3\)/s]. This is equal to nitric oxide flow divided by the initial nitric oxide concentration \( F_{NO}/[NO]_0 \). \( V_r/F_{tot} \) is the residence time [s] in the reactor.

Exact solutions of equation 3.11 are found for the two extremes. The first situation is at low conversion. The nitric oxide concentration is much higher than the nitrogen radical concentration. The conversion is linear to the energy input in this region (eq. 3.12).

\[
X_{NO} = \frac{2 * V_r}{[NO]_0 F_{tot} E_{dis}/f_{eff}} * W_{in}
\]

(3.12)

At a high conversion, the nitric oxide concentration is much lower than the concentration of nitrogen radicals (eq. 3.13). Here the conversion is an exponential function of the energy input with a limit of total conversion at infinite energy.

\[
X_{NO} = 1 - e^{-\frac{k_1 V_r}{F_{tot} \sqrt{\frac{2 W_{in}}{k_2 [M] E_{dis}/f_{eff}}}}}
\]

(3.13)

A numeric solution of equation 3.11 is shown in figure 3.1.
As expected the last nitric oxide molecules are difficult to remove, therefore working at high conversions is not very interesting for experiments. To reach higher conversions also the residence time can be increased. The result of this model is used to compare experiments with the same gas composition, but with different energy inputs.

We preferred to work at moderate conversions. The conversion can well be measured, but is still a linear function of the energy input. This is the best way to compare different experiments.
Chapter 4

Experimental

The experimental equipment is especially designed to study plasma induced catalytic reactions. The reactions are influenced by different parameters like the energy input, the gas mixture composition, the temperature and the catalyst.

Figure 4.1 gives a schematic view of the setup. The centre of the setup is the reactor. It is placed in an oven, which can be heated to 500 °C. The different reactors used are described in section 4.2. The reactor is supplied by a gas circuit to compose the gas mixture. The gas circuit is described in section 4.1. A high voltage pulse circuit is used for the plasma generation. The power supply is described in section 4.3. The products of the reactor are analysed in a quadrupole mass-spectrometer.

Figure 4.1: Schematic view of the experimental setup.
4.1 Gas Circuit

The gases are used directly from the cylinders, without further purification. They are supplied by "Hoek Loos". The used gases are helium, nitrogen, oxygen, 5% nitric oxide in helium, hydrogen and methane. The purity's of the gases can be found in table 4.1.

<table>
<thead>
<tr>
<th>purity</th>
<th>$H_2O$</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>Ar</th>
<th>CO</th>
<th>$N_2O$</th>
<th>NO</th>
<th>ch</th>
</tr>
</thead>
<tbody>
<tr>
<td>$He$</td>
<td>99.995</td>
<td>56</td>
<td>12</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>99.9</td>
<td>46</td>
<td>204</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$</td>
<td>99.9</td>
<td>1388</td>
<td></td>
<td>2585</td>
<td>739</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$He/NO$</td>
<td>99.995</td>
<td>1825</td>
<td>28</td>
<td>30</td>
<td>45</td>
<td>5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2$</td>
<td>99.5</td>
<td>0.2%</td>
<td>0.15%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CH_4$</td>
<td>99.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2%</td>
</tr>
</tbody>
</table>

*table 4.1 gas impurities in ppm or %*

Three electronic and two mechanic flow controllers are used at the gas manifold. The total flow is kept constant at 100 ml/min for all experiments (see section 5.1). A flow of 2 ml of a mixture helium with 5% nitric oxide is added to main flow to introduce 1000 ppm nitric oxide in the reaction mixture.

Water is introduced into the reaction mixture in two different ways. The first method is to saturate the gas mixture by flowing the complete gas mixture through water at different temperatures. This method is especially for high water concentrations. The concentration can be varied from 0.6 to 20% (0 to 60 °C). The second method is used for low water concentrations. Here, only a part of the bulk gas is led through water, controlled by a separate flow controller. This is a very appropriate way for introducing concentrations between 0 and 0.4%. This method is easier, because one can use water at room temperature. Other vapoured fluids, like hexane and iso-octane can also be introduced in the reactor this way. All tubing from the reactor to the mass-spectrometer can be heated to avoid condensation of the volatiles. This is not trivial because of the use of high voltage.

The gas mixture coming from the reactor is analysed in a quadrupole mass-spectrometer: A "Balzers QM420" with computer software to match. This results in a qualitative measurement of the reaction products. For quantitative interpretation much more calibration measurements are necessary, including the introduction of standards.

4.2 Reactors

An optimum combination of catalytic surface and discharge must be realised by the design of the reactor. The best condition for heterogeneous catalysis is a catalyst with a high surface area. In earlier research in this project the "fixed bed" reactor is the best possibility for a plasma induced catalytic reaction. The reactor is described further in chapter 4.2.1.
Also two other types of reactors are tried. No catalyst is used in these reactors, just the discharge. The idea of trying this type of reactor came from the parallel research of plasma induced catalytic reactions of methane. In this case the discharge is not a real corona discharge; it also contains a thermal part. The main advantage of this reactor is the cheap and reliable power supply, and the high energy input efficiency (above 80% is possible). The "capillary" reactor and the "gliding arc" reactor are described in the chapters 4.2.2 and 4.2.3.

4.2.1 The "Fixed Bed" Reactor

The "fixed bed" reactor has a so-called wire-cylinder electrode configuration. It consists of a quartz tube with a wire electrode through the centre of the catalyst bed. The fixed bed consists of catalyst particles. The catalyst is kept in position by two plugs of quartz wool. The grounded electrode is positioned around the tube. The wire electrode is covered by small glass tubes outside the catalytic bed to ensure that the corona discharge proceeds through the catalyst bed (see fig. 4.2). The self sustained discharge cannot penetrate into the micro pores of the catalyst, because ionisation is impossible in these small spaces. The discharge will proceed in between the support particles. The plasma in the bed is generated by the wire electrode and the grounded metal foil around the reactor. This is a wire to a dielectric barriered cylinder configuration. The quartz tube functions as a dielectric barrier. Due to the dielectric barrier a higher electric field than the breakdown field can be used under all the different gas compositions and temperatures. No arc discharge will occur. The discharge properties do not change much under different gas conditions and temperatures. This configuration is advantageous because of the wide range of experimental conditions that can be used. A pulsed or alternating voltage has to be used to create a repetitive discharge. The length of the bed is about 2 cm. The inner diameter of the reactor is 0.96 cm. The width of the external grounded electrode is 1 cm.

[Diagram of the fixed bed reactor]

\( \gamma \)-Alumina or silica with different particle sizes is used as catalyst. Also, dispersions of metal oxides on these materials are tried. The dispersions are made by a standard method of incipient wetness impregnation of the support materials using metal nitrates. Afterwards the catalyst is dried and calcinated to get the metal oxides. It is not important for us to make good catalysts with dispersion within the catalyst pores, because the discharge will not reach these micro pores. Another limitation is that the degree of metal covering cannot be too high, because the bed will become conductive. The
discharge will go over the surface instead of through the gas.

### 4.2.2 The "Capillary" Reactor

In the parallel research of plasma catalytic reactions with methane a new type of reactor is developed. This reactor only uses discharges and does not use any catalyst. In these reactors a very short, but intense treatment of the gas mixture is possible. The types studied are described in the next two paragraphs.

