AC/DC Power Modulation
for
Corona Plasma Generation

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Summary

The focus of this thesis is on AC/DC-pulsed power induced atmospheric streamer plasmas with application in chemical processing, especially the removal of odor from gasses. For industrial applications, a demonstration model has to be designed. This thesis describes the work performed on two assignments. The first assignment was to optimize the existing power modulator and the second assignment was to find the most optimal reactor configuration.

The first step for the optimization of the existing design of the power modulator was to study the present schematics and to determine the exact function of all the parts. Special attention was paid to the pulse transformer. Because this transformer is non-ideal (i.e., the coupling factor $k$ is not equal to one) a leakage inductance is introduced into the circuitry. It was found that the impedance of this leakage inductance is high enough for the resonant circuit. As a result, one of the additional inductors from the original design is not required anymore. Another aspect studied was the use of a bi-polar transformer, instead of a uni-polar one. For the AC/DC system, the transformer is used in discontinuous mode. Before the next pulse commences, the flux in the core will be at its residual value $B_{res} > 0$. The residual value limits the flux alternation and the transferable power. This is an undesirable effect for pulse transformers. Bi-polar use of a transformer does not have this disadvantage. Because of the bi-polar transformer, a full bridge rectifier is required at the output side, to obtain only positive voltages on the reactor. Although several high voltage diodes are required, tests have shown that no RC snubbers are needed for protection of these diodes.

For the second assignment (finding the optimal reactor configuration), electrical, optical and chemical measurements were performed and combined. The new system together with the new pulse transformer was not yet available for the measurements. Therefore, the original modulator with a uni-polar pulse transformer was used.

The AC/DC-pulse source consists of a two-stage resonant charging circuit, switched sequentially by thyristors, a pulse transformer, rectification and a reactor configuration. The experiments have been carried out with different reactor configurations (different electrode distance, number of reactors, extra applied capacitance) and different pulse repetition rates (100 – 800 pulses per second). Electrical waveforms were recorded with commercially available probes (North Star PVM-1 high voltage probe, Tektronix P5200 HV Differential probe and Pearson 110 and 6600 current probes). With the obtained voltage and current waveforms, the power, energy and energy transfer efficiency were determined. Ozone generation (measured using UV absorption technique at the exhaust of the reactor) was chosen as a monitor for the chemical processing efficiency. A chemical model was used to determine the actual $O^*$ yield through measurement of the produced ozone, the plasma volume, the relative humidity, the gas temperature and the plasma energy. The plasma volume is determined by using photographs made by a high speed ICCD camera.
Two criteria were derived which should be obeyed when high energy transfer efficiencies (i.e., well-matched systems) are required: 1) A high energy transfer efficiency of 95% is reached when the total high voltage capacitance $C_h$ is high (i.e., extra capacitors of around 12 nF have to be connected to the reactor); 2) A large $C_h$ is needed for the energy to be independent of the pulse repetition rate (i.e., again additional capacitors in the order of 12 nF are required).

The study of the ICCD photographs has resulted in an estimation of the plasma volume. A value of 0.5 dm$^3$ plasma volume per reactor was obtained. The plasma volume is a function of the applied voltage. The dependency is weak however. Therefore, this effect has not been taken into account in this thesis. Because of the measuring inaccuracy, an error is introduced, which has effect on the calculations of the oxygen radical yield. Calculations have shown that a change in volume of 5 times as small or 4 times as large results in a difference in the range of $\sim 0.5 - 12\%$. This error is low and acceptable.

For the study of the chemical yield, a key chemical process is monitored. Many pollutant (odor) removal processes are initiated by oxygen radicals. Ozone production from ambient air also depends on these oxygen radicals and is selected as an appropriate process. The ozone and oxygen radical yield (amount of radical per unit of energy) were monitored in a set of experiments where reactor settings were varied systematically. Typical ozone yields were found to be in the range of 10 – 40 g/kWh. These yields are good, especially when considering that the gas conditions are non ideal: relative humidity of 40%, not pure oxygen. Comparable yields are achieved with commercial ozone generators. Typical oxygen radical yields were found to be in the range of 1 – 4 mole/kWh. It was found that, to obtain high chemicals yields, a high energy ratio $E_p/E_t$ is required. $E_p/E_t$ is the ratio between the energy dissipated by the plasma during the charging of the high voltage capacitance and the total dissipated energy. A high energy ratio can be obtained when the high-voltage capacitance is limited. This criterion is opposite to the one required for obtaining a high energy transfer efficiency.

Based upon the results, it has become evident that a tradeoff has to be made between the contradicting design criteria. The exact value of the additional high-voltage capacitors has to be dimensioned based on this tradeoff.
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Acknowledgement
1. Introduction

Using pulsed power systems as a technology for pollution emission control is a promising application. Although there are several possible ways to generate streamers, here the focus is on AC/DC-pulsed power induced plasma. This promising method, recently introduced by the EPS group, nowadays attracts a lot of research, although the pulsed power method has by far a higher air cleaning capacity than non-pulsed methods (e.g., AC, RF, etc). The AC/DC modulator is simple compared to the high voltage pulse source. Less complicated high voltage components are necessary (i.e., no high voltage switch such as a spark gap and no pulse forming networks such as a TLT).

The principle of an AC/DC system is based on electrical discharges created by high voltage pulses. One of the possible appearances of the electrical discharges is called corona. Corona can sometimes be recognized as a crackling sound when being near high voltage lines in foggy weather. However, it is much more than just that. Corona is a plasma (a medium which properties are determined by the presence of free electrons). Under the right conditions, this plasma can create new electrons and ions, but also radicals. Plasma generation is often accompanied with light emission. The radicals enable several chemical conversion reactions: decrease molecular mass of hydrocarbons (tar-cracking), convert odor into non-smelling compounds (odor-removal), killing microorganisms in food (pasteurization). Other applications, like the surface activation of textiles or biogas conditioning, are now under investigation and will be available in the future.

To demonstrate the feasibility of the AC/DC technique, a demonstration model was designed. The system was designed to have a typically output power of 10 kW.

In the following section a description of the objectives of this thesis is given. Afterwards, a chapter overview is given.

1.1 Objectives

This thesis exists of two major assignments. The first part of the thesis is to study the necessity of the various components in the system and the possibility of using a bi-polar pulse transformer for the usage in the next generation of AC/DC-pulsed power modulators.

The second part of this thesis is to find criteria for the optimal reactor design. For the reactor design several parameters are important, like electrode distance, number of reactors, applied voltage and reactor capacitance. The optimal reactor should have a high energy efficiency as well as a high chemical yield.
1.2 Chapter overview

In order to reach 10 kW, it was determined to design the system in such a way that the pulse repetition rate is 2000 pulses per second with an average energy of 5 J/pulse. To investigate the necessity of the various components in the system and the possibility of using a bi-polar instead of a uni-polar pulse transformer, several experiments were carried out. This is described in the first part of this report.

In the second part of this thesis, the effort put into finding criteria for the optimal reactor design (electrode distance, number of reactors, applied voltage, reactor capacitance) is discussed. When designing the reactor both electrical and chemical efficiencies should be high. Different reactor settings were tested in order to obtain the relevant knowledge regarding the good matching between the energy input and output and the chemical processing efficiency.

A more detailed overview of the chapters is described below.

In Chapter 2, the experimental set-up and the experimental procedure are presented. The design of the power modulator and the employed diagnostic tools are discussed. General characteristics of the power modulator, plasma and ozone production are shown.

In Chapter 3, the optimization of the power modulator is discussed. The effect of the coupling factor of the transformer on the circuit and the energy transfer is discussed. Also the (dis-)advantages of bi-polar utilization of the pulse transformer are presented.

Chapter 4 presents the measurements to study the electrical behavior of the system. The measurements were performed to deepen the understanding of the modulator-plasma interaction.

For the determination of the oxygen radical concentration, the plasma volume has to be determined. In order to determine this plasma volume, optical measurements were performed. The results of these measurements are discussed in Chapter 5.

Chapter 6 presents the measurements to study the chemical efficiency. The measured ozone yield and the obtained plasma volume from the optical measurements were used to gather information about the oxygen radical concentration. Based on the results obtained from these measurements, criteria for achieving highly efficient plasmas are derived.

In Chapter 7, the important conclusions are summarized and recommendations for future research are presented. Criteria for the design of the future reactor are also given in this chapter.

This thesis also contains two appendices. In Appendix A, a list of the components of the used power modulator is given. In Appendix B, the program is presented that was used to determine the ozone concentration and the chemical reactions used for the kinetic model.
2. Experimental set-up

A schematic overview of the used AC/DC system is shown in Figure 2.1. Large parts of this system have already been under investigation in the EPS-group. A nice review of several important aspects can be found in [Yan2001]. A typical voltage waveform produced by this system is shown in Figure 2.2. A list of the component values can be found in Appendix A-I.

![Figure 2.1. A schematic overview of the AC/DC-pulsed power source [Nair2004].](image)

![Figure 2.2. Typical waveform of AC/DC pulsed power source.](image)
2.1 AC/DC source

Basically, the total system exists of two parts: a low voltage part and a high voltage part. In Figure 2.1 it can be seen that the pulse transformer TR separates the low voltage part from the high voltage part. The low voltage part is designed as a resonant charging unit. It consists of a mains filter, a set of rectifiers, two energy storage capacitors $C_0$ and $C_1$, three air-core inductors $L_1$, $L_2$ and $L_3$, the primary windings of the pulse transformer and three thyristors. The thyristors are protected for over voltage by RC snubbers and the voltage suppressor $S$. The thyristors are switched consecutively to charge the corona reactor and the capacitor $C''_h$.

The high voltage part consist of the secondary windings of TR, two diodes $D_1$ and $D_2$, two damping resistors $R_4$ and $R_5$ and an air-core inductor $L_4$. Diode $D_2$ and resistor $R_5$ are added for two reasons.

1) To protect diode $D_1$ by quenching the resonance between the secondary windings of TR and its parasitic capacitance.

2) For dissipating the energy remaining in the core as a result of the magnetization current.

The RC snubber is to protect $D_1$ during normal operation.

A two step process is used to generate the high voltage pulses. In the first step (see Figure 2.3), $C_L$ is resonantly charged via the energy storage capacitors $C_0$, the thyristor $T_{h1}$ and inductor $L_1$. Because of charge conservation and because $C_0 \gg C_L$, voltage doubling on $C_L$ is achieved. Typical voltage and current shapes on $C_L$ are shown is Figure 2.4 [PPT2006].

![Figure 2.3. a) Schematic overview of the first step. b) Equivalent electrical scheme [PPT2006].](image)

For illustration, in Figure 2.4 the waveforms are shown for all situations, i.e., also when $C_0$ is not excessively larger than $C_L$. When $C_0 = C_L$, the voltage on $C_L$ (labeled as $V_2$ in the figure), after the resonance will be the same as the initial voltage on $C_0$ (labeled as $V_1$ in the figure). The final voltage on $C_0$ will be zero. If $C_0 \approx C_L$, voltage doubling on $C_L$ is achieved. The relative change of the voltage on $C_0$ is negligible. If $C_0 \ll C_L$, the opposite is true. The relative change of voltage on $C_L$ is negligible and the voltage on $C_0$ reverses around 0 volt (assuming $C_L$ is initially not charged).
The following formulas can be used to determine voltage and current as function of time:

At $t = 0 \rightarrow V_1 = V_{10}$ and $V_2 = V_{20}$ \hspace{1cm} (2.1)

$C = \frac{C_0 \cdot C_L}{C_0 + C_L}$ \hspace{1cm} (2.2)

$\omega^2 = \frac{1}{L_1 \cdot C}$ \hspace{1cm} (2.3)

$I = I_0 \sin(\omega \cdot t)$ \hspace{1cm} (2.4)

$I_0 = \frac{V_{10} - V_{20}}{\omega \cdot L}$ \hspace{1cm} (2.5)

$V_1 = \frac{C}{C_0} (V_{10} - V_{20}) \cdot \{\cos(\omega \cdot t) - 1\} + V_{10}$ \hspace{1cm} (2.6)

$V_2 = \frac{C}{C_L} (V_{10} - V_{20}) \cdot \{1 - \cos(\omega \cdot t)\} + V_{20}$ \hspace{1cm} (2.7)

During the second step the high voltage capacitor, the reactor capacitance and the capacitance of the high voltage connections are resonantly charged via $C_L$, $L_2$, $TR$, $Th_2$, $D_1$ and $L_4$. When the charging voltage is higher than the plasma inception voltage, streamer formation inside the reactor is achieved. The high voltage diode $D_1$ prevents that the energy stored in the reactor and in $C^*_h$ flows back into the pulse transformer $TR$ and back into the low voltage part. For the charging of the reactor and of $C^*_h$, the same formulas as mentioned above can be used, of course the values of $C_0$, $C_L$ and $L_1$ have to be substituted with the appropriate values.

After charging of $C_h$ the voltage on $C_L$ can become negative (depending on system parameters). In the past [Yan2001] it was shown that this can result in large pulse-to-pulse instabilities (the variation in the amount of energy per pulse becomes large). To overcome this problem, the voltage on $C_L$ should be positive before it is charged again.
For this reason Th₃ was added to the circuit. A schematic overview of the voltage on Cₐ is shown in Figure 2.5.

![Figure 2.5. An overview of the voltage on Cₐ. The arrows refers to the closing of the corresponding thyristor [Yan2001].](image)

### 2.2 Plasma

During the second step the high voltage capacitor C’ₕ, the reactor capacitance Cₐ and the capacitance of the high voltage connections C cable are charged as described before. For convenience the total capacitance of C’ₕ, Cₐ and C cable is called Cₕ hereafter. During the charging period the voltage on Cₕ rises. When the voltage reaches the plasma inception voltage, streamer formation inside the reactor is initiated and plasma is created. This plasma dissipates the energy which has been transferred from Cₐ.

A distinction can be made between two plasma stages. The first stage occurs during the charging of Cₕ. When the plasma inception voltage is exceeded, plasma is formed and energy is directly dissipated. As a result of this additional current requirement, the voltage rise-rate decreases. After the charging, the second plasma stage commences. During this stage the energy stored in the high voltage capacitor C’ₕ, the high voltage connections C cable, and the reactor Cₐ is dissipated by the plasma.

As a first order approximation, the plasma can be modeled as a resistor. The resistance depends on the applied voltage. During the second stage a small current keeps on flowing through the reactor. Since Cₕ is not being charged anymore, the voltage on the reactor will drop. Because of the resistive nature of the plasma, the discharging can be roughly seen as a RC circuit with the plasma resistance and Cₕ. More details are discussed in Chapter 4. The voltage keeps on decreasing until:
1) The voltage becomes too low to maintain the plasma.
2) A new charging cycle commences.
In both cases, $C_h$ can not be completely discharged and the voltage will not decrease to 0 volt. As result a base voltage remains on $C_h$, which is referred to as DC voltage in this report. All of the above explains the typical waveform as shown in Figure 2.2.

