Design, construction and modelling of an air cleaning test rig

LOUISE FERNANDA STJERN
ABSTRACT

The cleaning technology for exhaust air is an area under constant development. In collaboration with Ozone Tech Systems the project resulted in a lab scale test rig for air cleaning units. The test rig was designed primarily to investigate the mechanisms of an UV reactor as well as the life times of a hydrogen sulphide absorption bed and an activated carbon bed. The thesis consisted in the design of the system, the acquisition of units and the construction of the system followed by the modelling of the pollutant elimination in the UV reactor. Fluid dynamics of the process flow is neglected, while the light distribution is numerically calculated. Two separate pollutants were considered, one being volatile organic compounds represented by acetaldehyde, and the other being hydrogen sulphide, chosen due to their prevalence in exhausts. An experimental plan is developed to validate the model, find model parameters and finally to investigate process parameters in the UV reactor.

SAMMANFATTNING

Luftföroreningar är ett mycket aktuellt problem, och tekniken för att rena luftströmmar är under ständig utveckling. I samarbete med Ozone Tech Systems designades och byggdes en testrigg för att undersöka olika luftreningssystem. De primära målen var att undersöka mekanismerna i en UV reaktor samt livslängden för två lika packade bäddar; en absorptionsbädd för divätesulfind samt en adsorptionsbädd av aktiverat kol. Examensarbete bestod av designmomentet, införskaffande av rätt enheter och konstruktionen av systemet. Även numerisk modellering av UV-reaktorn ingick i projektet, och denna gjordes med störst avseende på UV-ljusets fördelning i reaktorn medan flödesdynamiken försommades.

Två olika föroreningar valdes p. g. a. deras frekventa förekomst i luftströmmar som ska renas; divätesulfind och flyktiga organiska ämnen (representerade här av acetaldehyd). Rapporten presenterar även en experimentell plan för att validera modellen, hitta modellens semiempiriska parametrar, samt till slut för att med hjälp av faktoriell design undersöka interaktionen mellan olika faktorer i UV-reaktorn.
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>2</td>
</tr>
<tr>
<td>Sammanfattning</td>
<td>2</td>
</tr>
<tr>
<td>Introduction</td>
<td>5</td>
</tr>
<tr>
<td>Background</td>
<td>5</td>
</tr>
<tr>
<td>Purpose &amp; Aim</td>
<td>6</td>
</tr>
<tr>
<td>Scope</td>
<td>6</td>
</tr>
<tr>
<td>Workflow</td>
<td>6</td>
</tr>
<tr>
<td>Theory</td>
<td>7</td>
</tr>
<tr>
<td>Ozone</td>
<td>7</td>
</tr>
<tr>
<td>The pollutants</td>
<td>7</td>
</tr>
<tr>
<td>VOCs</td>
<td>7</td>
</tr>
<tr>
<td>Hydrogen Sulphide</td>
<td>8</td>
</tr>
<tr>
<td>Photochemistry</td>
<td>10</td>
</tr>
<tr>
<td>Absorption and transmission</td>
<td>11</td>
</tr>
<tr>
<td>Photolysis vs photooxidation</td>
<td>12</td>
</tr>
<tr>
<td>Radicals</td>
<td>14</td>
</tr>
<tr>
<td>Oxidation end products</td>
<td>14</td>
</tr>
<tr>
<td>The Activated Carbon</td>
<td>15</td>
</tr>
<tr>
<td>Ozone injection</td>
<td>15</td>
</tr>
<tr>
<td>Method - Design</td>
<td>17</td>
</tr>
<tr>
<td>Life time investigation</td>
<td>18</td>
</tr>
<tr>
<td>Efficacy investigation</td>
<td>19</td>
</tr>
<tr>
<td>Lines &amp; Turbulence</td>
<td>19</td>
</tr>
<tr>
<td>UV Reactor Design</td>
<td>20</td>
</tr>
<tr>
<td>Reactor chamber</td>
<td>25</td>
</tr>
<tr>
<td>Process control</td>
<td>25</td>
</tr>
<tr>
<td>Result &amp; Discussion – Construction</td>
<td>26</td>
</tr>
<tr>
<td>The lines</td>
<td>26</td>
</tr>
<tr>
<td>The life time system</td>
<td>26</td>
</tr>
<tr>
<td>The efficacy system</td>
<td>26</td>
</tr>
</tbody>
</table>
INTRODUCTION