The "capillary" reactor consists of two electrodes in a quartz capillary tube. One electrode is grounded, the other electrode is connected to the DC power supply (see section 4.3) [13]. The reactor is sketched in figure 4.3. The inner diameter of the reactor is only 0.8 mm. At 100 ml/min the gas flow is 4.2 m/s. The distance between the electrodes can be varied between 5 and 15 mm for the currently used voltage of up to 30 kV. Discharge frequencies from 5 to 25 kHz are observed.

![Figure 4.3: The "capillary" reactor.](image)

In this reactor the discharge is axial to the gas flow, through a capillary. The discharge current stops because of the induction of the DC power supply (see section 4.3). Then, breakdown is avoided by blowing away the hot ionised corona channel. The flow stabilizes the plasma. The electric field in the reactor is high enough to start a new discharge. The frequency and the energy input decrease (at a fixed voltage) and the breakdown voltage increases by increasing the flow. The frequency increases with the energy input. The gas treatment will be very intense, because both the gas and the discharge must go through the capillary.

### 4.2.3 The "Gliding Arc" Reactor

The second non-catalytical reactor is the "gliding arc". In this case the discharge is blown away in the perpendicular direction. The "gliding arc" was first used by Czernichowski [14] [15]. The reactor has two diverging electrodes. One is connected to the power supply, the other one is grounded (see fig. 4.4). Between the electrodes the gas is added through a nozzle. Just above the nozzle the
discharge appears. The discharge ignites where the distance between the electrodes is minimal at the
highest electric field, just above the nozzle. The flow blows the arc away. At the diverging part of
the electrodes the discharge channel becomes longer and non-equilibrium plasma. When the arc rises
high at the diverging electrodes, it dies. The distance between the electrodes becomes to large and
the electric field is too low [16].

![Diagram of a gliding arc reactor](image)

*Figure 4.4: The "gliding arc" reactor.*

At low flow rates a continuous discharge channel stays at a fixed position. When the flow is
increased, the arc glides over the entire electrodes. The discharge frequency is low. At high flows
the discharge frequency can become several hundreds Hz. Now the arc lives short and glides only
over a small part of the electrodes. The pulse frequency increases with a higher energy input.

A disadvantage of the "gliding arc" reactor is that only a part of the gas is treated. The other part is
used to blow the discharge away. When the reactor was constructed, we thought the gas would
circulate in the reactor, so a better gas treatment is obtained than expected. The disadvantage of a
large reactor is the large volume which makes the measurements more time consuming.

### 4.3 Plasma Power Supplies and Energy Input Measurements

A plasma is an ionized gas with high energy contents. The amount of energy added to the reactor is
very important for the plasma induced reaction. The characteristics of the discharge are mainly
determined by the reactor type and the gas composition and not by the power supply.

For the "fixed bed" reactor, a positive pulsed corona discharge has been chosen. Figure 4.5 gives a
schematic overview of the used electrical circuit. The high voltage power supply charges the capacitor
when the spark gap is open (fig. 4.6). The reactor is an open connection at this time. The charge time of the capacitor is about 1 ms. When the spark gap (S) is triggered, the circuit of minimal resistance contains the reactor with a corona discharge (fig. 4.7) \[16\] \[17\]. The corona discharge time is much faster: \(< 1 \mu s\).

\[\begin{align*}
&\text{Figure 4.5: The high voltage pulse circuit.} \\
&\begin{tikzpicture}
&\node [draw, shape=rectangle] (HV) at (0,0) {HV};
&\node [draw, shape=rectangle] (C) at (2,0) {C};
&\node [draw, shape=rectangle] (L) at (2,-1) {L};
&\node [draw, shape=rectangle] (S) at (0,-1) {S};
&\node [draw, shape=rectangle] (R1) at (-2,0) {R1 \(5 \text{ MOhm}\)};
&\node [draw, shape=rectangle] (R2) at (4,0) {R2 \(2 \text{ MOhm}\)};
&\node [draw, shape=rectangle] (166pF) at (2,-2) {166 \text{ pF}};
&\draw [->] (HV) -- (C);
&\draw [->] (C) -- (L);
&\draw [->] (L) -- (S);
&\draw [->] (S) -- (R1);
&\draw [->] (R1) -- (166pF);
&\draw [->] (166pF) -- (R2);
&\draw [->] (R2) -- (HV);
&\end{tikzpicture}
\end{align*}\]

The spark gap pulse circuit can give pulses to a maximum voltage of 30 kV with a voltage rise time of 50 ns. The maximum repetition frequency is 250 Hz. A "Tektronix CFG 250" pulse generator triggers a 400 V pulse transformer which triggers the spark gap. Most experiments are done at 25 kV and pulse frequencies between 10 and 200 Hz. The energy input into the reactor varies as a function of the pulse voltage and frequency. Typical values are 2 to 8 mJ per pulse.

The capillary reactors are supplied by a more simple circuit. The reactors do not have a dielectric barrier. The reactor is placed in series with a resistor \((R)\) and an induction \((L)\) (fig. 4.8). A positive DC corona discharge is used. High efficiency can be obtained at high voltages and low current. Up to 90% of the electrical energy can be transferred at a HV = 20 kV, I = 2 mA, R = 1 MOhm and L = 1 mH. The overall energy efficiency also depends on the internal resistance of the DC high voltage power supply. Voltages between 2 and 30 kV are used. Here, pulse frequencies to a maximum of 25 kHz occur.
The resistor must keep the arc current small enough to avoid a stable arc on long time scale. The current can be limited with the help of an inductance. The dissipation in the resistor can be minimized this way. Unfortunately an induction cannot replace the whole resistor.

To determine the energy input in the reactor the voltage and current are measured. It is important that the measurements are done close to the reactor to ensure good energy measurements. A Tektronix P6015A probe is used for the voltage measurements, and a "Pearson Electronics Inc 2877" probe for measuring the current. The measurements are performed by an oscilloscope, a "Tektronix 2440" at a bandwidth of 20 MHz. A personal computer calculates the energy input in the reactor from the measured values. The total discharge energy is defined as:

\[ E_{\text{tot}} = \int V(t) I_{\text{tot}}(t) \, dt \]  

(4.1)

To calculate the corona current, the total current, \( I_{\text{tot}} \), is corrected for the capacitive current in the circuit. The capacitive current is the product of the total capacity times the derivative of the voltage. The total capacity can be computed as the quotient of the total charge and the voltage. If the voltage is kept below the inception voltage the total charge is the integration of the capacitive current versus time when the reactor is an open connection. Now the corona energy, the effective energy in the reactor, is the integral of the voltage times the corona current as a function of time (eq. 4.2) [16] [17].

\[ E_{\text{cor}} = \int V(t) I_{\text{cor}}(t) \, dt \]  

(4.2)

The conversion of nitric oxide is measured with the mass-spectrometer. With the energy input, the gas composition and the flow the energy cost can be calculated. This is expressed in electron volts per molecule [eV/NO]. The equivalent of 1 eV/molecule is 96 kJ/mol.
Chapter 5

The Nitric Oxide Removal

The removal of nitric oxide from waste gases is studied. Experiments are performed in the three different reactors as described in section 4.2. First the results of the "fixed bed" reactor are presented. The influences of several parameters like gas composition, catalytic support and energy input are described in section 5.1. Firstly, the effect of conversion level was determined. Then the effect of the catalytic support was determined, then the energy input and the temperature. Thirdly the influences of some of the most important gases in flue gas; nitrogen, oxygen and water vapour were studied. Especially water can be important because of the formation of ·OH radicals by the plasma. Finally hydrogen, methane, hexane and iso-octane were tested as reductant or as radical chain reaction enhancer.