### 2.3 Matching

One of the goals of the research is to design the AC/DC system in such a way that most of the energy stored in $C_L$ is dissipated by the plasma. This can be accomplished by ensuring that the reactor is matched to the power modulator. Several design criteria can be derived that should be followed to ensure optimal energy transfer [Yan, Nair2005]. The criteria are derived based on the laws of energy (2.8) and charge (2.9) conservation:

\[
\frac{1}{2}C_L \cdot V_o^2 = \frac{1}{2}C_h \cdot (V_p^2 - V_{DC}^2) \tag{2.8}
\]

\[
C_L \cdot V_o = N \cdot C_h \cdot (V_p - V_{DC}) \tag{2.9}
\]

Substituting Equation 2.8 in Equation 2.9:

\[
N \cdot V_o = V_p + V_{DC} \tag{2.10}
\]

Substituting Equation 2.10 in Equation 2.9 gives:

\[
C_L = N^2 \cdot C_h \cdot \left(\frac{2 \cdot V_p}{N \cdot V_o} - 1\right) \tag{2.11}
\]

Or in terms of $V_{DC}$

\[
C_L = N^2 \cdot C_h \cdot \left(1 - \frac{2 \cdot V_{DC}}{N \cdot V_o}\right) \tag{2.12}
\]

where $N$ is the pulse transformer ratio, $V_o$ is the primary voltage, output from low voltage part, or input to the transformer, $V_p$ is the peak voltage and $V_{DC}$ is the DC voltage on $C_h$.

Although these equations give some theoretical background for the choices that have to be made when designing the system, there are some short comings with the assumptions made. The major problem can be found when considering that the charging and discharging of $C_h$ partly overlap in time. For both Equations 2.8 and 2.9 this implies that the term on the right-hand side is underestimated by a factor equal to the amount of energy resp. charge “consumed” by the plasma during charging of $C_h$. For future studies it is recommended that this contribution is taken into consideration when deriving equations like 2.11 and 2.12.
The equations indicate that good matching can be achieved when the proper value of $C_h$ is used. However, for the system design this is not the only aspect. Not only is it required that the energy which is discharged from $C_L$ is transferred efficiently into the reactor, but also that an as large as possible part of the energy stored in $C_L$ is used. Basically this implies that a reactor has to be used in which a sufficiently large amount of plasma can be generated (i.e. the electric field should be high and the reactor volume should be large enough). This will be systematically investigated in Chapter 4.

### 2.4 The reactor

A schematic overview of the reactor is shown in Figure 2.6. A parallel plate reactor was considered the most suitable for these experiments. The main reasons are:

1) The relative big volume compared e.g. to a cylindrical reactor.
2) This configuration permits optical access from the side and the top without disturbing the electric field.
3) The possibility to easily change the reactor dimensions (such as the number of reactors and the wire-plate distance).

The configuration of the reactor is as follows. Two aluminum plates of one by one meter are placed in parallel. These plates are connected to ground and they act as the collecting electrode. In between the plates high voltage electrodes are placed at a predetermined, fixed distance. During the experiments the distances were 5.0 cm and 5.5 cm.

The electrodes are installed vertically (at 48 millimeters intervals) between the plates. At the top and bottom these wires are supported using rods, which are field-controlled to prevent plasma activity and sparking. An example of an electrode is shown in Figure 2.7. As shown in the figure the electrodes have sharp points. On these points large electric field enhancement occurs. Because of this field enhancement, the voltage becomes very high locally. These high voltages are needed to achieve streamer formation.
A single electrode has a length of 80 cm (top to bottom) and a width of 1.35 cm (point to point). 168 sharp points are evenly distributed over the electrode, 84 on either side. A total of 18 electrodes are used per reactor. The reactor capacitance $C_r$ of a single reactor is around 0.230 nF.

During the experiments several parameters have been altered to study the effect on the system performance:
- $C_L$: 3μF and 6μF.
- The number of reactors: 1, 2 and 4 reactors.
- $C'_h$: 0nF, 0.5nF, 1nF, 1.5nF, 2nF, 4nF, 8nF and 12nF.
- Pulse repetition rate: 100-1000 pps in 10 steps of 100 pps.

2.5 Set-up and measurements

In Figure 2.8 a schematic overview of the complete experimental set-up is shown. The performed measurements can be divided into three categories: electrical, chemical and optical.
2.5.1 Electrical measurements

The measurement of fast, high amplitude voltage and current waveforms in an environment with large EM-fields is very difficult. EMC aspects should be taken into consideration.

For the visualization of the voltage and current waveforms a LeCroy Waverunner 2 oscilloscope (1 GHz, 4 GSamples/s) is used. The oscilloscope was placed in an EMC-cabinet. The energy from the grid is filtered before it enters the back of the EMC cabinet. The coaxial measurement cables were also connected to the back side of the EMC cabinet. From the inside they were connected to the scope.

For the measurement of the high voltage waveform on the reactor a North Star PVM-1 high voltage probe was used. This probe is an RC-divider with an attenuation factor of 1,000. The bandwidth of the probe is 80 MHz, where the maximal measured frequency is approximately 15 kHz. A typical voltage waveform as measured with this probe is shown in Figure 2.9 titled “Reactor Voltage”. The figure shows that the voltage rises to a maximum $V_p$. The voltage drops during the second stage to a DC voltage $V_{DC}$. The waveform is in agreement to the theoretical waveform shown in Figure 2.2.

For the measurement of the (floating) voltage on $C_L$ a Tektronix P5200 High Voltage Differential probe was used. This probe has an attenuation factor of 500. A typical waveform as measured with this probe is shown in Figure 2.9 titled “$C_L$ Voltage”. The figure shows that during charging of $C_L$ the voltage rises to a value $V_{CL+}$. During the discharging of $C_L$, it is possible that the voltage drops below zero. As discussed in Section 2.1, for output stability the voltage should be positive before the next pulse forming cycle commences. In the figure the voltage reversal, as caused by switching thyristor 3, can be seen clearly. The voltage on $C_L$ after switching of thyristor 3 is called $V_{CL-}$. The measured waveform is in agreement to the theoretical waveform shown in Figure 2.5.

For the current measurements two Pearson probes were used. To measure the current through $C_L$ a Pearson 110 was used. To determine the reactor current a Pearson 6600 was used. Both probes have an attenuation factor of 20. Typical current waveforms through $C_L$ and the reactor are shown in Figure 2.9 called “$C_L$ Current” and “Reactor Current” respectively. The reactor current is a sinusoidal function. After the charging of $C_h$, the current keeps flowing (see section 2.2), however with such a small amplitude that it cannot be seen in the figure. The current through $C_L$ shows three distinct sinusoidal peaks. The first is from charging $C_L$, the second is from discharging $C_L$ and the third is from reversing the voltage on $C_L$ by switching thyristor 3. The measured current waveforms are in agreement with the theoretical waveforms shown in Figure 2.4.
The following equations were used to calculate the different parameters:

The energy per pulse delivered by $C_L$:

$$ E_{C_L} = \frac{1}{2} \cdot C_L \cdot \left( V_{cL}^2 - V_{cL-}^2 \right) \quad (2.13) $$

The energy dissipated in the reactor is calculated in two parts. The energy per pulse during the charging period $E_p$ and the discharging period $E_H$ are calculated as described below. The total energy cannot be calculated as the time integral of the reactor power because the current during the discharging period is too small to be measured correctly.

$$ E_p = \int_{0}^{(V=V_p)} V \cdot I_t \cdot dt - \frac{1}{2} \cdot C_r \cdot \left( V_p^2 - V_{DC}^2 \right) \quad (2.14) $$

$$ E_H = \frac{1}{2} \cdot C_h \cdot \left( V_p^2 - V_{DC}^2 \right) \quad (2.15) $$

Adding Equations 2.14 and 2.15 gives the total energy per pulse $E_i$ of the high voltage part.
The efficiency $\eta$ of the transferred energy form $C_L$ to $C_h$:

$$\eta = \frac{E_r}{E_{C_L}}$$  \hspace{1cm} (2.17)

The electrical power $P$ dissipated by the corona plasma:

$$P = E_r \cdot \text{prr}$$  \hspace{1cm} (2.18)

where prr is the pulse repetition rate (pulses per second, pps).

### 2.5.2 Chemical measurements

The concentration of ozone $O_3$, in the exhaust of the reactor, can be used as a direct measure for the concentration of $O^*$ radicals which is produced by the plasma [Winands2007]. The ozone concentration was determined using a UV absorption technique (Figure 2.10) in the Hartley-band (230-290 nm). In this band the absorption of ozone is largest. As UV source, an Ocean Optics Deuterium light source was used. An HR2000 spectrometer also from Ocean Optics was used to acquire the spectra (wavelength 200-400 nm, resolution 0.1 mm). For the optical connection between the UV source, the measuring cell and the spectrometer laboratory-grade solarization-resistant optical fibers with a diameter of 400 $\mu$m were used. Two collimating quartz lenses were used to focus the light in the measuring cell. The optical path length $d$ in the measuring cell is 0.14 m. The cell was located in the exhaust pipe approximately 2 meters from the reactor.

![Figure 2.10. Schematic overview of UV absorption technique [Winands2007].](image)

The ozone concentration in the exhaust gas flow can be determined using Lambert-Beer’s law:

$$\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = c_{O_3} \cdot \varepsilon(\lambda) \cdot d$$  \hspace{1cm} (2.19)
Experimental set-up

where \( c_{O_3} \) is the ozone concentration (molecules/m\(^3\)), \( I(\lambda) \) is the absorption spectrum, \( I_0(\lambda) \) is the background spectrum (gas flow without ozone) and \( \varepsilon(\lambda) \) is the absorption cross-section of ozone as function of wavelength in m\(^2\)/molecule. The values for \( \varepsilon(\lambda) \) are in the order of approximately \( 1\cdot10^{-21} \) and can be found in the literature [e.g., Seinfeld 1986]. The ozone concentration multiplied by the constant of Avogadro (\( \text{Av} = 6.02214\cdot10^{-23} \)) gives the ozone concentration in the exhaust \( c_{O_3,\text{exh}} \) (mole/m\(^3\)).

The spectrometer is controlled via a personal computer. Before switching on the plasma, a background spectrum \( I_0(\lambda) \) is measured. Once the set-up is turned on, the absorption is monitored. After a while, 5-10 seconds, the spectrum reaches a stable value. This indicates a constant ozone production. The spectrum \( I(\lambda) \) can now be determined. After determining the spectrum, the set-up is switched off. The airflow in the reactor is maintained to remove all the ozone from its volume. Subsequently, a new measurement can be performed.

With the obtained spectra \( I_0(\lambda) \) and \( I(\lambda) \), in combination with Equation 2.19, the ozone concentration in the flow can be determined. To reduce measurement errors, calculations were performed at 15 different wavelengths in the range from 250 till 260 nm. The actual result was the average of those 15 points. The resulting measuring error is estimated to be less than 5%, as presented in [Winands2007].

During the chemical measurements the ambient air properties were monitored as well.

- The temperature was measured directly before and after a measuring sequence of about 20-25 minutes in the reactor. This temperature was determined using a standard temperature meter (ST-321). The temperature was found to be between 21-24 °C during all the measurements. No noticeable difference in temperature could be measured between the beginning and end of a measuring sequence.
- The relative humidity was monitored using a standard relative humidity meter (ST-321) in the open air approximately 2 meters from the reactor.
- The airflow rate was monitored in the exhaust of the reactor using a Testo 435 vane anemometer. During a measuring sequence the airflow was measured. The average value was used for the calculations.

Once the ozone concentration is determined, and the energy dissipated by the plasma is measured, the ozone yield can be calculated as:

\[
\text{Yield [g/kWh]} = \frac{c_{O_3,\text{exh}} \cdot M_{O_3} \cdot F \cdot 1000}{P} \tag{2.20}
\]

where \( c_{O_3,\text{exh}} \) is the concentration of ozone (mole/m\(^3\)) measured in the exhaust, \( M_{O_3} \) is the molar mass of ozone which is 48 g/mol, \( F \) is the average measured flow (m\(^3\)/h) and \( P \) is the electrical power (W).
Ozone is produced as a result of the reaction between oxygen radicals (as produced by the electrical discharge) and present oxygen molecules. Besides the concentration of these species the amount of ozone produced also depends on the relative humidity of the air and on the gas temperature. A Matlab program was developed that models the chemistry occurring in the reactor volume. Using this program, the amount of oxygen radicals produced by the discharge can be determined, using the ozone concentration in the exhaust, and several other parameters like humidity and temperature, as input parameters. The Matlab program is presented in Appendix B-I. The 71 chemical reactions, where 17 species are involved, used for the chemical model are listed in Appendix B-II.

One of the required model parameters is the H$_2$O concentration in the air. This parameter can be determined once the gas-temperature and the relative humidity are known:

$$c_{H_2O} = RH \cdot Av \cdot \left(\frac{3.1243 \cdot 10^{-6} \cdot T^{3} + 8.1847 \cdot 10^{-5} \cdot T^{2} + 3.2321 \cdot 10^{-3} \cdot T + 0.05018}{M_{H_2O} \cdot 10^{6}}\right)$$ (2.21)

where $c_{H_2O}$ is the concentration of water in air (molecules/cm$^3$), RH is the relative humidity (%), Av is the Avogadro constant ($6.02214 \cdot 10^{23}$), T is the temperature (°C) and $M_{H_2O}$ is the molar mass of water which is 18.0 g/mol. This equation is derived from information found on [www1].

Equation 2.21 has two boundary conditions:

1) The temperature has to be between 0 and 40 °C.
2) The relative humidity has to be between 0 and 100 %.

Besides the H$_2$O concentration, the program also requires other input parameters. Most notoriously is the (initial) O$^\cdot$ radical concentration as produced by the plasma. Basically, this is the unknown parameter. Below the iterative procedure is described that was adopted to find this initial concentration. Another input parameter that is required is the ratio between the concentration of O, N, OH and H radicals as produced by the electrical discharge. According to [Peyrous1990, Winands2007], the following ratio can be adopted:

$$O : N : OH : H = 1 : 0.06 : 0.6 \cdot 10^{-3} \cdot RH : 0.6 \cdot 10^{-3} \cdot RH$$

If the measured temperature, the measured relative humidity and an arbitrary concentration of oxygen radicals are entered into the model, the program calculates the ozone concentration in the plasma. The output ozone concentration, $c_{O_3, str}$, determined by the program can be compared to the measured ozone, $c_{O_3, exh}$. For this purpose the following relation should be used that links the concentration in the plasma and the concentration in the exhaust flow:

$$c_{O_3, exh} = \frac{c_{O_3, str} \cdot V_{str} \cdot f}{F}$$ (2.22)
where $C_{03,\text{exh}}$ is the concentration ozone (mole/m$^3$) measured in the exhaust, $C_{03,\text{str}}$ is the concentration ozone (mole/(m$^3$·pulse)) in the reactor, $V_{\text{str}}$ is volume of the plasma streamers (m$^3$), $f$ is the pulse repetition rate (pps) and $F$ is the airflow in the exhaust (m$^3$/s).

If the calculated $C_{03,\text{exh}}$ coincides with the measured concentration (within a difference of less than 0.1 %), the initial concentration of oxygen radicals has been chosen correctly. If there is a difference, the $O^*$ concentration has to be changed and the program has to recalculate the ozone concentration $C_{03,\text{str}}$. This procedure has to be repeated until a match within a good accuracy is obtained. Using this iterative routine, the actual amount of $O^*$ radicals produced by the discharge can be determined.

One of the parameters required to follow this procedure is $V_{\text{str}}$, which is unknown. By using ICCD photography it is tried to roughly determine this value. The ICCD set-up is described in the following section.