BACKGROUND

It is now long since the first notion of exhaust gas cleaning was brought to air and most regions, nations and industries are required by law to control their emissions. The air pollutants required to be removed can be harmful both to the environment and to people in a variety of ways such as having carcinogenic, mutagenic or toxic properties. Often, not only the pollutant itself but any derivatives resulting from spontaneous chemical reactions will also be dangerous, in some cases more so than the original pollutant. [2]

The World Health Organization defines air pollution as:

“Air pollution is contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere” – [3]

Those agents will hereafter be referred to as “pollutants”. Some common pollutants include very small particulate matter, nitrous dioxide and hydrogen sulphide (H₂S). Others are harder to pinpoint and are referred to in categories, such as the Volatile Organic Compounds (VOCs): a large family of hydrocarbons with different lengths, shapes and properties. Among the lesser issues of long term exposure to most pollutants, such as living in a polluted city, are the resulting risk for respiratory problems. [3]

The agricultural industry, the burning of fossil fuel or the manufacturing of potato chips are all examples of industries that cause a variety of air pollutants. As such, most air pollutants are man-made. Naturally, the major source will vary geographically. What will always remain constant however, is the need for abatement technologies. [3]

The air cleaning process must of course be suited to the pollutants to be removed. Existing technologies also commonly depends on the scale of the process, the possibility for heat integration etc. There are both physical, chemical and biological processes explored today. Some of the more common examples include scrubbers, filter bags, biological filters or incineration. Some are known for their low cost, their simple installation or their high efficiency. Many of the most efficient methods though, such as thermal or catalytic oxidation, require a significant amount of energy in the form of heat. Depending on where this energy originates from, the case might be that more environmental harm was done producing this energy than the positive impact the air cleaning unit has. [4] Others, like the activated carbon adsorption process is known to be highly efficient but maintenance-intensive if set to clean a highly contaminated stream since it consumed quickly, requiring frequent replacement.

Air pollution abatement is heading steadily forward today. One of the areas that has seen recent developments is known as Advanced Oxidation Processes (AOPs). It is suitable for the removal of both organic and inorganic but oxidizable pollutants. An AOP consists in producing hydroxyl radicals which subsequently reacts with the pollutant, the hydroxyl radical being a highly reactive oxidizing agent. The main difference between different AOPs is the way in which the radicals are produced. For example, ozone is often used in AOPs since its photolysis by UV leads to the production of this hydroxyl radical. The process can be carried out at normal temperature and pressure (NTP) and is thus a lot less energy intensive than many older alternatives.

AOPs were first considered in the 1980s for application in the wastewater treatment industry, and most research since have been focused on the water application. [5] Still today, UV reactors have been mostly used for disinfection purposes. In those cases UV-C (high-energy UV light) is used, which has the ability to
penetrate most microorganisms and disrupt their DNA, rendering them unable to replicate and thus no longer pathogenic. [6] This is obviously a case very different from the air pollution removal in this project and as such, known models and constants from the water research are not applicable to the air case.

Much of the work done on AOPs for the air application have been focused on the photocatalytic approach. The end result – produce hydroxyl radicals which react with the pollutant – is the same, but rather than thorough incineration or through the photolysis of ozone, the photocatalytic method uses water cleavage over a catalyst exposed to UV light, thus excluding the need for ozone entirely.[7] Given that ozone is a toxic compound with a very pungent odour, this approach would yield a safer environment for the operating engineer (see more in section Ozone). However, the photocatalyst is generally considered too sensitive for large scale applications where it may quickly become damaged by i.e. particles, or become poisoned. [4] For this reason, it is not viable for industrial cases. The road to large scale applications of air cleaning AOP systems thus starts with ozone and UV reactors.

PURPOSE & AIM

The thesis project is conducted at the R&D department of Ozone Tech Systems (Ozonetech) in Stockholm. Ozonetech sells air cleaning solutions and are therefore interested in extending the lifetime of their Activated Carbon (AC) beds. This is approached by increasing the cleaning efficacy before the AC bed, by the addition of different units. The methods chosen for further investigation are ozone injection, destruction of the pollutant in a UV reactor, and the combination of those.

Since the project is a collaboration between academic and industrial parties, focus was put on areas with a possible commercial application. Thus, this report will primarily consider hydrogen sulphide and VOCs, investigated separately. For the particular case of H₂S there is a type of absorption material also worthy of investigation, used sometimes in place of the AC beds. The life time of this material (Granular Metal Oxide (GMO)), and the effect of ozone injection on the AC bed is also a point of interest in this project. The system will not only be constructed for this project but will remain for future use at the company and will therefore be built with modularity in mind.