Except for experiments with the "fixed bed" reactor, also experiments are performed with two alternative reactor types: the "capillary" and the "gliding arc" reactor. Experiments with these reactors are described in section 5.2 and 5.3.

5.1 The "Fixed Bed" Reactor

5.1.1 The Nitric Oxide Conversion Levels

The total flow influences the nitric oxide conversion and thus the removal energy costs. The conversion of nitric oxide depends on the energy input, as shown in chapter 3. Higher flow rates with the same nitric oxide concentration will lead to a lower conversion at constant energy input because lower energy density as shown in figure 5.1. At the same conversions, the energy costs are lower at lower flows. The measurements are performed with nitrogen with 1000 ppm nitric oxide at three different pulse frequencies, but at a constant energy input. The experiments are performed with the "fixed bed" reactor filled with 125-250 μm silica Grace 332 as a catalyst.
At higher flows the energy costs are lower but the conversion is also lower. The conversion divided by the energy costs is for all experiments about the same, because the nitric oxide concentration as well as the energy input are kept constant. It is essential for accurate measurements (see chapter 3) to work at intermediate conversions, because the nitric oxide conversion is not measured accurately at low conversions. At high conversions the conversion is not anymore proportional to the energy input. Therefore, all measurements are performed with a 100 ml/min gas flow.

It should be noticed that the residence time changes by a packed bed in the reactor. In our case the gas is 0.6 seconds in the plasma zone instead of 1.1 seconds in the empty reaction sector. For dry gas mixtures this does not make much of a difference. The minor influence of the residence time for dry gas mixtures changes completely in presence of water vapour and oxygen. In corona flue gas cleaning this residence time is of great importance. For wet gas mixtures reactive radicals and ions can be covered with water molecules and have a much longer relaxation times. These radicals have the opportunity to react differently in the gas phase over a time period of more than 10 seconds. However, in our case the order of magnitude of the residence time does not change too much and we worked with dry gas mixtures.

5.1.2 The Effect of the Catalytic Support

In this section the influence of the catalytic support is determined: the material and the particles size. As support material highly porous γ-alumina (AKZO) and silica (Grace 332) is used. The empty tube is used as reference. Nitrogen with 1000 ppm nitric oxide is used as test gas. The reactor temperature is kept constant at 100 °C. The discharge frequencies used are 50, 100 and 200 Hz at a voltage of 25 kV. Firstly γ-alumina was studied with a particle size of 125-250 µm.
The experiment shown in figure 5.2 is performed with nitrogen containing 1000 ppm nitric oxide and 5% oxygen and a discharge frequency of 80 Hz. Nitric oxide does not react with γ-alumina in absence of the discharge. As soon as the discharge is switched on, the nitric oxide removal becomes nearly complete at an energy input of 50 eV/NO. The energy costs are a factor two lower when helium with 5% oxygen is used as bulk gas instead of nitrogen.

![Graph showing nitric oxide removal on γ-alumina](image)

**Figure 5.2:** The nitric oxide removal on γ-alumina in nitrogen containing 5% oxygen and 1000 ppm nitric oxide as a function of time.

The discharge induces a reaction of the nitric oxide with γ-alumina. After some time the nitric oxide conversion decreases and becomes equal to the level of the plasma induced homogeneous gas phase reaction (see figure 5.2). This plasma induced adsorption is enhanced by the addition of oxygen. Nitrates might be formed on the support surface.

Initially the nitric oxide signal decreases in steps because of the different discharge frequencies: 10, 20, 40 and 80 Hz of 6 mJ per pulse. The rise of the nitric oxide signal when the discharge is stopped (after 70 minutes) denotes a desorption of loose nitric oxide from the surface.

The saturated γ-alumina is studied immediately after the experiment by a temperature programmed desorption in helium from 50 to 440 °C at 6 °C per minute. Different desorption products can be distinguished. Firstly molecular nitric oxide desorb at 125 to 175 °C. At the second desorption process mainly oxygen and nitrogen dioxide desorbs (see fig. 5.3). The second desorption occurs above 400 °C. This is the dissociation of adsorbed NO₃⁻ groups at the γ-alumina.
The discharge enhances the adsorption of nitric oxide till the support area is saturated. The plasma induces a surface reaction on \(\gamma\)-alumina. It is measured that a part of the nitric oxide (\(\pm 25\%\)) converts into gaseous products like nitrogen and oxygen, but most of the nitric oxide is adsorbed at the support surface. However, a possible solution for nitric oxide removal from waste gases is the plasma induced adsorption of nitric oxide on \(\gamma\)-alumina. The removal is complete during a certain time proportional to the amount of \(\gamma\)-alumina. 1000 ppm nitric oxide in 100 ml nitrogen per minute can be removed for 0.4 W (50 eV/NO). After a certain adsorption degree the \(\gamma\)-alumina can be heated and the concentrated nitric oxide and nitrogen dioxide can be destructed with other methods.

The adsorption makes it very difficult to do good reproducible experiments. The effect \(\gamma\)-alumina as support material is also hardly measurable because the adsorption effect can hardly be distinguished from the catalytic removal reaction. The activity of the catalyst cannot be measured well when adsorption dominates. Experiments with \(\gamma\)-alumina were stopped after reaching this conclusion. The adsorption makes it impossible to see what happens during the experiments. The experiments do prove that a surface reaction can occur.

No adsorption is observed on silica Grace. This support is much better to use in the "fixed bed" reactor to measure the effects of a catalyst. The following parameter to be optimized is the particle size. The sieve fractions which are used are: 500-1000 \(\mu m\), 250-425 \(\mu m\), 125-250 \(\mu m\) and 30-90 \(\mu m\). An empty reactor is used as reference. The results of the experiments are plotted in figure 5.4 and figure 5.5. Nitrogen is used as bulk gas and contained 1000 ppm nitric oxide.

\[\text{Figure 5.3: The thermal desorption of NO, O}_2\text{ and NO}_2\text{ from} \]
\[\gamma\text{-alumina at a 6° per minute temperature programmed desorption experiment in pure helium.}\]
The results of the experiments show the advantage of the use of a catalyst bed. The use of the silica bed leads to lower energy costs. The different sieve fractions do not show much difference in energy costs and conversion, but are much better than the empty tube. The 30-90 \( \mu m \) is a little worse because the particles are blown away and the bed is not very stable. The catalytic surface has a positive effect on the rate of the decomposition reaction compared to the empty tube. The energy costs are lowered by a factor two. It is not yet clear if this is a catalytic effect or a plasma effect. In figure 5.5 the conversion is plotted as a function of the total energy input. This also shows the advantage of the use of catalytic bed.

Also different metal dispersions on the support are tried. This is done in combinations with reductants. More about these catalysts can be found in section 5.1.6.
5.1.3 The Influence of the Energy Input and Pulse Frequency

In this section the influence of the pulse frequency, as well as the pulse voltage is determined. In all experiments the voltage is kept at 25 kV and the energy input is varied with different discharge frequencies (mainly 50, 100 and 200 Hz). The energy input at 200 Hz is about four times higher than at 50 Hz.