### 2.5.3 Optical measurements

To visualize the plasma generated in the reactor and to determine the plasma volume $V_{\text{str}}$, photographs had to be made. For this purpose an intensified charged coupled device (ICCD) was used. In Figure 2.11 a schematic overview of the optical measurement is shown. A Princeton Instruments 576G/RB intensified CCD camera was used (180-800 nm, 576x384 pixels).

![Figure 2.11. Schematic overview of the ICCD system. Adequate EMC precautions have been taken to obtain reliable operation.](image)

To be able to photograph the plasma activity at a single point of the electrodes, a reactor had to be used in which only one electrode was constructed.

Two kinds of measurements were made: top-view and side view pictures. The side-view pictures were taken in order to visualize the shape of the plasma and the path of the individual streamers. The camera was placed approximately 1.5 meters from the electrode and was directly focused on the electrode. The top-view pictures were taken in order to
visualize the shape of plasma and to study the effects of neighboring electrodes (for this experiment, the number of electrodes in the reactor was increased from 1 to 18). A flat mirror positioned at an angle of 45 degrees was used to focus the camera on the plasma.

For these optical measurements the effect of two parameters on the plasma appearance were investigated: the applied voltage and the pulse repetition rate. The applied reactor voltage was regulated by the system’s input voltage (controlled by mean of a variac). The pulse repetition rate was set to 10 pulses per second and 100 pulses per second. The camera’s shutter time was set to 100 and 10 ms respectively in order to catch a whole period.

In Table 2.1 an overview is given of the reactor voltage as function of the input voltage (percentage of the maximum input voltage) and the pulse repetition rate.

<table>
<thead>
<tr>
<th>Input Voltage (%)</th>
<th>Pulse Repetition Rate (pps)</th>
<th>Pulse Peak Voltage $V_P$ (kV)</th>
<th>DC Voltage $V_{DC}$ (kV)</th>
<th>Pulse Repetition Rate (pps)</th>
<th>Peak Voltage $V_P$ (kV)</th>
<th>DC Voltage $V_{DC}$ (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10</td>
<td>28.3</td>
<td>15.2</td>
<td>100</td>
<td>31.9</td>
<td>20.3</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>27</td>
<td>15.2</td>
<td>100</td>
<td>29.6</td>
<td>20.2</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
<td>25.6</td>
<td>15.2</td>
<td>100</td>
<td>26.8</td>
<td>19.9</td>
</tr>
<tr>
<td>70</td>
<td>10</td>
<td>23.8</td>
<td>15.1</td>
<td>100</td>
<td>23.8</td>
<td>19.5</td>
</tr>
</tbody>
</table>

In Figure 2.12 a couple of pictures as produced by the intensified CCD camera are shown. With these pictures the streamer volume (as required for Equation 2.22) can be estimated. The results are discussed in Chapter 5.

**Figure 2.12.** Pictures made by ICCD camera. In photograph A, no voltage is applied. In photograph B the following voltages and pulse repetition rate were applied: $V_P = 31.9$ kV, $V_{DC} = 20.3$ kV and $prr = 100$ pps.
Figure 2.12 (continued). Photograph C shows the top part of the electrode. Photograph D shows a view from above. For both photographs, $V_p = 31.9$ kV, $V_{DC} = 20.3$ kV and $prr = 100$ pps was applied.

The pictures have a resolution of 486x271 pixels (shown along the axis). The actual size of the photographs is 6.5x3.6cm. The white line indicates the position of the grounded plate. The distance between the saw tooth shaped electrode and the plate is 5.5 cm.

In picture A the electrode configuration is shown. No voltage is applied here. The diamond shape structure that can be distinguished is caused the wall of the laboratory.

Picture B shows plasma activity as observed in the reactor. At first glance, it looks like the streamers pass the grounded plate. This is an artifact caused by the reflection in the aluminum plate caused by the perspective view of the camera. The bright white spots at the sharp point of the electrode have been removed from the picture (using Matlab software) in order to enhance the visibility of the streamers. For this typical example the applied voltage had a peak voltage of 31.9 kV and a DC voltage of 20.3 kV. The pulse repetition rate was 100 pps. It can be seen that, at the (four) sharp points of the electrode, streamers are produced. These streamers cross the complete gap to the plate. When the voltage is reduced no streamers will cross to the other side. Only short streamers are visible in the vicinity of the glow at the sharp points.

Picture C shows plasma activity as observed at the top part of the electrode. The pulse conditions where the same as above. Again streamers can be observed that cross the reactor gap. The streamers produced at the top-most point of the electrode follow a different path to the plate-electrode. Apparently, the streamer path is determined by the shape of the applied electric field and/or the vicinity of other streamers.

Picture D shows a top-view photo. At first glance, it looks like the grounded plate is at the wrong place. This is an artifact however caused (again) by the perspective view of the camera. For this typical example the applied voltage had a peak voltage of 31.9 kV and a DC voltage of 20.3 kV. The pulse repetition rate was 100 pps. In the picture, individual streamers cannot be distinguished, only the general shape of the plasma. No individual streamers could be distinguished, since:

1) A large number of streamers per meter is generated.
2) The depth resolution of the camera system is insufficient to focus over the complete wire.

Detailed information regarding the pictures will be presented in Chapter 5.
3. Optimization of the circuit

A part of this master thesis work was to investigate possible adjustments to the circuit in order to improve its performance. The studied subjects can be listed as:

1) The effect of the leakage inductance of the primary windings of the pulse transformer TR on the performance of the low voltage part.
2) The possibility of using a bi-polar pulse transformer (i.e. taking advantage of the complete B-H-curve of the magnetic core).
3) If a bi-polar transformer is used, a full bridge rectifier has to be used instead of the single diode D₁. A question that has to be answered is: are the RC-snubbers (to protect the individual diodes) still necessary?

3.1 Primary windings of the pulse transformer and L₂

In the design as presented in Figure 2.1 it has been assumed that the pulse transformer TR is ideal. Ideality implies that:

a) The ohmic losses of the windings are zero. No voltage drops and energy losses occur.

b) The hysteresis losses of the core are zero, as are the eddy currents.

c) All the fluxes produced by the primary and secondary windings are completely enclosed by the core. The coupling coefficient k is 1.

In reality the transformer will not be ideal. In this work the effect of having \( k < 1 \) was investigated. In Figure 3.1 a schematic overview is shown of a resonant charging circuit with a pulse transformer TR.

![Figure 3.1: Resonant charging circuit with TR.](image)

The circuit consists of \( C_L, L_2, TR, D \) and \( C_h \). The voltages over the primary and secondary coils can be derived as follows [Jongh1998, Liu2005]:

\[
V_1 = L_P \frac{dl_1}{dt} - M \frac{dl_2}{dt} = j \cdot \omega \cdot L_P \cdot I_1 - j \cdot \omega \cdot M \cdot I_2 \quad (3.1)
\]
\[ V_2 = -L_s \frac{dl_2}{dt} + M \frac{dl_1}{dt} = -j \cdot \omega \cdot L_s \cdot I_2 + j \cdot \omega \cdot M \cdot I_1 \]  

(3.2)

where \( V_1 \) is the voltage on primary windings, \( I_1 \) is the current through the primary windings, \( V_2 \) is the voltage on the secondary windings and \( I_2 \) is the current through the secondary windings. \( L_p, L_s \) and \( M \) are the primary, secondary and mutual inductance of TR respectively and \( \omega \) is the frequency (rad/s) which can be calculated using Equation 2.3. The primary current \( I_1 \) can be derived as:

\[ I_1 = \frac{V_1}{j \cdot \omega \cdot L_p} + I_2 \cdot \frac{M}{L_p} \]  

(3.3)

Eliminating \( I_1 \) by substituting Equation 3.2 in Equation 3.3 gives:

\[ V_2 = V_1 \cdot \frac{M}{L_p} - j \cdot \omega \cdot L_s \left( 1 - \frac{M^2}{L_p \cdot L_s} \right) \cdot I_2 \]  

(3.4)

Using \( n = M/L_p \) and \( k^2 = M^2/(L_p L_s) \) these equations can be rewritten into:

\[ I_1 = \frac{V_1}{j \cdot \omega \cdot L_p} + nI_2 \]  

(3.5)

\[ V_2 = nV_1 - j \cdot \omega \cdot L_s \left( 1 - k^2 \right) \cdot I_2 \]  

(3.6)

Equations 3.5 and 3.6 describe a circuit as shown in Figure 3.2. The pulse transformer TR is represented by an ideal transformer, with a transfer ratio of 1:n, and two uncoupled inductors \( L_p \) and \( (1-k^2) \cdot L_2 \). The other components are the same as in Figure 3.1.

![Figure 3.2. Equivalent circuit with an ideal transformer.](image)

In this figure \( L_p \) and \( L_s \) are the primary and secondary inductors of the pulse transformer respectively, the coupling factor \( (k) \) equals \( M/\sqrt{(L_p L_s)} \). Referred to the primary side, the circuit can be represented as shown in Figure 3.3. In this figure \( L \) is the leakage inductance of the transformer. This inductance is a result of a non-ideal coupling factor (i.e., \( k \) is not equal to one).
Although a transformer is never ideal, when care has been taken during the design, the coupling factor approaches 1. As a result the leakage inductance $L$ is significantly smaller than the primary inductance $L_p$. Consequently the equivalent circuit as shown in Figure 3.3 can be simplified as shown in Figure 3.4.

This figure is the same as the resonant charging circuit shown in Figure 2.3. The same formulas as derived in Chapter 2 can be used for the calculation of the different parameters. For this part of the thesis especially Equations 2.2 and 2.3 are important.

The equivalent capacitance $C$ can be derived as:

$$C = \frac{n^2 \cdot C_L \cdot C_h}{C_L + n^2 \cdot C_h}$$  \hspace{1cm} (3.7)

According to Equation 2.3, the frequency $\omega$ can be written as:

$$\omega = \frac{1}{\sqrt{(L_2 + L) \cdot C}}$$  \hspace{1cm} (3.8)

where $L$ is the leakage inductance which is defined as:

$$L = L_p \cdot \frac{1 - k^2}{k^2}$$  \hspace{1cm} (3.9)

In Figure 3.5 the behavior of $L$ as function of $k$ and $L_p$ is shown.
Two conclusions can be drawn from this figure:

1) A better coupling factor results in a small leakage inductance, independent of the primary inductance.
2) The larger the primary inductance $L_p$, the larger the leakage inductance $L$ for the same $k$.

During the design of a pulse transformer two boundaries of the leakage inductance must be taken into account:

1) The best way to design a transformer is with a coupling factor of one. However a small inductance has to be incorporated in the system to limit the current (especially for the thyristors).
2) The coupling factor should not be too low because this would result in pulses with a too large voltage rise-time, which (as will be shown) are not desirable from chemical efficiency point of view. (The value of $\omega$ decreases if $L$ is increased, see Equation 3.8)

It is within our capabilities to build a pulse transformer with a coupling factor of at least 0.996. The primary inductance $L_p$ will be in order of 3 mH. This means, (Figure 3.5) that the leakage inductance $L$ will be approximately 24 $\mu$H. In combination with the parameters discussed at the end of Section 2.4, Equations 3.7 and 3.8 and a transformation rate of 1:60, the frequency and the period time are calculated. The results are shown in table 3.1.
From this table it can be concluded that for $C_L = 3 \ \mu F$, $C_L$ is discharged in 15 to 26 $\mu$s for an increasing $C_h$. For $C_L = 6 \ \mu F$ the discharge time is in order of 17 till 35 $\mu$s.

In order to meet the first boundary as discussed above, the peak current through the thyristors is not allowed to be too high. The peak current can be calculated using Equation 2.4. In the worst case the peak current will be approximately 300 amperes (with $C_L = 3 \ \mu H$). Based on the specifications (voltage and current), two thyristors were found. For Th1 and Th3 TR 918 1150 20 was chosen. A fast thyristor with a maximum reversed voltage of 2 kV and an average current of 1148 Amperes. For thyristor 2, TR 918 850 30 was chosen. The choice for this one was based on the higher reversed voltage of 3 kV. The average on-state current is around 850 Amperes. For the new system ($C_L = 10 \ \mu F$), the peak current is around 600 Amperes. The thyristors are used in a save zone.

Based on this finding it can be concluded that there will be sufficient leakage inductance at the primary side of the transformer, purely as a result of the transformer being non-ideal. Consequently, the additional inductor $L_z$, as shown in Figure 2.1, is not required for the protection of the thyristor and consequently can be omitted from the circuit.

### 3.2 Bi-polar transformer

In the original design, a uni-polar transformer was used. Uni-polar utilization of a transformer occurs if the direction of the magnetic flux does not change during operation. The amplitude of the magnetic flux may vary but it will always be larger than zero. Since a transformer is always non-ideal, there will always be some leakage inductance, and consequently some inductive energy stored in its magnetic field. The energy stored in the pulse transformer’s magnetic field is dissipated as heat.

For the AC/DC system, the transformer is used in discontinuous mode. Before the next pulse begins, the flux in the core will be at its residual value (>0). The residual value limits the flux alternation and the transferable power. This is an undesirable effect for pulse transformers. An example of the B-H-curve of a pulse transformer used in uni-polar direction is shown in Figure 3.6.
The pulse transformer for the new system will be designed as a bi-polar pulse transformer. This means that the voltage and the current through the transformer alternate. Consequently, the magnetic field in the pulse transformer's core alternate between the positive and negative flux direction. The chosen core material is laminated Metglas 2605SA1. The typical hysteresis curve is shown in Figure 3.7.

Bi-polar utilization ensures that the flux in the core does not remain fixed above a certain value, but that it follows a much larger part of the B-H-curve. The most important advantage of bi-polar utilization compared to uni-polar utilization is that bi-polar utilization permits the use of a smaller core because of the larger change in the core's flux density.

The hysteresis losses (core losses) are a function of the area inside the loop. The area of the bipolar transformer is larger than the area of the uni-polar transformer. The core losses in a bi-polar TR will be higher than in a uni-polar TR (at least if the same core material is used). This additional loss however is only a small disadvantage compared to the advantage.
3.3 The full bridge rectifier

In order to use a bipolar pulse transformer and have positive polarity voltage on the reactor, a full bridge rectifier is required. The full bridge rectifier consists of four high voltage diodes as shown in Figure 3.8.

![Figure 3.8. Pulse transformer with full bridge rectifier.](image)

The “old” circuit rectifier has a RC-snubber over diode D₁ for protection (Figure 2.1). During the switching off of the diode a rapid voltage rise can be measured. This voltage rise (the recovery voltage) is caused by the stray capacitance of the diode (and its connections). The recovery voltage can seriously damage a diode. The RC-snubber makes sure that no charge can build up between the diode connections. It has to be investigated whether the RC-snubbers are still necessary when a full bridge rectifier is used.

A schematic overview of the used measuring circuit is shown in Figure 3.9. Since at the time of the measurements the bi-polar transformer was not yet available, the 1:60 uni-polar transformer had to be used. Several measurements have been performed in order to determine whether the snubbers are necessary. The high voltage diodes used during these measurements and (which are going to be in the future rectifier circuit) have a hold-off voltage of 50 kV.

![Figure 3.9. Schematic overview of full bridge rectifier measurement.](image)

In Figure 3.9, the D₁ till D₄ are the diodes, V₁ is the input voltage, Vₕ₊ is the rectified high voltage on the reactor wire and Vₕ₋ is the voltage on the plate electrodes. During the measurements the distance between the electrodes and the grounded plates was 5 cm. The maximum measured voltage on the reactor was 31 kV. An example of the measured waveform is shown in Figure 3.10. In this figure the voltage is measured on Vₕ₊ and V₁. The third waveform shown is for V₀. This is the difference between V₁ and Vₕ₊. As can
be seen in Figure 3.10, the voltage $V_-$ has a maximum of around 30 kV and $V_{DI}$ has a maximum of around –30 kV.