SCOPE

This project consists of the design, construction and modelling of a lab scale air cleaning rig. The rig shall include an UV reactor with ozone injection, AC adsorption beds and H₂S absorption beds as described above. Testing will not be included due to time constraints, but experimental plans are presented for future use. It is the hope that the model after validation will allow for future scaling to industrial dimensions, and that testing of the system will show the most important parameters and their interaction.

WORKFLOW

The project consists of 20 weeks of full time work. Being practical in nature, the project was initially developed iteratively, where scales, aims and goals changed almost weekly. By the sixth week all different goals, desired outcomes and limitations were collected and summarized, and a final design was set for the system layout and application. Even after the sixth week, much of the project plan relied on a number of suppliers to also stay on schedule. The time plan setup at the beginning of the project became irrelevant after parts of the equipment became the victim of an unfortunate accident. The time plan will thus not be presented here.
THEORY

OZONE

Ozone ($O_3$) is a highly reactive oxidizing agent present naturally in the upper layers of the atmosphere, where it absorbs some of the UV light irradiated by the sun. It is colourless with a smell similar to chlorine, and causes irritation in the respiratory tract already at 0.3 ppmv. [8] Ozone is highly selective, and if given the choice preferentially reacts with electron dense areas of other molecules (such as a double bond), due to its electrophilic nature. [9] [8]

It is photoactive and is naturally formed and decomposed by the absorption of UV light. The first reactions most relevant for this project are the ozone formation reactions (1 and 2), starting from oxygen. [10]

\[ O_2 + h\nu(185\text{nm}) \rightarrow 2O(3P) \]  
\[ O(3P) + O_2 \rightarrow O_3 \]  

There is also the decomposition reaction where the ozone molecule itself absorbs UV light at 254nm.

\[ O_3 + h\nu(254\text{nm}) \rightarrow O(1D) + O_2 \]  

The UV light being emitted by the lamps are at only these two wavelengths; 254nm and 185nm. Consequently, the UV lamps will be producing ozone if a gas stream containing oxygen is passed by the lamps.

The designation included in the parenthesis behind the radical refers to the energy level of the highest energy electron (the electron in the Highest Occupied Molecular Orbital, HOMO). As the reader might know, the oxygen radical from which ozone is formed ($O(3P)$) is at a higher energy level than the oxygen radical which is a decomposition product of ozone ($O(1D)$). The important role of this $O(1D)$ radical will become clear in subsequent sections. [11]

THE POLLUTANTS

The pollutants were chosen based on the demands on the market for air cleaning today (2018). In order to be of use to the company, the system needed to be somehow associated with the commercial situation. Both $H_2S$ removal and VOC abatement are commonly encountered on the market. Below, an overview will be given for each pollutant considered in this project. Note that at no point will both pollutants be removed at once; they will be considered and tested one by one.

VOCs

Volatile organic compounds are a collection of quite diverse hydrocarbons with the collective tendency to pass into gas phase at low temperatures, but no worldwide definition exists today. As put by Srivastava and Majumdar in their report on Air Quality Monitoring, an easily grasped definition is “VOCs are organic substances which are volatile and are photochemically reactive”. [12] The European union present a more detailed definition in their Directive 2004/42/CE:


“Volatile organic compound (VOC)’ means any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101,3 kPa”[13]

VOCs present a well known health hazard, particularly in indoor air, and regulatory bodies have therefore set mandatory emission limits for different industries. Since comparing the VOC concentration in the exhaust from a chimney to the concentration inside a factory does not yield any useful conclusions, different limits are set for indoor air quality and emission. [3]

Obviously, for the project at hand there is no perfect mixture of organic compounds ready to order. Neither can a field sample be used, since process control is an important aspect of the testing and any field sample from an arbitrary process will likely contain other compounds that might interfere.

It was decided that a single VOC would be used as a “VOC representative”. Possible candidates were determined by looking at common VOCs and also investigating VOC adsorption onto AC. Of course, not all VOCs adsorb equally well, and the adsorption varies with temperature, humidity, pressure etc. The VOC representative had to be neither extremely good nor terrible at adsorbing, which at first led us to the aromatic compounds. [2]

After briefly touching upon benzene, the path steered towards less carcinogenic compounds and started looking at toluene, a common VOC.[14] It was also known to be slightly better than average at adsorbing, and was initially accepted.