To determine the importance of the discharge frequency, an experiment is performed with a constant total energy input. The voltage of the pulses is adjusted to keep the total energy input constant at different frequencies (30-20 kV, 50-200 Hz). Helium with different percentages nitrogen and 1000 ppm nitric oxide is used as test gas. The oven temperature is kept constant at 100 °C.

Higher frequencies give slightly better conversion and thus lower energy costs (see fig. 5.6). Many little intensive steamers are better than a few intensive ones. This can also be seen from figure 5.1. A remarkable observation is that the production of nitrous oxide (N₂O) is always 4% from the 1000 ppm nitric oxide. Consequently the nitrous oxide production is not a function of frequency, but only of the total energy input and thus the nitrogen radical concentration. It is typically a discharge product.

![Figure 5.6: The nitric oxide conversion as a function of the energy costs. The arrow points to higher frequencies. The numbers in the graph refer to the N₂ percentage in helium.](image)

In chapter 3, a model is given that describes the relation between the conversion and the energy input. Experiments are performed to test this model. Different gas mixtures are used to determine the influence of the gas composition. All the experiments show the expected curve. Figure 5.7 shows the results of 1000 ppm nitric oxide in nitrogen with silica Grace 332 as catalyst at three different oxygen concentrations. Total conversion was not reached at the current possible energy inputs.
In practice it is very difficult to compare experiments with different energy inputs. Each gas mixture has its own kinetics and thus a specific conversion-energy input relation. It is better to compare results with the removal energy costs per molecule nitric oxide. More about the influence of the gas mixture can be found in section 5.1.4 and 5.1.5.

5.1.4 The Temperature in the Reactor

It is important to know if the reaction shows any temperature dependence, because of the different temperatures of waste gases. Therefore a temperature programmed experiment is performed in the empty "fixed bed" reactor. Helium with 1000 ppm nitric oxide is used as test gas mixture. The temperature is increased from 50 to 400 °C at a rate of 7 °C per minute. The corona discharge frequency is fixed at 100 Hz.

The conversion of nitric oxide appears to decrease with increasing temperature (see figure 5.8). The main part of the nitric oxide is converted to nitrogen and oxygen. Nitrogen dioxide is produced above 250 °C in presence of oxygen. Nitrous oxide is always produced in about the same amounts (30 to 50 ppm). It can be concluded that the experiments can best be done at relatively low temperatures.
The temperatures 300, 200, 100, 50 and 20 °C are chosen for the energy costs and the nitric oxide conversion measurements with silica Grace (125-250 μm) as catalyst. Three discharge frequencies are used: 50, 100 and 200 Hz (respectively about 0.3, 0.55, 1.1 W). The results are shown in figure 5.9 and 5.10.

**Figure 5.8**: Temperature programmed experiment of the nitric oxide conversion in helium with nitrogen and oxygen as reaction products.

**Figure 5.9**: The energy costs of the nitric oxide removal as a function of the temperature. Nitrogen with 1000 ppm nitric oxide is used as test gas.
These experiments also show better results at lower temperatures. Lower temperatures lead to lower energy costs and higher conversions. The plasma contains enough energy for the activation of the reaction. Higher temperatures lead kinetically to more nitrogen dioxide, in presence of oxygen.

Usually, exhausts of combustion processes are not at room temperature. Nowadays, one tries, for economical reasons, to decrease the exhaust temperatures. Considering these situations in practice, the best experimental temperatures will be between 50 and 150 °C.

Another problem is that the gas temperature will rise, because of the electric energy input. If all discharge energy is directly used to heat the gas, the temperature will rise several hundreds degrees (175 °C at 0.31 W and 525 °C at 1.1 W). In practice, convection and conduction of heat to the environment will be important. We decided to measure the temperature rise in the bed with a thermocouple. Figure 5.11 shows the temperature versus the time of the "fixed bed" reactor placed in an oven at 100 °C. Two different energy inputs are used: 0.31 W at a voltage of 25 kV and a frequency of 100 Hz and 1.10 W at a voltage of 27 kV and a frequency of 200 Hz. The experiments are done with nitrogen as bulk gas containing 1000 ppm nitric oxide.

Figure 5.10: The nitric oxide conversion as a function of the temperature. Nitrogen with 1000 ppm nitric oxide is used as test gas.
The part of the energy that converts into heat can be calculated from the initial temperature rising rate. No heat exchange occurs initially, because the temperature gradient is zero. The calculated part of the energy input that is needed for the temperature rise is in both cases only 17%. However, probably nearly all electric energy turns into heat. The conduction of the bed to the oven takes another part. A few photons will take some energy outside the reactor, but these will be transferred into heat in the oven.

The temperature in the reactor does not rise above 120°C. The excited gas is probably warmer because all discharge energy is transferred into heat. Creighton [8] measured a temperature rise of about 100°C. However, the heat of the gas is immediately transferred to the catalyst. The heat is transferred from the catalyst, through the reactor wall, to the oven. The oven temperature will not rise by this small amount of added energy. The temperature in the catalytic bed does rise, due to the heat production of the discharge. The maximum temperature rise is limited to 26 degrees, due to the heat exchange with the environment. It should be noticed that an oven temperature of 100°C corresponds with a gas temperature of 94°C in the bed.

5.1.5 The Influence of Nitrogen, Oxygen and Water Vapour

As mentioned in section 4.3 and 5, it is very important to know about the influences of different gases in the gas mixtures to the nitric oxide removal. The effect of the possible different gas components on the nitric oxide removal must be determined separately to know which reactions occur in the corona discharge. The following gases are investigated on the effect of nitric oxide removal: nitrogen, oxygen and water. In section 5.1.5 the influence of reductants is described. The "fixed bed" reactor is used for the experiments in this section. Silica grace 332 with a particle size of 125 to 250 μm is used as catalytic support.
Influence of Nitrogen

The influence of nitrogen on nitric oxide removal is determined by using different helium/nitrogen ratios. The oven temperature is fixed at 100 °C. The energy cost of the nitric oxide removal is shown in figure 5.12, the conversion of nitric oxide in figure 5.13.