![Figure 3.10. Measured voltages.](image)

The same kind of voltages waveforms are measured for the other diodes.

During the switching off of the diodes, the diodes go into recovery, no voltage build-up is recorded at all. The reason for this is that when a specific diode goes into its blocking state, at least two of the remaining three diodes are in their conducting state. As a consequence, no charge can built up. For this reactor setting (electrode-plate distance of 5 cm), approximately 31 kV is the highest voltage measured. It is expected that for lower and even higher voltages no voltage peaks will occur.

Since no voltage peaks occur, for various measurements, when the diodes stop conducting it can be concluded that the RC-snubbers are not necessary for circuit protection.

3.4 The new AC/DC system

A schematic overview of the new AC/DC system with bipolar pulse transformer and full bridge rectifier is shown in Figure 3.11. Compared to the schematic circuit shown in Figure 2.1, the new circuit comprises a few more components. The switching cycle has been extended compared to the system as shown in Figure 2.1.

1) The first pulse is generated by consecutively switching of thyristors 1, 2a and 3. Diodes $D_1$ and $D_3$ are in conduction mode.
2) The second pulse is generated by consecutively switching of thyristors 1, 2b and 3. Diodes D2 and D3 are in conduction mode. This sequence is repeated, for repetitive pulse generation.

The new system is not tested here. The new power modulator is still under construction and evaluated. For the measurements of this thesis, the power modulator as shown in Figure 2.1 was used.
4. Results of electrical measurements

In Section 2.5.1 the experimental set-up was discussed together with several design criteria that have to be followed to obtain an efficient system. To determine if these criteria are accurate, several measurements have been performed. The results of these measurements are discussed in this chapter. The results can be divided into the following three categories:

1) Energy measurements.
2) Efficiency measurements.
3) Power measurements.

Most of the results have been performed using a low voltage capacitance $C_L = 3 \, \mu F$. Some additional measurements, with $C_L = 6 \, \mu F$ are discussed in Section 4.4.

4.1 Energy measurements

One of the requirements for the system design is that as much energy as possible is dissipated by the plasma in the reactor. Figure 4.1 shows the dissipated plasma energy as function of the pulse repetition rate. Equation 2.16 was used to determine this energy.

![Figure 4.1. Energy as result of the pulse repetition rate.](image)

It is expected that the energy per pulse does not depend on the pulse repetition rate. In Figure 4.1 it can be seen however that this is not always the case. In this figure, three
different measurements of the energy per pulse are shown. It can be observed that if only 1 or 2 reactors are used, the energy per pulse decreases for increasing pulse repetition rate. If, however, 4 parallel reactors are used, the energy per pulse does not depend on the pulse repetition rate. The measured output voltages do not play a significant role. This finding indicates that the reactor volume is an important parameter. There has to be sufficiently space to allow for plasma generation.

Another observation that can be made is that the energy per pulse is always almost constant when the pulse repetition rate exceeds 550 pps. This is convenient for the future system, since the intention is to use high repetition rates, up to 2000 pps. In this regime the pulse repetition rate does not affect the energy per pulse significantly. In order to study the effect of the total high voltage capacitance $C_h$ on the performance system, the energy per pulse is averaged over the results for 550 till 800 pps.

Figure 4.2 shows the effect of the total high voltage capacitance on the average energy per pulse. The measurements have been performed for three reactor configurations.

![Figure 4.2. Average energy.](image)

In Figure 4.2 it can be seen that more energy is dissipated by the plasma when $C_h$ is increased. When $C_h$ increases, the DC voltage increases as well (see Figure 4.4). As was shown in [Yan2001] and [Winands2007], higher voltages result in reduced plasma resistances. More current can flow through the plasma which results in increased energy dissipation by the plasma. In Figure 4.2 it can also be observed that the number of reactors has a large effect on the dissipated energy. This finding again shows that the amount of energy the plasma can dissipate depends on the available space in the reactor. For the system design this implies that the reactor has to be designed sufficiently large.
As will be demonstrated in Chapter 6, an important parameter for the chemical efficiency of the plasma is the ratio between the energy dissipated by the plasma during the charging of the reactor $E_p$ and the total energy dissipated by the plasma $E_t$. A high ratio means that most of the available energy is dissipated in the charging period. A low energy ratio means that most of the available energy is dissipated during the discharging of the high voltage capacitance $C_h$.

In Figure 4.3 the effect of high voltage capacitance $C_h$ on the ratio $E_p/E_t$ is shown. Only measurements with a pulse repetition rate of 800 pps are shown.

![Figure 4.3. Energy ratio.](image)

From this figure it can be concluded that for lower values of $C_h$, a significant part of the energy is already dissipated during the charging of the reactor. This effect can be explained by studying Equation 2.3. A low value for $C$ results in a high value for $\omega$. The higher $\omega$ becomes the shorter the voltage rise time on the reactor. High voltage amplitudes are obtained soon after charging has commenced, and the plasma can ignite in an early stage. Consequently, a large portion of the energy is already dissipated during the charging of the reactor.

Not only the dissipated energy, but also the reactor voltage is affected by the value of the high voltage capacitance. This effect is shown in Figure 4.4. The peak voltage $V_p$ decreases as the capacitance increases. This effect can also be explained by Equation 2.3 as stated above. Because of the short rise time, the voltage can rise to a value that is higher than the plasma inception voltage, obtaining higher values than would be the case if the plasma would ignite sooner. If the short rise time (and a high $dV/dt$) results in a higher ignition voltage requires time-resolved measurements. The DC voltage increases as the high voltage capacitance increases. This can be explained by the discharging curve.
from Figures 2.2 and 2.9. The discharging of $C_h$ is like a RC-network. If the capacitance increases, the RC-time increases. A small $C_h$ and a large difference between $V_p$ and $V_{DC}$ results in a high $dV/dt$ (shown in Figure 4.5).

Figure 4.4. The effect of the high voltage capacitance on the peak and DC voltage, the pulse repetition rate is 800 pps.

Figure 4.5. The effect of the high voltage capacitance on the $dV/dt$, the pulse repetition rate is 800 pps.
In Figure 4.4 the peak voltage is shown by the blue diamantes. The DC voltage is shown by the pink color. The squares (Vdc1) are the DC voltage measurements with one reactor. The triangles (Vdc2) and crosses (Vdc4) are the measurements with two and four reactors respectively. No distinction can be made between the number of reactors when considering Vp. VDC however is influenced by the number of reactors. It can clearly be seen that the DC voltage is lower when the number of reactors increases.

The DC voltage is the remaining voltage after discharging of the high voltage capacitance Ch. This discharging can be described with a RC time. The decreasing DC voltage for an increased number of reactors indicates a smaller RC time. Since for an increased number of reactors the capacitance increases as well, this can only be explained by a decreased plasma resistance R. This conclusion is logical when considering that the resistance is determined by the amount of plasma. More reactors imply more space for the plasma, i.e., more streamers can be produced. Each streamer has a resistance. Since all of the streamers are in parallel, the total plasma resistance decreases if the number of streamers increases. In [Winands2007] it is shown that an increase in peak voltage results in a decrease of the plasma resistance. However, in Figure 4.4 the peak voltage is rather constant that this effect can not be determined.

In Figure 4.5 the dV/dt decreases as Ch increases. This is comparable to the effect of the high voltage capacitance on the energy ratio Ep/Ei. The voltage rate of rise was determined between 20 – 80 % of the voltage slope from the DC voltage to the peak voltage. In order to obtain a high dV/dt, the high voltage capacitance Ch has to be kept low.

Figure 4.6 shows the plasma resistance as function of the number of reactors. The plasma resistance is fitted from the RC time. It is clearly visible that the resistance decreases when the number of reactors increases. The jitter on the measurements is very low; around 10 to 15 %, which is in the range of the measurement inaccuracy.
From the energy point of view the following conclusions can be drawn:

- To transport as much energy from the low voltage side into the reactor, the reactor should be sufficient large.
- To transport as much energy from the low voltage side into the reactor, a high capacitance of $C_h$ is preferred.
- Increasing $C_h$ results in a shift in energy dissipation from the rising slope of the voltage ($E_p$) to the discharging stage ($E_h$).
- Increasing $C_h$ results in a decreasing $dV/dt$.
- A high energy in the slope means a high peak voltage and a low DC-voltage.

### 4.2 Efficiency measurements

Not only is the dissipation of as much energy as possible desired, also a high energy transfer efficiency is required. This efficiency is calculated by using Equation 2.17. In Figure 4.7 an overview is shown of the effect of $C_h$ on the efficiency. The efficiency is averaged over the pulse repetition rate from 550 till 800 pps. $C_L = 3 \ \mu F$. 
In this figure all the measurements with $C_L = 3 \mu F$ were used. No difference in energy transfer efficiency was found between the measurements with 1, 2 or 4 reactors. In Section 4.1 it was shown that changing the number of reactors has an effect on the reactor capacitance $C_r$ and the voltages, especially the DC voltage. From Figure 4.7 however it can be concluded that the energy transfer efficiency only depends on the total high voltage capacitance $C_h$ and not on the number of reactors or the output voltages. The overall efficiency is around 92% with a 6% deviation. In the higher region of the $C_h$ values, some of the measurements have a higher efficiency than 100%. This is caused by the measurement inaccuracy.

The conclusions that can be drawn for the efficiency are as follows:
- The efficiency is high: around 92%, and for all parameters an excellent matching can be obtained.
- The efficiency slightly increases with increasing $C_h$.

### 4.3 Power measurements

The new system is designed for an average power up to 10 kW. According to Equation 2.18, the power can be calculated as the product of the energy per pulse and the pulse repetition rate. Increasing the power to 10 kW can be achieved by increasing these parameters. The goal is to obtain a situation with 5 J/pulse at 2000 pps.
For the system as used in this thesis, Figure 4.8 gives an overview of the effect of the high voltage capacitance on the power. The pulse repetition rate is set up at 800 pps and $C_L = 3 \mu F$. In this figure also the effect of the number of reactors on the plasma power is shown. For the situation with four reactors, the power is relatively stable around 1000 W. When decreasing the number of reactors, also the amount of power dissipation decreases. This effect was already discussed in the preceding section: the reactor volume should be sufficiently large to allow for plasma generation.

![Figure 4.8](image)

*Figure 4.8. The effect of the capacitance on the dissipated power.*

Ideally the power is a linear function of the pulse repetition rate. Figure 4.9 shows the average power as function of the pulse repetition rate and $C_h$, when two reactors are used. The pulse repetition rate was varied from 100 till 800 pps. Although for the high values of $C_h$ the relation is nearly linear, this is not the case for situations with low values of $C_h$. The power starts to saturate for pulse repetition rates exceeding ~ 600 pps. Apparently, for these conditions the energy per pulse decreases.
In Figure 4.10 the results of a similar measurement are shown, only now for a situation with four reactors. The linear relation as function of the pulse repetition rate is more pronounced now. For the lower repetition rates the power is almost identical. For the higher pulse repetition rates the power starts to saturate, especially when $C_h$ is low. The saturation effect is far less than shown in Figure 4.9, with two reactors.
A maximum amount of power of \(~1.1\) kW was obtained with the configuration: \(C_L = 3\ \mu\text{F}\), four reactors and \(C'_h = 12.49\ \text{nF}\). In this case however, the voltage on the reactor is almost a DC voltage (see Figure 4.4 \(V_p - V_{DC} < 2\ \text{kV}\)). As will be shown in Chapter 6, this is not advantageous from chemical processing point of view.

The conclusions can be summarized as follows:

- If the dimensions of the reactor are too small, the power saturates as function of the pulse repetition rate.
- The maximum amount of power is dissipated when \(C'_h\) is large.

### 4.4 Measurements with \(C_L = 6\ \mu\text{F}\)

Similar measurements as presented in the preceding sections have also been performed for the situation where \(C_L = 6\ \mu\text{F}\). Ideally, the power and energy per pulse should be twice the amount as obtained for \(C_L = 3\ \mu\text{F}\). Several of the observed trends as discussed above were also obtained for this new situation. However, many of the required measurements could not be performed as a result of excessive electrical breakdown in the reactor volume. For the experimental conditions: number of reactors = 1, \(C'_h = 0\) until 12 nF and the pulse repetition rate exceeding 100 pps, it was not possible to perform measurements as result of sparking. For the experimental conditions: number of reactors = 2, \(C'_h = 0\) until 8 nF and the pulse repetition rate exceeds 600 pps, it was not possible to perform measurements as result of sparking. For these experimental conditions the system had also difficulties closing thyristor 2 (see Figure 4.11). This phenomenon is undesired because it results in uncontrolled switching behavior.

![Voltage and Current Waveform](image)

**Figure 4.11.** Voltage and current waveform on \(C_L\) where A) is the voltage waveform and B) is the current waveform.
At first it was believed that the excessive amount of breakdowns was caused by insufficient flow in the reactor. If this would be the case, too much energy is dissipated in the gas leading to a situation in which too many ionized species are created in the reactor. Different experiments were performed to obtain information regarding the effect of the flow. During the experiments the input voltage was reduced (by mean of a variac) in order to do measurements without breakdowns.

The results of the first experiment are shown in Figure 4.12. During this test two reactors were connected and $C'_{h}$ was 8 nF. The test was performed with two different flows: 275 and 600 m$^3$/h.

![Figure 4.12. The effect of the flow on the electrical power with two connected reactors.](image)

The conclusion which can be drawn from this is experiment is that the amount of power dissipated in the reactor is not increased if the flow is doubled. Apparently, for these experimental conditions, the flow has no effect on the power.

The results of the second experiment are shown in Figure 4.13. During this experiment only one reactor was connected and $C'_{h} = 0$. The flow through the connected reactor was varied 550, 275 and 140 m$^3$/h.
In this figure it can be observed that the flow does have an effect on the power. If the flow through the reactor is high, the plasma is able to dissipate much power. At lower flow rates, the amount of dissipated energy decreases. The explanation for this phenomenon cannot be provided. However possibly the presence of ionized/exited species in the gas are responsible for the changed power. In order to get a total overview of the effect of the flow additional experiments are required, preferably with a larger range of flows e.g. from 0 to 1000 m³/h.

Nevertheless, when combining the findings from Figure 4.11 and 4.12 one thing becomes evident: the reactor should be sufficiently large. But also: the airflow has to be sufficiently large.

4.5 Conclusions and recommendations

For the new system the following aspects are important from an electrical point of view:
- As much as possible of the energy has to be dissipated by the plasma (high efficiency).
- The energy per pulse should not depend on the pulse repetition rate.

From all the aspects discussed above the most important conclusion that can be drawn is that the plasma needs sufficient space (see Figure 4.2). The reactor is than able to handle the available energy without causing electrical breakdowns and/or decreased energy dissipation.
In order to get the highest efficiency the $C'_{h}$ should be large in the order of 12 nF. The corresponding efficiency is 95% (see Figure 4.6).

To obtain a linear relation between the average power and the pulse repetition rate, the reactor needs to be sufficiently large and the extra $C'_{h}$ is also necessary. The extra high voltage capacitance should be in the order of 12 nF as well.