However, toluene has a boiling point of 110.6°C, which meant that in the system, at NTP, much toluene would be liquid. A liquid, as the reader of course realises, causes some issues in an air cleaning system.[15] One solution would be to evaporate the toluene before starting the process, but considering the additional work involved it was preferred to find a more suitable VOC instead. The investigation was thus started again, and the next candidate to be settled on was acetaldehyde, which has previously been successfully used as a VOC representative. [7, 16]

Acetaldehyde has a boiling point at 21°C, thus removing the issue of having to evaporate a liquid VOC before starting the system.[17] The compound is a strong reduction agent and belongs to the group of odorous chemicals known as aldehydes, and is commonly encountered in the industry of odour abatement technology (air cleaning). The structure of acetaldehyde is shown in Figure 2 – Illustration of the chemical structure of acetaldehyde

Care should be taken when handling the gas, as 15 minutes of exposure at concentrations around 50 ppm will result in irritation in the respiratory tract and high-level exposure could result in death. [18]
Hydrogen sulphide gas has the unfortunate odour of rotten eggs. This odorous property of H_{2}S is one main reason why it often presents a problem already at low concentrations, having an odour threshold as low as 0.002 ppm. United States Department of Labour [19], [20] H_{2}S is normally encountered in gaseous phase, where it might be breathed in and reach our respiratory system. Not only does it have a pungent odour, it also presents a grave health hazard, where concentrations of 500 ppm or above will lead to death within half an hour. In the master thesis by Lorenza Gilardi, the table below is presented to show the human body's physiological responses to different concentrations of H_{2}S. [20]

### Table 1 - The physiological response to different concentrations of H_{2}S as presented by Lorenza Gilardi[20]

<table>
<thead>
<tr>
<th>Concentration [ppm]</th>
<th>Effect on human health</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002-0.003</td>
<td>Odour threshold</td>
</tr>
<tr>
<td>3-10</td>
<td>Obvious unpleasant odour</td>
</tr>
<tr>
<td>20 - 30</td>
<td>Strong offensive odour (&quot;rotten eggs&quot;)</td>
</tr>
<tr>
<td>30</td>
<td>Sickening sweet odour</td>
</tr>
<tr>
<td>50</td>
<td>Conjunctival irritation</td>
</tr>
<tr>
<td>50 - 100</td>
<td>Irritation of respiratory tract</td>
</tr>
<tr>
<td>100 - 200</td>
<td>Loss of smell (olfactory fatigue)</td>
</tr>
<tr>
<td>150 - 200</td>
<td>Olfactory paralysis</td>
</tr>
<tr>
<td>250 - 500</td>
<td>Pulmonary edema</td>
</tr>
<tr>
<td>500</td>
<td>Anxiety, headache, dizziness, stimulation of respiration, amnesia, unconsciousness (&quot;knockdown&quot;)</td>
</tr>
<tr>
<td>500 – 1 000</td>
<td>Respiratory paralysis leading to death, immediate collapse, neural paralysis, cardiac arrhythmias, death</td>
</tr>
</tbody>
</table>

Obviously, the need to remove H_{2}S from any air intended for breathing is great but the execution is not always easy since it is highly corrosive and can damage downstream piping and equipment. Especially when dealing with higher concentrations of H_{2}S, special materials such as stainless steel or Teflon piping are required.

A common source of H_{2}S is biogas production sites. Briefly explained, biogas is a methane-carbon dioxide mix, where the methane is produced by microorganisms in a large reactor called a digester. However, not only methane-producing microorganisms are represented in the digester; some microorganisms, known as sulphur reducing bacteria compete with the methane producing bacteria and produce H_{2}S as a metabolic by-product. Thus it is not uncommon for biogas producers to require abatement technologies.

In this report, the hydrogen sulphide will be referred to as H_{2}S for clarity.
There is already an H$_2$S abatement unit at the company; a packed bed reactor filled with GMOs[1]. The reason this specific absorption material was chosen is because of its simultaneous absorptive and regenerating properties. Usually for an absorption material, there will have to be fairly frequent periods of planned maintenance where the material is either regenerated or exchanged for new material. Not so for this GMO.