![Diagram 5.12: The effect of increasing nitrogen concentration on the nitric oxide conversion versus the energy costs. The arrow points in the direction of 0%, 5%, 10%, 15% to 20% nitrogen in helium.](image)

![Diagram 5.13: The energy costs of the nitric oxide removal versus nitrogen in helium.](image)

It appears that increasing the amount of nitrogen in helium leads to lower energy costs and a higher nitric oxide conversion. The energy costs of the nitric oxide removal do not depend much on the nitrogen concentration when above 5% nitrogen. But, the conversion decreases a little at a higher nitrogen concentrations.
The reaction products are mainly nitrogen and oxygen. Nitrous oxide is found proportional to the energy input. Around 20, 40 and 70 ppm nitrous oxide is found at respectively energy inputs of 0.3, 0.55 and 1.1 W. Nitrous oxide is, as expected, a typical discharge product. Nitrogen dioxide is not found. The three reactions that are likely to occur are [18]:

\[
\begin{align*}
N^* + NO & \rightarrow N_2 + O^* & k_a = 1 \cdot 10^{-10} \\
N_2 + O^* + M & \rightarrow N_2O + M & k_b = 5 \cdot 10^{-38} \\
N^* + NO + M & \rightarrow N_2O + M & k_c = ? \\
N^* + N^* + M & \rightarrow N_2 + M & k_c = 1 \cdot 10^{-32}
\end{align*}
\]

The reaction rate constants are given in \([\text{cm}^3/\text{molecules s}]\) or \([\text{cm}^6/\text{molecules}^2 \text{s}]\). Reaction 5.1a is the main reaction for nitric oxide removal. The formed mono-oxygen radicals can recombine to molecular oxygen or stick to the silica. The formed mono-oxygen radical can also react with nitrogen and form nitrous oxide (eq. 5.1b). At higher energy input more mono oxygen radicals are produced. Reaction 5.1c must occur, because of the low mono-oxygen radical concentration, but is unknown in the literature. Reaction 5.1c has to be proved with labelled nitric oxide ($^{18}$NO). The recombination reaction of nitrogen radicals (eq. 5.1d) of course also occurs and is important for the nitrogen radical concentration. To work in more realistic situations, the following experiments are done in nitrogen.

**Influence of Oxygen**

Oxygen, as an oxidizer, will probably have a bad influence on the nitric oxide reduction. Discharge energy is transferred to the dissociation of oxygen because oxygen has a lower dissociation energy than nitrogen. The formed mono oxygen radicals are not very reactive towards nitric oxide. The experiments are performed in nitrogen with 1000 ppm nitric oxide at 50, 100 and 150 °C. Only small concentrations of oxygen were used: 1, 3 and 5%. The results are shown in figure 5.14.

**Figure 5.14:** The conversion as a function of the energy costs at different oxygen concentrations and three different energy inputs.
It can be concluded that oxygen leads to lower nitric oxide conversions as well as higher energy costs (see figure 5.14). The energy costs of the nitric oxide removal in presence of small concentrations oxygen are 1½ to 3 times higher than in pure nitrogen. Also the formation of nitrogen dioxide is measured. This can be up to 15 ppm of the original nitric oxide amount at a conversion of about 20%. At 5% oxygen, the conversion of nitric oxide is nearly complete from nitric oxide to nitrogen dioxide. The selectivity of the reaction to nitrogen dioxide is difficult to measure because of the low nitric oxide conversion. The nitrous oxide production is the same as in pure nitrogen. Two reactions with the mono oxygen radical can occur (eq. 5.2a and 5.2b) and one with oxygen (eq. 5.2c and eq. 5.2d).

\[
\begin{align*}
O^- + NO &\rightarrow O_2 + N^- & k_a = 1 \cdot 10^{-18} \\
O^- + NO (+ M) &\rightarrow NO_2 (+ M) & k_b = 3 \cdot 10^{-11} \\
N^- + O_2 &\rightarrow NO + O^- & k_c = 1.4 \cdot 10^{-11} \\
O_2 + O^- (+ M) &\rightarrow O_3 (+ M) & k_d = 3 \cdot 10^{-12}
\end{align*}
\]

(5.2)

The reaction rate constants are given in \(\text{cm}^3/\text{molecules s}\) or \(\text{cm}^6/\text{molecules}^2 \text{s}\). The reaction 5.2a is considered too slow to occur, so no extra nitric oxide can be removed. The rate of reaction 5.2b increases at higher oxygen concentrations, and thus more mono oxygen radicals. This is a three particle collision. Reaction 5.2c regenerates a nitric oxide molecule. Reaction 5.2d forms an ozone molecule that is considered stable at present pressure and temperature.

**Influence of Water Vapour**

Flue gases, effluent gases from a nitric acid factory and exhausts from combustion processes always contain water. The first series of experiments in this section were performed with a gas mixture containing 0.4% and 4% water. 125-250 µm silica (Grace 332) is used as catalytic support. Experiments are also performed with a gas mixture containing both water vapour and oxygen. All experiments are performed in nitrogen with 1000 ppm nitric oxide. The energy costs and nitric oxide conversions are shown in figure 5.15 and figure 5.16.

![Figure 5.15: The effects of the addition of water and/or oxygen on the energy costs of the nitric oxide removal.](image-url)
At higher energy inputs, the energy costs are the sum of the energy costs of the oxygen and 0.4% water experiments. Only 0.4% water vapour has about the same result as 3% oxygen; the energy costs are 2 to 3 times higher than in pure nitrogen. The nitric oxide conversions in presence of water vapour do not depend so much on the energy input like in the presence of oxygen and remain low. Oxidation to nitrogen dioxide is more important in presence of oxygen but the nitric oxide conversion is too low to measure the selectivity.

The negative effect of water vapour and oxygen in combination with a catalytic support on the conversion and energy costs seems in contradiction to the results to the pure gas phase pulsed corona research. This is the result of reactions of the silica surface with ·OH and ·O radicals. To know more about these reactions, the role of water vapour and oxygen is studied in an empty "fixed bed" reactor. Also higher water concentrations are used in these experiments. It appeared that helium as bulk gas shows slightly better results than with nitrogen. Thought only the experiments with nitrogen, 5% oxygen and different water concentrations are shown here because this is a more practical situations and therefore more relevant to the project. The results are shown in figure 5.17.

Low water concentrations have the same negative effect as in case with a silica filled reactor. Higher water concentrations lead to higher conversions as well as lower energy costs. It is observed that nitric oxide reacts to nitric dioxide. Afterwards nitrogen dioxide is converted to products which could not be measured with the mass-spectrometer. Formation of aerosols might explain the missing fraction of NO$_x$. Another possibility is that nitrogen dioxide converts to nitric acid, but that solves in condensed water in the mass-spectrometer and is not measured. It is also possible that the hot water and nitric acid react with the steal tubing.
Figure 5.17: The nitric oxide conversion versus the energy costs as a function of the water concentration in nitrogen containing 5% oxygen and 1000 ppm nitric oxide.

The •OH-radicals are very important for the reaction in the empty tube. In the reaction mechanism also the oxygen concentration is important, however not yet well understood. Figure 5.18 and 5.19 show the oxygen dependence of the nitric oxide removal energy costs and conversion. The experiments are done in nitrogen with 1000 ppm nitric oxide. The reactor temperature was 100 °C and all tubings were heated to prevent condensation of water.

Figure 5.18: The energy costs as a function of the oxygen percentage at different water concentrations.
The conclusion for an empty "fixed bed" reactor is different of the one with silica support. At water concentrations above 5%, the energy costs decrease and the conversion increases for higher oxygen concentrations. At intermediate water concentrations, the energy costs and conversion are independent of the oxygen concentration. At higher oxygen concentration, 100% conversion can be obtained. Even all nitrogen dioxide can be converted.

It can be concluded that water vapour as well as oxygen has a positive effect on the nitric oxide removal, but not in combination with a catalytic bed. Probably the \( \cdot \text{OH} \) and \( \cdot \text{O} \) radicals are quenched on the silica. This is not possible in the gas phase in the empty tube, where the reactive radicals can do their destructive work. Oxygen appears to be very important. Its role is not yet elucidated. In literature many radical reactions and chain reaction are known with \( \cdot \text{O}, \cdot \text{OH}, \cdot \text{O}_2\text{H}, \) etcetera. The reaction mechanism is very complex.