The effect of the flow has to be examined more closely. A possibility is to repeat the experiment at different flow settings.
5. Results of optical measurements

For the calculation of the amount of oxygen radicals $O^*$ as produced by the plasma, the initial concentration of the ozone in the streamer volume ($c_{O_3,\text{str}}$) has to be known. This initial concentration can be calculated by using Equation 2.22. It can be seen that the plasma volume is one of the parameters that has to be known to be able to determine $c_{O_3,\text{str}}$. To determine the plasma volume several optical measurements were carried out.

In Section 5.1 the experimental method is explained. The effects of the applied voltage and the pulse repetition rate on the plasma appearance are discussed in Sections 5.2 and 5.3 respectively. To determine the actual streamer volume (as discussed in Section 5.6) the streamer width and the shape of the plasma have to be investigated. Results are presented in Sections 5.4 and 5.5 respectively.

5.1 The plasma volume

In order to determine the plasma volume photographs were taken with the ICCD camera. As discussed in Section 2.5.3, two kinds of photographs were taken: top-view and side-view pictures. For the side-view pictures, a reactor with only one electrode was used. For the top-view pictures, two experimental conditions were recorded: a reactor with only one electrode and a reactor (fully loaded) with 18 electrodes. As result of this last experiment it will be possible to comment on the effect of the presence of adjacent streamers on the plasma generation.

During the optical measurement the effect of two parameters on the plasma appearance were investigated: the applied voltage and the pulse repetition rate. As discussed in Section 2.5.3, the reactor voltage was regulated by decreasing the input voltage. For an overview of the reactor as function of the input voltage and the pulse repetition rate, see Table 2.1.

The photographs from the ICCD camera are in grayscale. Using a computer, this grayscale is translated into a colormap which closely resembles the actual color of the plasma. One of the problems encountered when studying the pictures was that the light intensity near the sharp points of the high voltage electrode was too large. As a result, the visibility of the less intensive streamers is limited, as can be seen in Figure 5.1a. By using the developed software, the bright spots can be removed from the picture, thereby increasing the quality of the picture. This effect is visualized in Figure 5.1b.
Figure 5.1. A) The picture before white spot removal. B) The same picture after white spot removal. The white line is the grounded plate-electrode. The distance between the saw tooth shaped electrode and the plate is 5.5 cm. It looks like the streamers pass through the grounded plate. This is an artifact caused by the reflection in the aluminum plate caused by the perspective view of the camera. The pictures have a resolution of 486x271 pixels (shown along the axis). The actual size of the photographs is 6.5x3.6 cm.

Using pictures similar to the ones shown in Figure 5.1 it is possible to determine the width of the streamers. In this report, the width (which was determined by the developed software) is defined as the full width at 80 percent of the maximum light intensity value.

5.2 The effect of the applied voltage

In Figure 5.2 four typical examples of the plasma appearance are shown. As can be seen, the appearance depends on the applied voltage and thus on the average electric field in the reactor gap. For these measurements the pulse repetition rate was 100 pps and the shutter time was 10 ms. In the pictures the bright spots near the electrode points have been removed from the pictures.

Figure 5.2. The effect of the applied reactor voltage on the plasma appearance. A) Applied reactor voltage: \( V_p = 31.9 \text{ kV} \) and \( V_{DC} = 20.3 \text{ kV} \). B) Applied reactor voltage: \( V_p = 29.6 \text{ kV} \) and \( V_{DC} = 20.2 \text{ kV} \).
Picture A shows plasma activity as observed in the reactor when the peak voltage $V_p$ was 31.9 kV and the DC voltage $V_{DC}$ was 20.3 kV. A number of streamers can be seen, some of which reach the grounded plate-electrode on the other side.

In picture B, again some of the streamers cross to the plate-electrode. However, compared to the streamers in picture A, their intensity is less. The reason for this difference is the lower voltage used: $V_p$ was 29.6 kV and $V_{DC}$ was 20.1 kV. For these conditions, many of the streamers that start at the sharp point stop propagating halfway the electrode gap. This has to be caused by the lower electric fields in the gap.

In picture C the reactor voltage was reduced to: $V_p = 26.8$ kV and $V_{DC} = 19.9$ kV. As a result of the low voltage, the streamers cannot cross the complete electrode gap. The streamers start at the point electrode, but quench after they traveled approximately one third of the total distance. This results in that only a kind of glow is visible near the pointed electrodes.

In picture D only short streamers are visible in the vicinity of the glow at the sharp points. The voltage was reduced to $V_p = 23.8$ kV and $V_{DC} = 19.5$ kV. The streamer concentration has reduced as well, the glow is less dense.

The conclusion that can be drawn from these pictures is that the streamers need a high electric field to cross the complete electrode gap. In other words, high voltages or short electrode distances are required. When the voltage is reduced, the total plasma volume decreases slightly.

### 5.3 The effect of the pulse repetition rate

During the optical measurements, two pulse repetition rates were used in order to investigate the effect of the pulse repetition rate on the plasma appearance. The pulse repetition rates used were 10 and 100 pps.
In Figure 5.3, two photographs are shown. In picture A, prr = 10 pps. In picture B, prr = 100 pps.

![A and B](image)

**Figure 5.3.** Effect of pulse repetition rate on plasma appearance. A) 10 pps, with an applied voltage on the reactor of \( V_p = 28.3 \text{ kV} \) and \( V_{DC} = 15.2 \text{ kV} \). B) 100 pps, with an applied reactor voltage of \( V_p = 31.9 \text{ kV} \) and \( V_{DC} = 20.3 \text{ kV} \).

There are some differences as function of the pulse repetition rate. When the prr is 10 pps, no streamers cross the gap completely. The situation is different when the prr is 100 pps; some streamers do cross the gap. Also, for the 10 pps measurements, the intensity of the light is (about five times) larger than for the 100 pps measurements. A possible explanation for this phenomenon is the longer shutter time for the 10 pps measurements. By keeping the shutter open for a longer time period, the exposure time of the photograph is increased. Because of the large contribution of the glow discharge, the streamers cannot be seen anymore.

A second explanation for the fact that the '10 pps' streamers cannot cross the complete gap might be found in the effect of the applied voltage. For both measurements the input voltage (voltage on \( C_0 \)) was kept equal. However, as a result of the different pulse repetition rates, the reactor voltages differ. For 100 pps, \( V_p \) and \( V_{DC} \) were 31.9 and 20.3 kV respectively. For 10 pps, \( V_p \) and \( V_{DC} \) were 28.3 and 15.2 kV. As mentioned in Section 5.2, when the voltage is decreased, no streamers are able to cross the complete electrode gap.

Because of these two effects, a well founded conclusion regarding the effects of the pulse repetition rate cannot be made. In order to increase the relevant knowledge, it is advised to perform time-resolved measurements.

### 5.4 Streamer width

In some of the pictures in Figure 2.12 (B and C) and Figure 5.2 (A and B) a few streamers crossing the complete gap can be seen. In the other pictures only a glow is visible. From the first type of pictures, the streamer width can be determined. Using the pictures, the streamer width could be determined to be between 680 and 760 μm. The
lowest widths were measured for the lower output voltage. The streamer width increases, when the reactor voltage increases. The difference in the measured widths is very small, in the order measurements inaccuracy. The average streamer width was determined to be 737 \mu m.

### 5.5 Plasma shape

Figure 5.4 shows the top-view pictures of the plasma appearance. Picture A shows the plasma shape when only one electrode is present in the reactor. Picture B shows the situation when there are multiple electrodes (separated 48 mm).

As seen from the top, the plasma shape resembles that of an onion. In the center of the onion, where the light is the brightest, the streamer concentration is the highest. Further outward the light intensity decreases as does the streamer concentration. Figure 5.4b is focused on two electrodes. A space between the plasma of the adjacent electrodes is clearly visible. It is not clear if this space is the result of a mutually repelling (e.g. Lorentz) force or the fact that the distance between the electrodes is too large. In order to investigate if the electrodes can be positioned closer together (to increase the number of electrodes per reactor volume), additional measurements are required.

With the data as presented so far, it is possible to develop a schematic representation of the plasma shape (see Figure 5.5). The side-view is shown in drawing A and the top-view drawing is shown in B. In drawing A, the sharp points where the streamers start are 9 mm apart from each other. From the points the streamers move outwards a little. At a distance of about 9 mm from the sharp points, streamers generated at two adjacent points start to overlap. From this point forward, the streamers move in a parallel direction, straight towards the plate electrode. Usually they stop propagating as a result of a too low local electric field. It may appear that some of the streamers cross each other, or merge together. This however is an artifact caused by the relative long shutter time.
As seen from the top, the streamers can expand further because the sharply pointed conductors are at a distance of 48 mm from each other. Neighboring electrodes are too far away to influence each other. An onion like shape can be recognized. The maximum width of the onion shape is 28 mm. At the widest point, around 6 mm from the sharp points, the first streamers stop to propagate. Separate streamers can not be distinguished since on the pictures, too many streamers overlap.

![Figure 5.5. Schematic figures of streamer shapes. A) A schematic view from the side. B) A schematic view from the top. The figures are not in scale.](image)

The plasma volume exists primarily out of the plasma in the core. The streamers that cross the complete gap hardly contribute to the plasma volume. Using Figure 5.5 an estimation of the plasma volume can be made. A schematic view of the plasma volume is shown in Figure 5.6.

![Figure 5.6. A schematic overview of the plasma volume.](image)
Results of optical measurements

5.6 Plasma volume

With the model shown in Figure 5.6 and the streamer width from Section 5.4 the plasma volume $V_{str}$ was estimated as follows.

- As stated in Section 5.4 the streamer width is $737 \mu m$. The cross-section of a streamer is therefore $0.427 \text{ mm}^2$.
  The total volume of the shape as shown in Figure 5.6 can be determined to be $3.444 \text{ cm}^3$.
- It was estimated (by globally counting the number of streamers) that about 5 to 20 percent of this volume is filled with plasma, i.e., the plasma volume per sharp point ($V_{pin}$) is in the range of 0.2 to 0.7 cm$^3$.
- In one reactor 18 high voltage electrodes are positioned, each having 168 sharp points. As a result, the total plasma volume $V_{str}$ per reactor is $\sim 0.5$ to $2.0 \text{ dm}^3$.

With this plasma volume, the O$^*$ yield can be determined. The effect of different plasma volumes is discussed in Chapter 6.

5.7 Conclusions and recommendations

The average streamer width is determined to be $737 \mu m$. With this streamer width an estimate for the plasma volume was made: $\sim 0.5$ to $2.0 \text{ dm}^3$/reactor.

The effect of the output voltage on the streamer appearance is significant. If the output voltage is reduced, a decreasing number of streamers is able to cross the gap between the two electrodes. Also, the intensity of the plasma glow decreases. It is anticipated that the plasma volume decreases as well for reduced voltages. In this report however, this effect is not taken into account. For all the calculations a plasma volume of $0.5 \text{ dm}^3$ per reactor has been adopted.

It was not possible to determine if there is an effect of the pulse repetition rate on the plasma appearances. Additional time-resolved measurements are required.

In order to study the effects of the output voltage and the pulse repetition rate, more measurements are required. A camera with a higher resolution is preferable, as is the possibility to determine the time-resolved generation of the streamers.

As discussed in Section 5.5, it appears that neighboring electrodes are too far from each other. Possibly, in future reactor designs it is possible to place the high voltage electrodes closer to each other. The advantage of placing the electrodes closer together is that more plasma volume is available and the reactor capacity $C_r$ rises. More energy can be dissipated in the same space.
6. Results of chemical measurements

Besides the electrical behavior, also the chemical performance of the system is of great importance. For the industrial application, it is important to have the best chemical efficiency, together with the best electrical efficiency.

For the application especially the oxygen radicals (O*) are required. Unfortunately, O* can not be measured directly in the exhaust since these radicals are too reactive. In a fraction of a second, all oxygen radicals have disappeared as a result of the chemical reactions as shown in Appendix A-II.

As discussed in [Winands2007], it is possible to determine the O* concentration indirectly: by first determining the amount of ozone produced. Together with other parameters that can easily be determined, and by the use of a developed Matlab routine (Appendix A-I) the O* concentration can be calculated.

First, in Section 6.1, the effect of the plasma volume $V_{str}$ on the ozone concentration in the plasma $C_{O_3,str}$ is determined. From these tests an estimate for the error, introduced as a result of the inaccuracy of the plasma volume determination, on the calculations is derived.

In Section 6.2 details regarding the ozone production are discussed. The influence of the gas temperature and humidity on the ozone production is analyzed. Finally, in Section 6.3 information regarding O* radicals is presented.

6.1 The effect of the plasma volume

As was concluded in Chapter 5, it is extremely difficult to determine the exact plasma volume. Some assumptions have to be made. These assumptions will determine the exact value of the ozone concentration $c_{O_3,str}$. As was discussed in Chapter 2, the various reaction pathways depend on the concentration of the various species. The kinetic model is used to determine the initial O* concentration, based (among others) on $c_{O_3,str}$. If an error is made in the determination of this last value, automatically an error is introduced in the calculated O* concentration. To determine the sensitivity of the results on the inaccuracy of the plasma volume determination, several calculations have been performed.

In Chapter 5 it was shown that, on average, the plasma volume per reactor is in the range of 0.5 – 2.0 dm$^3$. For the calculations for the sensitivity of the plasma volume, two different plasma volumes were chosen in this range (0.5 and 2.0 dm$^3$/reactor) and one outside this range (0.1 dm$^3$/reactor). With these values for the plasma volume, the effect on $c_{O^*}$ can be determined, i.e., the effect on $c_{O^*}$ when the plasma volume can be 5 times...
Chapter 6

as low or 4 times as high as the estimated plasma volume. The error introduced by the inaccuracy of the plasma volume is demonstrated in Figure 6.1.

For the calculation from Figure 6.1, it was assumed that the pulse repetition rate was 800 pps, the relative humidity 40\% and the temperature was 20 °C. The ozone concentration was between 0.1 and 0.6 mmole/m³. Concentrations between these values were measured during the actual experiments.

The experiments have been performed using $V_{str} = 0.5$ dm³ per reactor (solid line). If in reality the plasma volume is four times as high, or five times as low, different results are obtained, as indicated by the dotted lines. The biggest difference is obtained when the plasma volume would be five times as low as the used. The relative difference, over the whole range of $C_{O_3,exh}$ (0.1 - 0.6 mmole/m³), varies from ~ 2 \% to 12 \%. When the plasma volume would be four times as high as the used $V_{str}$, the difference is much smaller. The relative difference for this measurement varies from ~ 0.5 \% to 3 \%. It can be concluded that that the overall error varies from ~ 0.5 \% to 12 \%. This error is small, even though the assumed variation in $V_{str}$ is considerable.

### 6.2 Ozone production

In Figure 6.2 results regarding the ozone yield are shown. The experimental set-up for the chemical measurements was discussed in Chapter 2.5.2. In Figure 6.2a the yield is plotted
Results of chemical measurements

as a function of the energy ration $E_p/E_t$, since it was found that this is an important parameter (see below). In Figure 6.2b the yield is plotted as a function of the voltage rise rate $dV/dt$; also an important parameter. The maximum energy intensity is $13 \ J/L$. For these low energy densities, the ozone concentration dependency on energy density is linear. Although, the gas is mixed well between pulses, ozone deconstruction is not significant in this regime. It is found that energy densities of $>100 \ J/L$ are required to change the linear dependency of ozone on energy density [Braun1990].