The absorption process and the regeneration process summarized and described by the following total reaction:

$$3H_2S + 1.5 O_2 \rightarrow \frac{3}{8} S_8 + 3H_2O$$

Reaction 4

Theoretically, the only upper limit to the life time of the material would be the gradual build-up of solid sulphur S$_8$ formed in Reaction 4 turning the material from orange to black. Of course though, there will be other more practical limits such as fouling the sulphur clogging of internal pores in the GMO will also affect the total life time.

Careful study of the material by the manufacturer showed that the mechanism of absorption started only when the H$_2$S was dissolved in water, creating hydrogen sulphide ions, which then react with the iron hydroxide. However, to add water in its liquid state to the system is highly detrimental to the pellets and could even dissolve them. Therefore, the moisture must come from the gas. Research indicated a minimum gas moisture of 40%RH. Note that this moisture is also used as a reactant in the regeneration reaction.[1]

**PHOTOCHEMISTRY**

When considering the reactions of a molecule with UV light, the light is imagined to arrive at the site as a photon of a specific energy. For a wavelength $\lambda$, the energy $E_\lambda$ of a photon is calculated as

$$E_\lambda = h \frac{c}{\lambda} \ [J]$$

Equation 1

Where $c$ is the speed of light and $h$ is Planck’s constant.

As for most chemical reactions, it’s not enough for the reactants to be present in each others’ vicinity. They must collide the correct way in order to react. Additionally, the absorption of a photon is not guaranteed. It is expressed as a probability of absorption, where $\kappa_i^\lambda$ is the absorption coefficient of species $i$ at NTP for wavelength $\lambda$. [21, 22]

**Probability of $i$ absorbing a photon of wavelength $\lambda$ is:**

$$1 - e^{-x_i^\lambda \cdot x_i \cdot L}$$

Equation 2

Where $x_i$ is the mole fraction of species $i$ in the media, and $L$ is the depth of the media. For example, for a single cylindrical lamp in a cylindrical reactor, $L$ would be the distance from lamp to reactor wall. [21, 22]

For the photochemical reactions 1 and 3, the absorption coefficients are presented in Table 2 below.
Table 2 – Presentation of the absorption coefficients used in the project

<table>
<thead>
<tr>
<th>Species</th>
<th>Absorption coefficient [cm⁻¹]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>( K_{O_2}^{185} = 0.75 )</td>
<td>[23]</td>
</tr>
<tr>
<td>Ozone</td>
<td>( K_{O_3}^{254} = 133.1 )</td>
<td>[24]</td>
</tr>
</tbody>
</table>

The quantum yield is a number that both encompasses the stoichiometry and the photochemical conversion. The quantum yield for formation of ozone (Reaction 1 and Reaction 2) is reported as 2.0[25], while for the decomposition of ozone the quantum yield, it has been shown to be largely dependent on the amount of ozone. However, for the present concentrations of ozone, it can be assumed to be unity. [26][10, 27]

ABSORPTION AND TRANSMISSION

As a light beam of wavelength \( \lambda \) travels from its source and outwards, it will become attenuated by any material that absorbs light at \( \lambda \). The degree to which a material absorbs light at \( \lambda \) can be expressed either as an absorption coefficient (cm⁻¹) or as a constant known as the absorption cross section (cm² per molecule).

As explained by Blatchley, [28], the absorbance \( A(\lambda) \) for path length \( L \) is related to the absorption coefficient \( a(\lambda) \) by

\[
A(\lambda) = \frac{a(\lambda)}{\ln 10} \times L
\]

Equation 3

Furthermore, the absorbance is also related to the concentration of the species and its molar absorption coefficient \( \epsilon \) (M⁻¹·cm⁻¹) by the Beer-Lambert Law.

\[
A(\lambda) = \epsilon(\lambda) \times c \times L
\]

Equation 4

Conversely, the transmittance of light, the fraction of light at \( \lambda \) allowed to pass through the material, is expressed as

\[
T(\lambda) = 10^{-A(\lambda)}
\]

Equation 5

Consider the case of one light source in the middle of a sphere (left part of Figure 4). A point close to the middle will of course be exposed to more light than a point at the sphere surface due to dissipation and absorption of the light. How much light reaches the sphere surface is of course dependent on the media inside the sphere and the radius of the sphere.