Better results are obtained with helium in the empty tube reactor. The energy input is used more efficiently for the dissociation of oxygen and water. Not much nitrogen will be dissociated at high water and oxygen concentrations because water vapour and oxygen have much lower dissociation energies, but some energy will be lost. The \( \cdot \text{OH} \) and \( \cdot \text{O} \) radicals can react better with nitric oxide in helium because the radicals cannot react with helium. But, nitrogen is a better bulk gas than helium in presence of a catalytic bed. The nitrogen radicals seem to be stabilised at the silica surface. The recombination of two radicals is prohibited. The good results of helium in combination with a catalytic bed have to do with the discharge energy that is transferred more efficiently directly to the nitric oxide molecule. Here we probably have a surface reaction of activated or dissociated nitric oxide. \( \cdot \text{OH} \) and \( \cdot \text{O} \) radicals react at the silica surface and are lost for further reaction with nitric oxide.
5.1.6 Addition of Reductants

Waste gases will nearly always contain oxygen. In plasma catalytic reactions it is already shown that it is very difficult to remove nitric oxide in the presence of oxygen. Addition of a reductant can have two possible advantages on the nitric oxide removal. Firstly, nitric oxide may be reduced directly by the reductant and secondly the oxygen may be removed by the reductant. Using metal oxides on the catalytic support can be interesting in this case. A known catalytic process for nitric oxide removal is based on a combination of copper oxide as a catalyst and ammonia as a reductant.

First a temperature programmed experiment is performed. Except for pure silica grace 332 (125-250 µm), the following oxides on silica Grace 332 are tried; 10 weight% cobalt-, iron-, chromium- and copper oxide. Nitrogen with 1% oxygen, 1000 ppm nitric oxide and 1% hydrogen or 1% methane is used as a test gas. The temperature was increased from 50 to 400 °C (7 °C/min). The experiment shows the same temperature dependence as in section 5.1.2. A little higher conversion and a little lower energy costs at lower temperatures are obtained. The temperature for the next experiments, is kept constant on 100 °C.

The oxygen concentration dependence is determined for the different catalysts used. The experiments are performed with a gas mixture of nitrogen, 1% hydrogen and 1000 ppm nitric oxide containing 0, 1, 3 or 5% oxygen. In figure 5.20 and figure 5.21 the results are shown for the different catalysts.

![Figure 5.20: The nitric oxide removal energy costs versus the oxygen concentration for different catalysts.](image-url)
In presence of oxygen the metal oxide catalysts show better results than pure silica. Without oxygen, the pure silica gives the best results. Fe$_2$O$_3$ is the best of all metal oxide catalysts. This effect is even more clear at higher oxygen concentrations. It seems that hardly any hydrogen is oxidised. Burning away the oxygen does not happen.

Different reductants are tested with Fe$_2$O$_3$ on silica as catalyst. Hydrogen, methane, hexane and iso-octane are used as reductants. Hexane and iso-octane are also tried because of the possibility of the formation of stabilised radicals or ions. These radicals are important in the gas phase reaction as a homogeneous catalyst [19]. Removing the oxygen is already out of the question since no carbon dioxide was measured in the methane experiments. Gas mixtures of nitrogen with 1000 ppm nitric oxide, 0 to 5% oxygen and different percentages of hydrogen, methane, hexane or iso-octane are tested. The mixture without a reductant is used as reference. The results are shown in the figures 5.22 and 5.23 with 1% hydrogen or methane, or 0.1% hexane or iso-octane.
Unfortunately the presence of the reductants hardly influences the reaction. Slightly better conversions are obtained, but at somewhat higher energy costs. Methane is worse, the other reductants have about the same conversions and energy costs. When hexane or iso-octane was used as reductant, we could not detect partial oxidation products. It seems that stabilised ions or radicals are not formed.

Addition of 0.4% water and a reductant has the same negative influence as in section 5.1.4. The energy costs are increasing, the nitric oxide conversions are decreasing. The conclusion is that the slightly better results of the 10 weight% $\text{Fe}_2\text{O}_3$ on silica support are not caused by a reductant. In figure 5.24, the results are shown of the comparison of pure silica to silica with 10 weight% iron at different oxygen concentrations.

**Figure 5.23:** The nitric oxide conversion versus the oxygen concentration for different reductants.

**Figure 5.24:** The nitric conversion versus the nitric oxide removal energy costs as a function of the oxygen concentration (0%, 1% and 3%) for pure silica and 10 weight% iron on silica.
The nitric oxide conversion with 10 weight% Fe$_2$O$_3$ catalyst is not so much influenced by a higher oxygen concentration. However in presence of oxygen the 10 weight% Fe$_2$O$_3$ catalyst gives slightly higher conversions against lower energy costs. Also we observed, that pure silica needs higher voltages for a stable discharge. Probably the iron particles influence the discharge. Already at lower pulse voltages a good discharge can be made. A lower pulse voltage induces a lower energy per pulse, which is usually more efficient in exciting the gas.

5.2 The "Capillary" Reactor

This reactor is totally different from the "fixed bed" reactor. The discharge is between two point electrodes without a dielectric barrier. The electrodes are positioned in a narrow quartz capillary (see section 4.2.2). This configuration gives a very intense gas treatment. The DC-power supply, as described in section 4.3, was used with a resistor of 2.5 Mohm. An induction was used of approximately 1 mH.

In the blanco experiments, gas mixtures with nitrogen and small percentages oxygen are treated to find out if any nitric oxide is produced. The experiments are performed with different electrode separations: 5, 10 and 15 mm. For each experiment two different discharge currents are used. This is realised by using two different voltages. An increasing voltage does not have to increase the energy input but increases the discharge current. An increasing current increases the dissipation in the resistance and decreases the voltage over the electrodes which can lead to a lower energy input in the reactor. Nitrogen with 0%, 1%, 3% or 5% oxygen was used as test gas. The total flow was 100 ml per minute. The results are shown in figure 5.25.

![Figure 5.25: The nitric oxide production of nitrogen with oxygen at three different electrode distances and two energy inputs.](image-url)
No nitric oxide production is seen in the experiment without oxygen. Figure 5.25 shows an increasing nitric oxide production at an increasing oxygen concentration and at larger electrode distances. The gas treatment time increases at a longer discharge length and seems to result in a larger nitric oxide production about proportional to the reaction time. But the energy input also increases because much higher voltages which were necessary to obtain the desired discharge. Nitrous oxide is formed in very low concentrations. Nitrogen dioxide is only formed in presence of 5% oxygen, but also in very low concentrations.

A higher voltage gives higher currents and higher pulse frequencies. Higher discharge frequencies lead to a higher nitric oxide production when the discharge does not change. This is not always true; for instance at the 1% oxygen in nitrogen experiment, 5 mm electrode distance (see figure 5.25). Here a lower nitric oxide production occurs at a higher energy input and a higher frequency (17 versus 13 kHz, 4.8 W versus 4.3 W). This effect has to do with the type of discharge. When a glow discharge or arc occurs the thermal character causes the production of nitric oxide instead of removal.