Figure 6.2. a) Ozone yield as function of the energy ratio. b) Ozone yield as function of $dV/dt$. 
In Figure 6.2a four measurements are shown, two with an electrode-plate distance of 5.5 cm (blue and pink) and two with an electrode-plate distance of 5 cm (green and red). It can be seen that (globally), the points follow the same trend. No significant difference can be observed between the yield of 5 cm and 5.5 cm or between a $C_L$ of 3 $\mu$F and 6 $\mu$F.

In Figure 6.2b two measurements are shown with an electrode-plate distance of 5.5 cm. Also in this figure, it can be seen that (globally), the points follow the same trend. No significant difference can be observed between a $C_L$ of 3 $\mu$F and 6 $\mu$F.

Perhaps the most important conclusion that can be drawn from this figure is that the yield is a function of the ratio $E_p/E_i$ and $dV/dt$. The higher this ratio, the higher the yield and the higher the $dV/dt$, the higher the yield. This implies that ozone is created more efficiently when the energy is dissipated during the charging stage of the reactor. A high ratio $E_p/E_i$ also means that $C_h$ is low as shown in Figure 4.3. For the best results this means that $C'_h$ should be chosen as small as possible. The same can be concluded for the voltage rate of rise as shown in Figure 4.5. The most efficient plasma is made with a high peak voltage and a low DC voltage, i.e., more liked pulsed plasmas. Notice that the requirement for $C'_h$ is in this case opposite to the one required to obtain high energy transfer efficiencies.

Typical yields of 35 g/kWh are excellent, especially when considering that the gas conditions are non ideal: relative humidity of 40 %, not pure oxygen. Comparable yields are achieved with commercial ozone generators.

### 6.3 Relative humidity and temperature

As can be concluded when studying the reaction kinetics, the chemistry depends on the relative humidity and the gas temperature. To study the effects of these two parameters on the calculation of the $O^*$ concentration, several experiments have been performed.

Figure 6.3 shows the effect of the relative humidity and the temperature on the calculated ozone concentration. For the initial $O^*$ concentration a value of $1 \cdot 10^{-9}$ mole/cm$^3$ was chosen because all the concentrations obtained during the experiments are around this value.

From Figure 6.3 it can be concluded that the humidity has a negative effect on the ozone production. The same can be concluded for the temperature. These results show that it is important to determine these two parameters accurately. A small error already introduces significant errors in the determination of the ozone concentration.
Since the experiments are performed with different conditions (temperature and humidity vary from day to day), it is obvious that the measured ozone yield of the various experiments cannot be compared directly. If experiments are performed on a ‘wet’ and ‘hot’ day, the amount of produced ozone will be smaller than for a ‘dry’ and ‘cold’ day, even if the amount of oxygen radicals produced by the plasma is the same.

It is anticipated that when the actual O* yields are calculated, the influence of the humidity and temperature vanishes. As a result it then becomes possible to compare the various results.

In Figure 6.4 results regarding the effect of the humidity are shown. Two measurements were performed on two different days, on which the humidity differed significantly:

The parameters of the first test were as follows:
Number of reactors = 1, $C_L = 3 \, \mu F$, $C'_h = 1.6 \, nF$, temperature = 22.6 and 22 degrees Celsius respectively and the relative humidity = 33.8 and 41.1 % respectively.

The parameters of the second test that is repeated are as follows:
Number of reactors = 2, $C_L = 3 \, \mu F$, $C'_h = 0 \, nF$, temperature = 22 and 23.6 degrees Celsius respectively and the relative humidity = 40.3 and 54 % respectively.

For both tests all other parameters (voltage, $C_h$, flow, etc) were not varied.

In Figure 6.4 the ozone concentration in the streamers is shown. This concentration was calculated by using Equation 2.22, assuming a streamer volume of 0.5 dm$^3$/reactor. As
can seen, for both cases the ozone streamer concentrations are not exactly the same. As mentioned above, it is expected that part of these differences are caused by the variation in temperature and humidity.

![Figure 6.4. The ozone concentration in the streamer.](image)

In Figure 6.5 the calculated O* concentration is shown for the same markers as shown in Figure 6.4. Still differences can be observed. However, compared to the results in Figure 6.4, the differences have become smaller, as expected.
When looking at the ozone production measurements, the average difference between the two measurements was 23% and 18% for the one and two reactor experiment respectively. This difference was reduced to an average of 11% and 13% when the results were recalculated to the $O^*$ concentration. Apparently, the adopted reasoning is valid.

### 6.3 Oxygen radicals

Basically it is the $O^*$ yield that is the important parameter, not the ozone yield. For all the performed measurements the $O^*$ yield is calculated. The results are shown in Figure 6.6. Figure 6.6a shows the $O^*$ yield as function of the energy ratio $E_p/E_t$ and in Figure 6.6b the $O^*$ yield as function of the voltage rate of rise $dV/dt$ is shown. Please note that the $O^*$ yield is presented in [mole/kWh].
The same shapes as in Figure 6.2 is observed. The highest yields are acquired at high values of $E_p/E_i$ and $dV/dt$. The main difference with Figure 6.2 however, is that in this figure, the jitter on the measurements is far less. By calculating the results back to the initial condition, the effect of temperature and humidity can be corrected for. Not only does this result in a more universal indication regarding the chemical efficiency of the system, but also can experiments be compared that have been performed during different experimental conditions.

Figure 6.6. a) $O^*$ yield as function of the energy ratio. b) $O^*$ yield as function of $dV/dt$
6.4 Conclusions and recommendations

In Chapter 5, it was concluded that the plasma volume $V_{str}$ per reactor is in range of 0.5 to 2.0 dm$^3$/reactor. In this chapter the consequences of a possible error on the determination of the plasma was determined. The error varies from $\sim 0.5\%$ to $12\%$. This error is low, even though the assumed variation in $V_{str}$, four times as high and five times as low as the assumed plasma volume, is considerable.

The yield calculations have shown that the effect of the plasma volume is reasonable. The jitter on the measurements has become far less compared to the measurements before the calculations.

A high $O^*$ is preferred for industrial applications. The highest yields are obtained for high energy ratios, $E_p/E_t$. As discussed in Chapter 4, this experimental condition can be obtained when $dV/dt$ is chosen high. A high $dV/dt$ can be obtained when $C'h$ and the leakage inductance of the transformer is low. The criterion for the capacitance is opposite to the one derived in Chapter 4. Apparently a tradeoff has to be made. This is discussed in Chapter 7.
7. Conclusions and recommendations

In this thesis, the optimization of the AC/DC pulse power modulator was discussed. Several experiments were performed to obtain the relevant information. The system was studied from electrical and chemical point of view. Based on the obtained results, relations between the various system parameters and the electrical and chemical performance of the system were derived. The obtained information can be used as a guideline for future design of gas cleaning systems. In this chapter, the main conclusions are summarized. Based on these conclusions, some recommendations for future research and system usage are addressed.

7.1 Optimization of the AC/DC pulse source

For the next generation odor cleaning systems, an AC/DC power generator was developed. During this study, the original system was analyzed and changes to the design were made. The complete system, from low-voltage part to high-voltage part was evaluated.

One of the first aspects to investigate was the effect of the coupling factor $k$ of the pulse transformer $TR$ not being equal to one (i.e., having a non-ideal transformer). Because of this non-ideality, a leakage inductance is introduced into the circuitry. In order to have fast energy transfer, the inductance has to be kept low (Equations 2.3 and 3.8). It is possible to build a pulse transformer with a coupling factor exceeding 0.996. With a coupling factor of 0.996, the leakage inductance is large enough in order to leave $L_2$ (the inductor used in the past design to limit the peak current) out of the circuit.

The future pulse transformer $TR$ will be a bi-polar transformer. Bi-polar utilization ensures that the flux in the core does not remain above a certain value, but that it follows a much larger part of the B-H-curve. The most important advantage of bi-polar utilization compared to uni-polar utilization is that bi-polar utilization permits the use of a smaller core because of the larger change in the core’s flux density.

Because of the bi-polar utilization of the transformer a full bridge rectifier is needed in order to have only positive pulses on the reactor. RC-snubbers are not required to protect these diodes.

The schematic overview of the new circuit is shown in Figure 3.11. The system is still under construction. Measurements will have to be performed to establish the feasibility of the proposed adjustments.
7.2 Electrical measurements

Measurements were performed in order to investigate the mechanisms involved when trying to achieve a high energy transfer efficiency from the power modulator to the reactor. The following conclusions were made.

An efficiency of around 95% can be achieved by adding a capacitor in parallel to the reactor with a value of approximately 12 nF. The transfer efficiency does not depend on the number of reactors.

Ideally, the energy per pulse should not depend on the pulse repetition rate. In order to obtain a linear relationship between the power and the pulse repetition rate, additional capacitors in parallel to the reactor of approximately 12 nF are necessary. However, this is not the only criterion. Another criterion is that the reactor needs to be sufficiently large. A sufficiently large reactor is able to handle the available energy without causing electrical breakdowns and/or decreased energy dissipation.

7.3 Optical measurements

To determine the amount of O* radicals produced by the plasma, a computer program was developed. This program requires several input parameters, such as the ozone concentration in the reactor \( c_{O_3,itr} \), the gas temperature and the relative humidity. The \( c_{O_3,itr} \) was calculated using Equation 2.22. This equation has an unknown parameter; the plasma volume \( V_{itr} \). With photographs taken with the ICCD camera, the following conclusion could be drawn about the plasma volume.

The average streamer width is \( \sim 737 \, \mu m \). With this streamer width an estimate for the plasma volume was made: \( \sim 0.5 \) to \( 2.0 \, dm^3 \).

There is an effect of the output voltage on the streamer appearance. If the output voltage is reduced, a decreasing number of streamers is able to cross the gap between the two electrodes. Also, the intensity of the plasma glow decreases. It is anticipated that the plasma volume decreases as well for reduced voltages. In this report however, this effect is not taken into account. For all the calculations a plasma volume of \( 0.5 \, dm^3 \) per reactor has been adopted.

7.4 Chemical measurements

The oxygen radicals are the most important particles for the removal of the pollutants from the gas. With the derived plasma volume, the concentration of O* radicals, \( c_{O^*} \), can be determined. Because of the measuring inaccuracy in \( V_{itr} \), an error in the determination of \( c_{O^*} \) is introduced. Calculations showed that the error varies from \( \sim 0.5 \% \) to \( 12 \% \). This
error is low, even though the assumed variation in $V_{str}$, four times as high and five times as low as the assumed plasma volume, is considerable.

A high $O^*$ is preferred for industrial applications. The highest yields are obtained for high energy ratios, $E_p/E_t$ (the ratio between the energy dissipated by the plasma during the charging of the high voltage capacitance and the total dissipated energy). This experimental condition can be obtained when $dV/dt$ is chosen high. A high $dV/dt$ can be obtained when the capacitance of the high-voltage part (reactor plus additional capacitors in parallel) and the leakage inductance of the transformer are low. The criterion for the capacitance is opposite to the one derived for the electrical measurements.

### 7.5 Recommendations

During the measurements with a low-voltage capacitance $C_L$ of 6 $\mu$F several problems (e.g., many electrical breakdowns and decreased energy dissipation) were encountered. One of the parameters that was considered responsible for these problems is the flow through the reactor. The effect of the flow needs to be examined more closely.

Although it was possible to estimate the plasma volume $V_{str}$, not all the effects of different parameters on the plasma volume could be determined. For instance, it was not possible to establish the effect of the pulse repetition rate on the plasma appearance. Additional time-resolved measurements are required. A camera with a high spatial and temporal resolution is preferable.

The neighboring electrodes in a reactor are positioned too far from each other. Possibly, they can be positioned closer together. The advantage of placing the electrodes closer together is that more plasma volume is available for the same reactor size, and that the reactor capacity $C_r$ increases. More energy can be dissipated in the same volume. The effect on the plasma of placing the electrodes closer together has to be determined.

For the chemical measurements it might be possible to use a regulated air mixture. This mixture would have predefined gas concentrations ($N_2$, $O_2$, etc) and a fixed temperature and relative humidity.

### 7.6 Future reactor design

The reactor is the most difficult part of the new system that has to be designed. Based on the measurements as presented in this thesis the following can be said. The reactor needs to be sufficiently large. For a high chemical yield, a high energy ratio $E_p/E_t$ is desired. This experimental condition can be obtained when $dV/dt$ is high. A high $dV/dt$ can be obtained when the capacitance of the high-voltage part and the leakage inductance of the transformer are low. As can be seen in Figure 4.4, the DC-voltage decreases when the
number of reactors is increased. This effect is caused by a decreased plasma resistance. At some point however, increasing the number of reactors will not result in lower plasma resistance anymore, and hence de DC-voltage will also not drop any further. This turning point is considered to coincide with the ideal number of reactors.

The electrodes in the reactor should be placed closer together, if no disadvantageous effects are discovered. This will save reactor dimensions and the reactor will have a higher capacitance.

For the transformer used in this thesis \((n = 60)\), a wire-plate distance of 5 to 5.5 cm could withstand the applied voltage. In order to withstand the voltage with the new pulse transformer \((n = 80)\), a distance of 6 to 7 cm will be required. The ideal wire-plate distance has to be determined in preliminary experiments.

A trade-off has to be made between a high energy efficiency and a high chemical yield. For the safety of the new system, it is preferred that the system is electrically safe. This means that extra capacitors have to be installed in parallel to the reactor. If no capacitors are installed, the chance for electrical breakdowns in the reactor increases considerably.
### Appendix A-I Component values

The following components were used in the AC/DC-pulsed power modulator as shown in Figure 2.1:

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_1, L_2$</td>
<td>$10-30 \mu H$</td>
<td>Toroid, air core, $L_2$ taken out</td>
</tr>
<tr>
<td>$C_0$</td>
<td>3.3 mF</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>$C_L$</td>
<td>3-6 $\mu F$</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>$C_{\text{cable}}$</td>
<td>0.17 nF</td>
<td>Coaxial HV cable (100 pF/m)</td>
</tr>
<tr>
<td>$C'_h$</td>
<td>0-12 nF</td>
<td>Murata</td>
</tr>
<tr>
<td>$C_r$</td>
<td>0.230-0.920 nF</td>
<td>Reactor configuration (1, 2 and 4 reactors)</td>
</tr>
<tr>
<td>Pulse Transformer</td>
<td>1:60 winding ratio</td>
<td>Homemade, oil filled</td>
</tr>
<tr>
<td>$R_5$</td>
<td>10-15 k$\Omega$</td>
<td>Non-inductive, linear disc resistor</td>
</tr>
<tr>
<td>$D_1, D_2$</td>
<td>40 kV hold-off, 8 A conducting current</td>
<td>Fast recovery diodes</td>
</tr>
</tbody>
</table>
Appendix B-I Kinetic model

The kinetic model for the calculation of the ozone concentration \( \text{c}_{03, sr} \) consists out of a main program and two sub-programs. All the programs are listed below.