To obtain a pulsed discharge, the voltage had to be increased at increasing electrode separation:
\[ \pm 9-10 \text{ kV for 5 mm, } \pm 11-13 \text{ kV for 10 mm and } \pm 13-14 \text{ kV for 15 mm.} \]
The discharge frequency decreases at an increasing electrode distance:
\[ \pm 15-25 \text{ kHz for 5 mm, } \pm 10-16 \text{ kHz for 10 mm and } \pm 7-13 \text{ kV for 15 mm.} \]
The energy input for the different electrode distances is typically:
\[ \pm 4.3-7.0 \text{ W for 5 mm, } \pm 7.6-12.0 \text{ W for 10 mm, and } \pm 9.8-18.7 \text{ W for 15 mm.} \]

We studied nitric oxide removal, in this reactor. Nitrogen containing 1000 ppm nitric oxide and different oxygen concentrations are used as test gas mixtures. The same experiments are performed with 0.4% water added to the gas mixture (see figure 5.26). The total flow was kept constant at 100 ml per minute.

![Graph](image_url)

*Figure 5.26: The nitric oxide concentration with nitrogen, oxygen and 0.4% water at three electrode distances and two energy inputs.*
The measurements are performed at two energy inputs by using two voltages. The applied voltages, measured frequencies and energy inputs are respectively:

- **5 mm**: 8.0-13.5 kV; 15-28 kHz; 3.0-5.0 W,
- **10 mm**: 10.0-13.5 kV; 10-12 kHz; 8.0-12.0 W,
- **15 mm**: 13.0-18.0 kV; 5-14 kHz; 12.0-27.0 W.

Low water vapour concentrations do not influence the nitric oxide removal reaction, but oxygen does. In absence of oxygen the nitric oxide removal is complete, however the energy input is ten times higher than in the empty "fixed bed" reactor (about 500 eV/NO). The presence of small amounts of oxygen still leads to some nitric oxide removal, but above 3% oxygen, the nitric oxide removal is counterbalanced by nitric oxide production. The production of nitrogen dioxide and nitrous oxide is the same as in the experiment without nitric oxide.

The pulsed discharge is not stable in the current conditions. The voltage had to be adjusted during the experiments to keep the discharge pulsing. The stabilisation depends on the gas mixtures. Addition of hydrogen makes it even impossible to keep the discharge pulsing. Further, the metal of the electrodes evaporates under operating conditions and condensates at the wall of the capillary which became conducting. After a few experiments the reactor had to be cleaned. The reactor becomes hot because the discharge is partially thermal. The pulsed discharge is transformed into a thermal arc when the reactor becomes very hot at high discharge currents. An example of the transformation from pulsed to thermal arc is seen in figure 5.26 in the middle of the experiment with 1% oxygen and a 5 mm electrode distance.

The "capillary" reactor is successful in the nitric oxide removal, but not in the presence of oxygen. However, the removal in pure nitrogen is also very expensive compared to other methods. The pulsed discharge is not stable, but this problem can be solved by adjusting the power supply.

### 5.3 The "Gliding Arc" Reactor

In the "gliding arc" reactor a thermal arc is blown away by the gas (see section 4.2.3). The "gliding arc" reactor consists of two diverging electrodes with a high gas flow in the direction of the diverging part of the electrodes. The applied voltage must be sufficient high to induce a discharge channel at the smallest electrode separation. The high gas flow blows the thermal discharge channel to the diverging part, where the discharge becomes non-equilibrium. In the power supply, as described in section 4.3, a resistor of 2.5 Mohm is used. The inductance is different from the one used for the "capillary" reactor. Different gas mixtures are tested; Nitrogen containing 1000 ppm nitric oxide with 0%, 1% or 3% oxygen, both with and without 0.4% water. The results are shown in figure 5.27.
Figure 5.27: The nitric oxide concentration at different oxygen concentrations in nitrogen with and without water.

In these experiments not much nitric oxide removal appeared, even in the absence of oxygen only a conversion of 50% is obtained for energy costs of about 1000 eV/NO. A net nitric oxide production occurs above 1% oxygen. In the presence of water vapour a somewhat higher nitric oxide production is observed. Hardly any nitrous oxide or nitrogen dioxide is produced with this reactor type at all gas mixtures. The energy input is about 10 times higher than with the "fixed bed" reactor.

The total flow appeared to low to make the arc glide over the full length of the electrodes. Even the highest possible flows of the gas circuit are too low for the "gliding arc" reactor. A pulse frequency of about 8 kHz was observed. This frequency is not caused by the flow, but by the power supply. The frequency always continued, even without a flow. A voltage of 6.5 kV was used. This was about the only voltage the discharge would glide nicely. This voltage gave a current of 1.8 mA (0% oxygen), 1.6 mA (1% oxygen) and 1.5 mA (3% oxygen). The current gives an energy input of respectively 3.6 W, 4.0 W and 4.5 W.

Considering the nitric oxide production, experiments with this reactor were stopped. A thermal plasma produces nitric oxide.
Chapter 6

Conclusions

In this chapter the main conclusions about the nitric oxide removal are summarised as a result of the experiments as described in chapter 5. Firstly, the hypothesis (see chapter 2) will be evaluated. Secondly the results of the three used reactors (see section 4.2) will be evaluated. Finally some recommendation will be given.

Our hypothesis was to make vibrationally excited nitric oxide molecules react at the surface of a catalyst. This reaction should make the removal of nitric oxide from waste gases more efficient than in the homogeneous gas phase. A low temperature plasma should excite the nitric oxide vibrationally via the bulk gas since, the concentration of nitric oxide is low.

However, the experiments show importance of radical reactions and not of vibrationally excited molecules. The importance of the radicals is learned from the experiments with the empty tube reactor with over 5% water vapour and over 3% oxygen (see section 5.1.4). It is well known that water easily forms radicals in a plasma, e.g. ·OH, ·H, ·O and ·O₂H. These radicals can react in many ways with the nitric oxide, although we do not understand exactly how. A part of the nitric oxide reacts to nitrogen and oxygen, but also nitrogen dioxide is formed, which reacts further to nitric acid or aerosols. In dry gas mixtures without oxygen hardly any reaction is observed because no radicals can be formed. In case of the empty tube reactor helium appears to be a little better bulk gas than nitrogen in presence of water vapour and oxygen. Energy is used more efficiently for dissociation of water and oxygen. In presence of nitrogen hardly any nitrogen radicals are formed because nitrogen has a higher dissociation energy than water and oxygen.

In combination with the catalytic support the situation is different, but here also radicals are of great important. In presence of water and oxygen the formed ·OH and ·O radicals are quenched at the surface in this case. The radicals react with -OH and -H groups at the silica surface to water. The energy input is lost in making radicals which react with themselves or the silica surface. When a catalytic support is used in dry gas mixtures without oxygen, nitrogen radicals appear to be important. In case of the use of silica nitrogen is a better bulk gas than helium. The nitrogen radicals are somehow not quenched, but stabilised on the catalyst surface. The nitrogen radicals are not lost and
can react again from the surface. A dispersed transition metal oxides can make it even a little easier to stabilise the nitrogen radical, especially iron oxide.

The radical reaction mechanism also explains the results when γ-alumina is used as catalytic support. In this case a plasma induced adsorption occurs of nitric oxide. Nitrates are formed on the γ-alumina surface in presence of nitric oxide and oxygen. The nitrates are formed by a reaction with nitric oxide and oxygen radicals on the γ-alumina surface.