**Main program**

clear all; clc;

to = 0;
te = 0.001;
tspan = (to: 1e-8:te);
Av = 6.02214e23; % Constant of Avogadro

Temp = {'Enter the temperature in Celsius: (Temp < 40!!!!!!)', 'Enter the relative Humidity in %', 'Concentration O in mol/cm3'};
dlg_title = 'Input Parameters';
num_lines = 1;
def = {'20','40','1e-9'};
answer = inputdlg(Temp, dlg_title, num_lines, def);
if isempty(answer),
    return
end

T = str2num(answer{1})+273; % Temperature in Kelvin
Tc = str2num(answer{1}); % Temperature in Celsius
RH = str2num(answer{2});
    [3.1243e-6·Tc^3+8.1847e-5·Tc^2+3.2321e-3·Tc+0.05018]/(1e6·(18.0118/Av)); % Concentration water in molecules/cm^3
R = str2num(answer{2}); % RH [%]
X = str2num(answer{3}); % Concentration O* in mole/cm^3
X2 = 1e6 · X; % Concentration O* in mole/m^3
k = [];
run constants

% INITIAL CONCENTRATIONS [mole/cm^3, Av = molecules/cm^3]
O_0 = X · Av; % Supposed O* concentration
O_0 = 0 · Av;
N_0 = 0.06 · O0; % O3
NO_0 = 0 · Av; % N
NO_2 = 0 · Av; % NO
N_2O_0 = 0 · Av; % NO2
\[
\text{NO}_3\_0 = 0 \cdot \text{Av}; \quad \% \text{NO}_3 \\
\text{N}_2\text{O}_5\_0 = 0 \cdot \text{Av}; \quad \% \text{N}_2\text{O}_5 \\
\text{H}_2\text{O}\_0 = \text{RH}; \quad \% \text{H}_2\text{O} \\
\text{OH}\_0 = 0.6\text{e}-3 \cdot \text{R} \cdot \text{O}0; \quad \% \text{OH} \\
\text{H}\_0 = 0.6\text{e}-3 \cdot \text{R} \cdot \text{O}0; \quad \% \text{H} \\
\text{HO}_2\_0 = 0 \cdot \text{Av}; \quad \% \text{HO}_2 \\
\text{H}_2\text{O}_2\_0 = 0 \cdot \text{Av}; \quad \% \text{H}_2\text{O}_2 \\
\text{HNO}_2\_0 = 0 \cdot \text{Av}; \quad \% \text{HNO}_2 \\
\text{HNO}_3\_0 = 0 \cdot \text{Av}; \quad \% \text{HNO}_3 \\
\text{O}_2\_0 = 8.92\text{e}-6 \cdot \text{Av}; \quad \% \text{O}_2 \\
\text{N}_2\_0 = 3.57\text{e}-5 \cdot \text{Av}; \quad \% \text{N}_2 \\
\]

\[z\_0 = [\text{O}\_0 \text{O}_3\_0 \text{N}_0 \text{NO}_0 \text{NO}_2\_0 \text{N}_2\text{O}_5\_0 \text{NO}_3\_0 \text{N}_2\text{O}_5\_0 \text{H}_2\text{O}\_0 \text{OH}_0 \text{H}_0 \text{HO}_2\_0 \text{H}_2\text{O}_2\_0 \text{HNO}_2\_0 \text{HNO}_3\_0 \text{O}_2\_0 \text{N}_2\_0 ];\]

options = odeset ('Reltol', 1e-140, 'AbsTol', 1e-140);
[t,z] = ode15s (@differential_equations, tspan, z_0, T, k, options);

% PLOTS

figure (1);
subplot (3,1,1);
loglog (t,z(:,1));
title ('Concentratie O in molecules/cm^3');
axis auto;
grid minor;
subplot(3,1,2);
loglog(t,z(:,2));
title ('Concentratie O_3');
axis auto;
grid minor;
subplot(3,1,3);
loglog(t,z(:,3));
title ('Concentratie N');
axis auto;
grid minor;

% CONCENTRATION OXYGEN RADICALS [ppm]

ppmO = 1e6 \cdot z(100001,1) / (z(100001,1) + z(100001,2) + z(100001,3) + z(100001,4) +
        z(100001,5) + z(100001,6) + z(100001,7) + z(100001,8) + z(100001,9) +
        z(100001,10) + z(100001,11) + z(100001,12) + z(100001,13) + z(100001,14) +
        z(100001,15) + z(100001,16) + z(100001,17));
% CONCENTRATION OZONE [ppm]

ppmO3 = 1e6 \cdot z(100001,2) / (z(100001,1) + z(100001,2) + z(100001,3) + z(100001,4) + z(100001,5) + z(100001,6) + z(100001,7) + z(100001,8) + z(100001,9) + z(100001,10) + z(100001,11) + z(100001,12) + z(100001,13) + z(100001,14) + z(100001,15) + z(100001,16) + z(100001,17));

Co3 = 1e6 \cdot z(100001,2) / Av;

% Concentration in mole/(m^3 pulse)

display(['ppm O = ', num2str(ppmO)]);
display(['ppm O_3 = ', num2str(ppmO3)]);
display(['Concentration O_3,5tr = ', num2str(Co3), ', mole/(m^3 pulse)']);
display(['Concentration O* = ', num2str(X2), ', mole/(m^3 pulse)']);

Constants

The constants are shown in Appendix A-II under Rate-coefficient.

Differential equations

function df = differential_equations(t,z,k,T);

O = z(1); O_3 = z(2); N = z(3); NO = z(4); NO_2 = z(5); N_2O = z(6); NO_3 = z(7); N_2O_5 = z(8); H_2O = z(9); OH = z(10); H = z(11); HO_2 = z(12); H_2O_2 = z(13); HNO_2 = z(14); HNO_3 = z(15); O_2 = z(16); N_2 = z(17);

df = zeros(17,1);

df(1) = -2 \cdot O^2 \cdot (N_2 + O_2) \cdot k(1) - O \cdot (O_2)^2 \cdot k(2) - O \cdot O_2 \cdot N_2 \cdot k(3) - O \cdot O_2 \cdot O_3 \cdot k(4) - O \cdot O_2 \cdot H_2O \cdot k(5) - O \cdot O_2 \cdot O \cdot k(6) + O \cdot O_2 \cdot k(7) + (O_2)^2 \cdot k(8) - NO \cdot (N_2 + O_2) \cdot k(9) + N \cdot O_2 \cdot k(10) + N \cdot NO \cdot k(13) + N \cdot NO_2 \cdot k(14) - NO \cdot O \cdot N_2 \cdot k(15) - NO \cdot O \cdot O_2 \cdot k(16) - NO \cdot N_2 \cdot O \cdot k(17) + NO \cdot O_2 \cdot k(20) - NO_2 \cdot O \cdot k(21) - NO_2 \cdot O \cdot (N_2 + O_2) \cdot k(22) - NO_3 \cdot O \cdot k(27) - N_2O \cdot O \cdot k(31) + N_2 \cdot O_2 \cdot k(32) - N_2O \cdot O \cdot k(33) - N_2O_3 \cdot O \cdot k(34) - H_2O \cdot O \cdot k(37) - O \cdot OH \cdot k(38) + O_2 \cdot H \cdot k(39) + (OH)^2 \cdot k(41) - HO_2 \cdot O \cdot k(46) - H_2O_2 \cdot O \cdot k(50) + H \cdot O_2 \cdot k(53) + H \cdot HO_2 \cdot k(55) - HNO_3 \cdot O \cdot k(70);

% dO*/dt

df(2) = O \cdot (O_2)^2 \cdot k(2) + O \cdot O_2 \cdot N_2 \cdot k(3) + O \cdot O_2 \cdot O_3 \cdot k(4) + O \cdot O_2 \cdot H_2O \cdot k(5) - O \cdot O_3 \cdot k(6) - O_2 \cdot O_2 \cdot k(7) - (O_2)^2 \cdot k(8) - N \cdot O_3 \cdot k(11) - NO \cdot O_3 \cdot k(18) - NO_2 \cdot O_2 \cdot k(23) + NO_3 \cdot O_2 \cdot k(28) - OH \cdot O_3 \cdot k(40) - HO_2 \cdot O_3 \cdot k(47) - H \cdot O_3 \cdot k(52) - H \cdot O_3 \cdot k(53);

% dO_3/dt
\[
df(3) = -N'O(N_2+O_2)k(9) -N'O_2k(10) -N'O_3k(11) - 2(N)^2(N_2+O_2)k(12) - N(NO)k(13) - N(NO_2)k(14) - N'OHk(58); \\
\%
\]\[
\[
df(4) = N'O(N_2+O_2)k(9) + N'O_2k(10) + N'O_3k(11) - N'NOk(13) - NOO·N_2k(15) - NOO·O_2k(16) - NOO·N_2O_2k(17) - NOO·O_2O_2k(18) - 2NO^2O_2k(19) - NO'O_2k(20) + NO_2O·k(21) + 2(NO_2)^2k(24) + NO_2NO_3k(25) - NOO·NO_2k(29) + 2·N_2O·O·k(33) + N'OHk(58) - NOOHk(59) - NOOH(N_2+O_2)k(60) - NOHO_2k(61) - NOHO_2O_2k(62) - NOH_2O_2k(63) + NO_2H·k(64); \\
\%
\]\[
\[
df(5) = -N'O_2k(14) + NOO·N_2k(15) + NOO·O_2k(16) + NOO·N_2O_2k(17) + NOO·O_2k(18) + 2(NO)^2O_2k(19) + NOO·O_2k(20) - NOO·O_2O_2k(21) - NOO·(N_2+O_2)k(22) - NOO·O_2k(23) + 2(NO_2)^2k(24) - NOO·NO_3(N_2+O_2)k(26) + NOO·O_2k(27) + NOO·O_2k(28) + 2NOO·NO_2k(29) + 2(NO_3)^2k(30) + 2N_2O_3·O·k(34) + N_2O_3·N_2k(35) + N_2O_3·O_2k(36) + NOOHk(59) - NOHO_2k(61) - NOH·H_2O_2k(64) - NOOH(N_2+O_2)k(65) - NOH·NO_2O_2k(66) + HNO_2·OH·k(69); \\
\%
\]\[
\[
df(6) = N'O_2k(14) - N_2O·O·k(31) + N_2O·O_2k(32) - N_2O·O·k(33) + N_2·OHk(57); \\
\%
\]\[
\[
df(7) = NOO·O(N_2+O_2)k(22) + NOO·O_2k(23) - NOO·NO_3k(25) - NOO·NO_3(N_2+O_2)k(26) - NOO·O_2k(27) - NOO·O_2k(28) - NOO·NO_2k(29) - 2(NO_3)^2k(30) + N_2O_3·N_2k(35) + N_2O_3·O_2k(36) - NO_3·H_2Ok(67) + HNO_3·O·k(70) + HNO_3·OH·k(71); \\
\%
\]\[
\[
df(8) = NOO·NO_3(N_2+O_2)k(26) - N_2O_3·O·k(34) - N_2O_3·N_2k(35) - N_2O_3·O_2k(36) - N_2O_3·H_2O·k(68); \\
\%
\]\[
\[
df(9) = -H_2O·O·k(37) + (OH)^2k(41) + OH·HO_2·k(44) + OH·H_2O·k(45) - HO_2H_2O·k(49) + H·HO_2·k(55) + H·H_2O·k(56) - NO_2·H_2O·k(67) - N_2O_3·H_2O·k(68) + HNO_2·OH·k(69) + HNO_2·OH·k(71); \\
\%
\]\[
\[
df(10) = 2H_2O·O·k(37) - O·OH·k(38) + O_2·H·k(39) - OH·O_2k(40) - 2(OH)^2k(41) - 2(OH)^2(N_2+O_2)k(42) - 2(OH)^2k(43) - OH·HO_2·k(44) - OH·H_2O·k(45) + HO_2·O·k(46) + HO_2O·k(47) + HO_2·H_2O·k(49) + H_2O_2·O·k(50) + H·O_3·k(52) + 2H·HO_2·k(54) + H·H_2O·k(56) - N_2·OH·k(57) - N·OH·k(58) - NO·OH·k(59) - NO·OH(N_2+O_2)k(60) + NO·HO_2·k(61) + NO·H_2O·k(63) + NO·H·k(64) - NO_2·OH(N_2+O_2)k(65) + NO_3·H_2O·k(67) - HNO_2·OH·k(69) + HNO_3·O·k(70) - HNO_3·OH·k(71); \\
\%
\]\[
\[
\%
\]
df(11) = O·OH·k(38) - O₂·H·k(39) + (OH)²·k(43) - H·O₂·(N₂+O₂)·k(51) - H·O₃·k(52) - k(53) - H·HO₂·k(54) + N·OH·k(55) + NO·OH·k(56) - NO₂·H·k(57) - NO₂·H·k(58) + NO·OH·k(59) - NO₂·H·k(60); % dH/dt

df(12) = OH·O₃·k(40) + (OH)²·k(43) - OH·HO₂·k(44) + OH·H₂O₂·k(45) - HO₂·O·k(46) - H₂O₂·O·k(47) + 2·(OH)²·k(48) - HO₂·H₂O·k(49) + H₂O₂·O·k(50) + H·O₂·(N₂+O₂)·k(51) + H·O₃·k(52) + H·H₂O₂·k(53) + H·HO₂·k(54) + k(55) - NO·HO₂·k(56) + NO·HO₂·k(57) - N·O·H·k(58) - NO·O·k(59) - NO·O₂·H·k(60) - NO·O₂·H·k(61); % dH₂O₂/dt

df(13) = (OH)²·(N₂+O₂)·k(42) - OH·H₂O₂·k(45) + (HO₂)²·k(48) + HO₂·H₂O·k(49) - H₂O₂·O·k(50) - H·H₂O₂·k(51) - NO·H₂O₂·k(62); % dH₂O₂/dt

df(14) = NO·OH·(N₂+O₂)·k(60) + NO·H₂O₂·k(63) + NO₂·H₂O₂·k(64) - HNO₂·OH·k(65); % dHNO₂/dt

df(15) = NO·H₂O₂·k(62) + NO₂·OH·(N₂+O₂)·k(65) + NO₃·H₂O·k(66) - HNO₃·O·k(67) - HNO₃·OH·k(68); % dHNO₃/dt

df(16) = (O)²·(N₂+O₂)·k(1) - O·(O₂)²·k(2) - O·O₂·N₂·k(3) - O·O₂·O₃·k(4) - O·O₂·H₂O·k(5) + 2·O·O₃·k(6) + O₃·O₂·k(7) + (O₃)²·k(8) - N·O₂·k(10) + N·O₃·k(11) + NO·O₃·k(12) - (NO)²·O₂·k(13) - NO·O₂·k(14) + NO₂·O·k(15) + NO₂·O₃·k(16) + (NO₂)²·k(17) + NO₂·O₃·k(18) + NO₂·O₂·k(19) + NO₂·O·k(20) + NO₂·O₃·k(21) + NOO·O·k(22) + NOO·O₃·k(23) + NOO·O₂·k(24) + NOO·O·k(25) + NOO·O₃·k(26) - NOO·O₂·k(27) + NOO·O·k(28) + (NOO)²·k(29) + NOO·O₃·k(30) + NOO·O₂·k(31) - N₂·O₂·k(32) + N₂O₃·O·k(33) + O·OH·k(34) + O·O·k(35) - O₂·H·k(36) + N·O·O·k(37) - H·O₂·N₂·k(38) + H·O₂·O·k(39) + H·O₂·N₃·k(40) + H·H₂O₂·k(41) + H·H₂O₂·k(42) + H·HO₂·k(43) + H·HO₂·k(44) + H·HO₂·k(45) + H·HO₂·k(46) + H·HO₂·k(47) + H·HO₂·k(48) + H·HO₂·k(49) + H·HO₂·k(50) + H·HO₂·k(51) + H·HO₂·k(52) + H·HO₂·k(53) + H·HO₂·k(54) + H·HO₂·k(55) - NO·HO₂·k(56) - NO·HO₂·k(57) + NO·HO₂·k(58) - NO·HO₂·k(59) - NO₂·H·k(60) - NO₂·H·k(61) - NO₂·H·k(62) - NO₂·H·k(63) - NO₂·H·k(64); % dO₂/dt

df(17) = (N)²·(N₂+O₂)·k(12) + N·NO·k(13) + N₂O·O·k(31) - N₂·O₂·k(32) - N₂·OH·k(57); % dN₂/dt
Appendix B-II Reactions used in kinetic model

Reaction rates are in cm$^3$/s and cm$^6$/s for tow and three body collisions respectively. T is the absolute temperature in K. Reactions taken from Peyrous 1990 and Winands 2007.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate-coefficient</th>
<th>k( )</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O + O + M \rightarrow O_2 + M$</td>
<td>$M = N_2, O_2 \quad \frac{3.8 \times 10^{-30}}{T} \cdot \exp[-170/T]$</td>
<td>1</td>
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<tr>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
<td>$M = O_2 \quad 6.9 \times 10^{-34} \cdot (300/T)^{3.25}$</td>
<td>2</td>
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<tr>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
<td>$M = N_2 \quad 6.2 \times 10^{-34} \cdot (300/T)^2$</td>
<td>3</td>
</tr>
<tr>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
<td>$M = O_3 \quad 4.6 \times 10^{-35} \cdot \exp[1050/T]$</td>
<td>4</td>
</tr>
<tr>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
<td>$M = H_2O \quad 9.9 \times 10^{-34} \cdot \exp[510/T]$</td>
<td>5</td>
</tr>
<tr>
<td>$O + O_3 \rightarrow O_2 + O_2$</td>
<td>$1.8 \times 10^{-11} \cdot \exp[-2300/T]$</td>
<td>6</td>
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<tr>
<td>$O_3 + O_2 \rightarrow O + O_2 + O_2$</td>
<td>$7.3 \times 10^{-10} \cdot \exp[-11400/T]$</td>
<td>7</td>
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<tr>
<td>$O_3 + O_1 \rightarrow O + O_2 + O_3$</td>
<td>$1.65 \times 10^{-9} \cdot \exp[-11400/T]$</td>
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</tr>
<tr>
<td>$N + O + M \rightarrow NO + M$</td>
<td>$M = N_2, O_2 \quad 1.8 \times 10^{-31} \cdot T^{-0.5}$</td>
<td>9</td>
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<tr>
<td>$N + O_2 \rightarrow NO + O$</td>
<td>$4.4 \times 10^{-12} \cdot \exp[-3220/T]$</td>
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<tr>
<td>$N + O_3 \rightarrow NO + O_2$</td>
<td>$2.0 \times 10^{-11} \cdot \exp[-1070/T]$</td>
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<tr>
<td>$N + N + M \rightarrow N_2 + M$</td>
<td>$M = N_2, O_2 \quad 8.3 \times 10^{-34} \cdot \exp[500/T]$</td>
<td>12</td>
</tr>
<tr>
<td>$N + NO \rightarrow N_2 + O$</td>
<td>$3.1 \times 10^{-11}$</td>
<td>13</td>
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<tr>
<td>$N + NO_2 \rightarrow N_2O + O$</td>
<td>$2.1 \times 10^{-11} \cdot \exp[-800/T]$</td>
<td>14</td>
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<tr>
<td>$NO + O + M \rightarrow NO_2 + M$</td>
<td>$M = N_2 \quad 1.2 \times 10^{-31} \cdot (T/300)^{1.82}$</td>
<td>15</td>
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<tr>
<td>$NO + O + M \rightarrow NO_2 + M$</td>
<td>$M = O_2 \quad 8.6 \times 10^{-32} \cdot (T/300)^{1.82}$</td>
<td>16</td>
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<tr>
<td>$NO + O + M \rightarrow NO_2 + M$</td>
<td>$M = N_2O \quad 1.7 \times 10^{-32} \cdot \exp[620/T]$</td>
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<tr>
<td>Reaction</td>
<td>Rate-coefficient</td>
<td>k( )</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>----------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>( NO + O_3 \rightarrow NO_2 + O_2 )</td>
<td>( 3.6 \cdot 10^{-12} \cdot \exp[-1560/T] )</td>
<td>18</td>
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<tr>
<td>( NO + NO + O_2 \rightarrow NO_2 + NO_2 )</td>
<td>( 3.3 \cdot 10^{-39} \cdot \exp[530/T] )</td>
<td>19</td>
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<tr>
<td>( NO + O_2 \rightarrow NO_2 + O )</td>
<td>( 2.8 \cdot 10^{-12} \cdot \exp[-23400/T] )</td>
<td>20</td>
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<tr>
<td>( NO_2 + O \rightarrow NO + O_2 )</td>
<td>( 1.7 \cdot 10^{-11} \cdot \exp[-300/T] )</td>
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</tr>
<tr>
<td>( NO_2 + O + M \rightarrow NO_3 + M )</td>
<td>( M = N_2, O_2 ) ( 9.0 \cdot 10^{-32} \cdot (T/300)^2 )</td>
<td>22</td>
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<tr>
<td>( NO_2 + O_3 \rightarrow NO_3 + O_2 )</td>
<td>( 1.2 \cdot 10^{-13} \cdot \exp[-2450/T] )</td>
<td>23</td>
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<tr>
<td>( NO_2 + NO_2 \rightarrow NO + NO + O_2 )</td>
<td>( 3.3 \cdot 10^{-12} \cdot \exp[-135400/T] )</td>
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<tr>
<td>( NO_2 + NO_3 \rightarrow NO + NO_2 + O_2 )</td>
<td>( 2.3 \cdot 10^{-13} \cdot \exp[-1000/T] )</td>
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<tr>
<td>( NO_3 + NO_3 + M \rightarrow N_2O_5 + M )</td>
<td>( M = N_2, O_2 ) ( 3.7 \cdot 10^{-30} \cdot (T/300)^{4.1} )</td>
<td>26</td>
</tr>
<tr>
<td>( NO_3 + O \rightarrow O_2 + NO_2 )</td>
<td>( 1.0 \cdot 10^{-11} )</td>
<td>27</td>
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<tr>
<td>( NO_3 + O_2 \rightarrow O_3 + NO_2 )</td>
<td>( 7.0 \cdot 10^{-34} )</td>
<td>28</td>
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<tr>
<td>( NO_3 + NO \rightarrow NO_2 + NO_2 )</td>
<td>( 2.0 \cdot 10^{-11} )</td>
<td>29</td>
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<tr>
<td>( NO_3 + NO \rightarrow NO_2 + NO_2 + O_2 )</td>
<td>( 5.0 \cdot 10^{-12} \cdot \exp[-3000/T] )</td>
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<tr>
<td>( N_2O + O + M \rightarrow N_2 + O_2 )</td>
<td>( 1.7 \cdot 10^{-10} \cdot \exp[-14100/T] )</td>
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<tr>
<td>( N_2 + O_2 \rightarrow N_2O + O )</td>
<td>( 1.1 \cdot 10^{-10} \cdot \exp[-55200/T] )</td>
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<td>( N_2O + O \rightarrow NO + NO )</td>
<td>( 7.2 \cdot 10^{-11} )</td>
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<td>( N_2O_3 + O \rightarrow NO_2 + NO_2 + O_2 )</td>
<td>( 1.0 \cdot 10^{-16} )</td>
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<td>( N_2O_3 + M \rightarrow NO_2 + NO_3 + M )</td>
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<tr>
<td>( N_2O_3 + M \rightarrow NO_2 + NO_3 + M )</td>
<td>( M = O_2 ) ( 2.0 \cdot 10^{-2} \cdot (T/300)^{-0.1} \cdot \exp[-11080/T] )</td>
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<tr>
<td>( H_2O + O \rightarrow OH + OH )</td>
<td>( 1.0 \cdot 10^{-11} \cdot \exp[-550/T] )</td>
<td>37</td>
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<tr>
<td>Reaction</td>
<td>Rate-coefficient</td>
<td>(k())</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>-------------------------------------------------------</td>
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<tr>
<td>(O + OH \rightarrow O_2 + H)</td>
<td>(2.3 \cdot 10^{-11} \cdot \exp[110 / T])</td>
<td>38</td>
</tr>
<tr>
<td>(O_2 + H \rightarrow O + OH)</td>
<td>(3.7 \cdot 10^{-10} \cdot \exp[-8450 / T])</td>
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<tr>
<td>(OH + O_3 \rightarrow HO_2 + O_2)</td>
<td>(1.9 \cdot 10^{-12} \cdot \exp[-1000 / T])</td>
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<tr>
<td>(OH + OH \rightarrow H_2O + O)</td>
<td>(4.5 \cdot 10^{-12} \cdot \exp[-275 / T])</td>
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<tr>
<td>(OH + OH + M \rightarrow H_2O_3 + M) (M = N_2, O_2)</td>
<td>(6.5 \cdot 10^{-31} \cdot (T / 300)^{0.7})</td>
<td>42</td>
</tr>
<tr>
<td>(OH + OH \rightarrow HO_2 + H)</td>
<td>(2.0 \cdot 10^{-11} \cdot \exp[-20200 / T])</td>
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<tr>
<td>(OH + HO_2 \rightarrow H_2O + O_2)</td>
<td>(8.3 \cdot 10^{-11} \cdot (T / 335)^{0.25})</td>
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<tr>
<td>(OH + H_2O \rightarrow H_2O + HO_2)</td>
<td>(2.9 \cdot 10^{-12} \cdot \exp[-160 / T])</td>
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<tr>
<td>(HO_2 + O \rightarrow OH + O_2)</td>
<td>(8.0 \cdot 10^{-11} \cdot \exp[-500 / T])</td>
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<tr>
<td>(HO_2 + O_3 \rightarrow HO_2 + O_2 + O_2)</td>
<td>(1.4 \cdot 10^{-14} \cdot \exp[-600 / T])</td>
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<tr>
<td>(HO_2 + HO_2 \rightarrow H_2O_2 + O_2)</td>
<td>(4.0 \cdot 10^{-14} \cdot \exp[1200 / T])</td>
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<tr>
<td>(HO_2 + H_2O \rightarrow H_2O_2 + OH)</td>
<td>(4.7 \cdot 10^{-31} \cdot \exp[-16500 / T])</td>
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<tr>
<td>(H_2O_2 + O \rightarrow HO_2 + OH)</td>
<td>(1.0 \cdot 10^{-11} \cdot \exp[-2500 / T])</td>
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<td>(H + O_2 + M \rightarrow HO_2 + M) (M = N_2, O_2)</td>
<td>(5.9 \cdot 10^{-32} \cdot (300 / T))</td>
<td>51</td>
</tr>
<tr>
<td>(H + O_3 \rightarrow OH + O_2)</td>
<td>(1.1 \cdot 10^{-10} \cdot \exp[-480 / T])</td>
<td>52</td>
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<tr>
<td>(H + O_3 \rightarrow HO_2 + O)</td>
<td>(1.0 \cdot 10^{-11} \cdot \exp[-480 / T])</td>
<td>53</td>
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<tr>
<td>(H + HO_2 \rightarrow OH + OH)</td>
<td>(4.2 \cdot 10^{-10} \cdot \exp[-950 / T])</td>
<td>54</td>
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<tr>
<td>(H + HO_2 \rightarrow H_2O + O)</td>
<td>(9.0 \cdot 10^{-13})</td>
<td>55</td>
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<tr>
<td>(H + H_2O_2 \rightarrow OH + H_2O)</td>
<td>(5.0 \cdot 10^{-12} \cdot \exp[-1900 / T])</td>
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<tr>
<td>(N_2 + OH \rightarrow N_2O + H)</td>
<td>(5.4 \cdot 10^{-12} \cdot \exp[-40000 / T])</td>
<td>57</td>
</tr>
</tbody>
</table>
### Kinetic model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate-coefficient</th>
<th>k( )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N + OH \rightarrow NO + H)</td>
<td>(3.8 \cdot 10^{-11} \cdot \exp[85/T])</td>
<td>58</td>
</tr>
<tr>
<td>(NO + OH \rightarrow NO_2 + H)</td>
<td>(5.2 \cdot 10^{-12} \cdot \exp[-15000/T])</td>
<td>59</td>
</tr>
<tr>
<td>(NO + OH + M \rightarrow HNO_2 + M), (M = N_2O_2)</td>
<td>(6.5 \cdot 10^{-31} \cdot (T/300)^{-2.4})</td>
<td>60</td>
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<tr>
<td>(NO + HO_2 \rightarrow NO_2 + OH)</td>
<td>(3.7 \cdot 10^{-12} \cdot \exp[240/T])</td>
<td>61</td>
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<tr>
<td>(NO + HO_2 \rightarrow HNO_3^*)</td>
<td>(1.4 \cdot 10^{-13})</td>
<td>62</td>
</tr>
<tr>
<td>(NO + H_2O_2 \rightarrow HNO_2 + OH)</td>
<td>(1.0 \cdot 10^{-20})</td>
<td>63</td>
</tr>
<tr>
<td>(NO_2 + H \rightarrow NO + OH)</td>
<td>(5.8 \cdot 10^{-10} \cdot \exp[-740/T])</td>
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<td>(NO_2 + OH + M \rightarrow HNO_3 + M^*), (M = N_2O_2)</td>
<td>(2.6 \cdot 10^{-30})</td>
<td>65</td>
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<tr>
<td>(NO_2 + HO_2 \rightarrow HNO_2 + O_2)</td>
<td>(2.0 \cdot 10^{-14})</td>
<td>66</td>
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<td>(NO_3 + H_2O \rightarrow HNO_3 + OH)</td>
<td>(5.0 \cdot 10^{-21})</td>
<td>67</td>
</tr>
<tr>
<td>(N_2O_3 + H_2O \rightarrow HNO_3 + HNO_3)</td>
<td>(5.0 \cdot 10^{-21})</td>
<td>68</td>
</tr>
<tr>
<td>(HNO_2 + OH \rightarrow NO_2 + H_2O)</td>
<td>(1.3 \cdot 10^{-13})</td>
<td>69</td>
</tr>
<tr>
<td>(HNO_3 + O \rightarrow NO_3 + OH)</td>
<td>(5.0 \cdot 10^{-15})</td>
<td>70</td>
</tr>
<tr>
<td>(HNO_3 + OH \rightarrow NO_3 + H_2O)</td>
<td>(1.5 \cdot 10^{-14} \cdot \exp[650/T])</td>
<td>71</td>
</tr>
</tbody>
</table>

* Reaction and rate taken from NIST chemical database
Bibliography


[www1] Relative Humidity, see webpage: http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/relhum.html.


[Yan] Internal communication about the work of K. Yan.

Acknowledgement

Finally I can start writing my acknowledgement, exactly one year after the day I started (with a seven week holiday to the US of A in between) with this thesis at EPS within the faculty of Electrical Engineering of Eindhoven University of Technology.

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Without my friends I would not have made it. Although I don’t see you very much, the weekends with the drinks and parties are a great relief. It is nice to know that I’m always welcome.

As last I want to thank my next of kin. My parents always supported my study in many ways. Also Linda and her family were always supportive during this period.