No evidence is found for the reactivity of vibrationally excited molecules. These are probably quenched before reaching the catalytic surface. Vibrationally exited molecules appear to have a too low energy to activate gas phase reactions. All reactions in the current plasma reactors originally form radicals.

The Reactors

The "Fixed Bed" Reactor

The "fixed bed" reactor is a tube reactor containing a catalytic active bed with an electrode in the centre. First the reactor was filled with silica Grace 332. In this case the reactor is more efficient in dry, pure nitrogen for the removal of nitric oxide. In 100 ml/minute nitrogen containing 1000 ppm nitric oxide a conversion of 90% can be obtained, with energy costs of 120 eV/NO. Every impurity of oxygen or water vapour makes the reaction more energy intensive. Addition of 0.4% water vapour or 3% oxygen lead to 2 to 3 times higher energy costs and half of the conversions compared to in dry nitrogen. Hydrogen, methane, hexane and iso-octane were tested as a reductant. Addition of reductants hardly has any influence on the removal reaction. No direct reduction of nitric oxide occurs, neither burning the oxygen from the gas mixture.

This reactor cannot be applied succesfully for practical gas mixtures. Nearly always we have to do with mixtures containing water vapour or oxygen. The energy costs are high compared to other known methods. We could not improve the efficiency of existing homogeneous gas phase plasma treatment. No future is seen for plasma induced catalytic removal of nitric oxide in this configuration.

The use of γ-alumina as catalytic support in the "fixed bed" reactor has a different effect. This support material can be used for a plasma induced adsorption of nitric oxide. In dry nitrogen with 5% oxygen and 1000 ppm nitric oxide over 95% nitric oxide is adsorbed for energy costs of 50 eV/NO. In helium with 5% oxygen the energy costs are even lower: 25 eV/NO. Optimisation of the discharge parameters can probably reduce the energy costs for nitrogen. Nitric oxide appeared to be reaction adsorbed as nitrates on the γ-alumina surface. The γ-alumina can be recovered by thermal desorption at 400 °C. The desorption energy costs are not included in the 50 eV/NO. This may be an interesting way to remove or reconcentrate nitric oxide.

The homogeneous plasma induced reaction is the most energy efficient in the empty "fixed bed" reactor. Nitrogen containing 1000 ppm nitric oxide, more than 5% water vapour and more than 3% oxygen are necessary for a efficient removal reaction. A conversion of 90% can be reached at energy
costs of 50 eV/NO. A selective oxidation to nitrogen dioxide and nitric acid and probably aerosols occur. The empty "fixed bed" reactor seems to be very promising in nitric oxide removal. Further research is necessary, especially the influence of the wall effect and the residence time.

**The "Capillary" Reactor**

The "capillary" reactor consists of two electrode in a narrow quartz capillary. In this reactor type the discharge is stabilised by an axial gas flow. Unfortunately the "capillary" reactor produces nitric oxide, even at low oxygen concentrations. Only in pure nitrogen containing 1000 ppm nitric oxide (100 ml/minute) a complete conversion can be reached at 4 W input power (500 eV/NO). Low water vapour concentrations do not have any influence at the reaction. This reactor may be tried at higher water vapour concentrations in presence of oxygen, but the reactor probably gets too hot and thus the plasma too thermal for nitric oxide removal. Also the energy consumption is too high to be competitive with other methods. The high pressure drop in the small reactor volume makes it difficult to use this type for industrial purposes.

**The "Gliding Arc" Reactor**

The second capillary reactor is the "gliding arc" reactor. This reactor consist of two diverging electrodes. The discharge is blown away in the direction of the diverging electrodes. The "gliding arc" reactor is also not very useful for nitric oxide removal. Nitric oxide in pure, dry nitrogen is only partially removed (50%) for 3.6 W (1000 eV/NO). Water vapour and oxygen have a bad influence on the removal reaction and lead to nitric oxide production. The thermal character of the reactor makes the gas too hot to remove nitric oxide. The reactor consumes also a lot of energy compared to other methods.
Recommendations

It is known that radicals are the driving force for plasma induced reactions. These radical reactions are very important for the removal of nitric oxide. A combination of a catalytically active surface and radicals is not desirable, because active radicals, like ·OH and ·O, loose their activity on these surfaces. A possibility for nitric oxide removal is the selective oxidation to nitrogen dioxide. Nitrogen dioxide can easily be extracted from the waste gas. This is also a good possibility for plasma induced reactions in presence of more than 5% water vapour and more than 3% oxygen. For industrial applications more research is needed to non-catalytic plasma induced radical reactions. Also the influence of the wall effect and the residence time need to be determined for further application.

In some processes it may be desirable to concentrate the nitric oxide or nitrogen dioxide. Plasma induced adsorption on γ-alumina can be a good possibility in this case. The desorbed nitric oxide and nitrogen dioxide from adsorbed nitrates on the γ-alumina can be recycled, for instance in the nitric acid production. More research is needed to know exactly how the adsorption process works and what the adsorption capacity of γ-alumina is. Also the desorption process and the desorption energy costs have to be determined.

I certainly think there is a future for using low temperature plasma techniques in environmental chemistry. Removal of nitric oxide is one, but many more pollutants can be destructed by plasma induced reactions like dioxines and poly aromatic compounds. Vibrationally excited species should not be considered important in these reactions, all reaction will be based on radical reaction mechanisms. This combination of chemical kinetics, electrotechnical engineering and theoretical physics needs a good cooperation of chemists and electrotechnics and physicists.
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Wie dit leest is gek

De titel die hier boven staat
is slechts bedoeld als goede raad
en dwars is hij of zwak van geest,
die desondanks nog verder leest.
Wie hier niet stopt verknoeit zijn tijd
aan zoute zee aardigheid,
want wat nu volgt heeft kop nog staat
en is het sop in de kool niet waard.
Verder lezen heeft geen zin,
er staat geen zinnig woord meer in.
Dwing dus U zelf hier om te stoppen,
de rest is slechts om U te foppen,
om U - gelijk men doet met gekken -,
diep door de cacao te trekken,
erger nog, om U te honen,
door zwart op wit hier aan te tonen,
dat U geen flinke meid of vent
doch slechts een slap slak weekdier bent,
een ouwe bet, die ernstig lijdt
aan ziekelijke nieuwsgierigheid,
die niet wil luisteren naar mijn raad,
doch plompverloren verder gaat
mijn oorden aan zijn laars te lappen
en wederom er in te trappen.
Hoe nu? Zit U nu nog te lezen?
Dan doet mij dit het ergste vrezen.
Recht van leden, ja, recht van lijk,
maar hebt U ze wel alle vijf?
Wat moet het akelig donker zijn
daar binnen in dat vogelrek!
Hier valt U lelijk door de mand
met dit vertoon van onverstand,
dit staaltje onbenulligheid
dat werkelijk ten hemel schreit.

Gelukkig slaat dit niet op U,
want mensen met een hoog I.Q.,
dat zijn de lui die beter weten,
die deze kul het raam uit smeten,
en wel onmiddelijk bij 't begin,
die mensen trapen er niet in.
Alleen de lui die verder lezen,
am, tsjaa, dat zijn dan ook de dwazen,

want knettergek moet je toch wezen
om dit tot hier te blijven lezen.

Moral: Gebrek aan intellectuele standing
leidt zelden tot een happy ending

john o'mill, bonny ballads