Now consider an identical sphere located a short distance away. Any point in the vicinity of both spheres will be irradiated by two different light sources, and the sum will be the total irradiation at that point. An infinite amount of individual light sources along a line of length \( L \) could then represent a cylindrical lamp of length \( L \). This is illustrated below.
This method, known as the point source summation model, was first defined by Jacob and Dranoff [29] and then further developed by Blatchley [28]. Bolton later uses this model to develop an expression for the fluence rate at any given point in a cylindrical reactor. This method of approaching a model of the UV light distribution in UV reactors has been often used in literature and will also be used here.

PHOTOLYSIS VS PHOTOOXIDATION

Photodegradation, the science behind UV induced reactions for air cleaning can be split into two categories; the direct interaction between the UV light and the pollutant (photolysis), and the indirect oxidation of some other species which then proceeds to react with the pollutant (photooxidation). Not all literature on the subject have distinguished between the two; with the main goal of often simply eliminating a pollutant the exact mechanism of how it is eliminated is not always of interest.

In the case of this project, two aspects must be considered. Firstly, if the pollutant engages in photolysis rather than reacting with radicals the expression for the reaction rate of the pollutant must take this into account. Secondly, if the photons produced by the UV lamps are absorbed by the pollutant on their way to produce a radical, the expression for the production rate of radicals cannot be equal to the probability of absorption of said photons.

THE VOC

The direct interaction between the UV light (at 185nm and 254nm) and the VOCs (photolysis) was investigated in a study by Kang and Hu [30]. It was shown that for most common VOCs, the photolysis was of less import than the photooxidation; that is, VOC removal by UV is mainly due to the hydroxyl radical production, not due to the photolysis. When considering the reactions the VOC participates in, the photolysis of VOCs will be considered negligible.

THE H₂S

It is known that H₂S is photoactive at the wavelength 185nm, as shown in the work of Lorenza Gilardi [20]. In this case, the H₂S is photolysed according to Reaction 5 below:[31]

\[ H_2S + h\nu(185\text{nm}) \rightarrow H^+ + HS^- \]

Reaction 5
A study by Jianhui et al. showed that the role of photooxidation is much more significant than photolysis in degrading the H$_2$S molecule.[32] Based on this, it can be assumed that when considering the reactions the H$_2$S participates in, the photolysis of H$_2$S will be negligible.

**THE PHOTONS**

Another way of seeing the matter is whether or not all the photons can be assumed to participate in Reaction 1 and Reaction 3 or if they react with the pollutants or the water vapour in the air.

To compare different species' ability to absorb light at a specific wavelength, one can compare the species' absorption cross section [cm$^2$ per molecule], a commonly used measurement of the probability of absorption. The comparison was made for the species at hand, and the result is shown in Table 3 below.

In the column marked Note the absorption probability of the respective species at the current concentrations are compared to the absorption probability of oxygen (for 185nm) or ozone (for 254nm). To achieve a representative comparison, not only the absorption cross sections are not compared directly, but are multiplied with the concentration per volume of each species. The products are then compared to see if some species are likely to absorb more than oxygen or ozone. If this were the case, then Reaction 1 and Reaction 3 would have to compete with other photochemical reactions.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength [nm]</th>
<th>Cross sections [cm$^2$/molecule]</th>
<th>Note</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>254</td>
<td>1.14*10$^{-17}$</td>
<td>At 273K, not room T, but also not very T-dependent.</td>
<td>[34]</td>
</tr>
<tr>
<td>Oxygen</td>
<td>185</td>
<td>6.2294*10$^{-21}$</td>
<td>Middle of the Schuman-Runge non continuous absorption bands.</td>
<td>[35]</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>185</td>
<td>1.26*10$^{-17}$</td>
<td>Around a hundredth as absorbent as oxygen</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>254</td>
<td>1.52*10$^{-28}$</td>
<td>Negligible compared to ozone</td>
<td>[37]</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>185</td>
<td>3.42*10$^{-18}$</td>
<td>Around a hundredth as absorbent as oxygen</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>254</td>
<td>1.47*10$^{-28}$</td>
<td>Negligible compared to ozone</td>
<td>[39]</td>
</tr>
<tr>
<td>Water vapour</td>
<td>185</td>
<td>7.14*10$^{-28}$</td>
<td>Around three millionths as absorbent as oxygen</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>254</td>
<td>-</td>
<td>Not applicable</td>
<td>[41]</td>
</tr>
</tbody>
</table>

The general trend observed from Table 3 is that both the 254nm-photon and the 185nm-photon will mainly be consumed by Reaction 1 and Reaction 3.
RADICALS

A radical is an atom or a molecule with at least one unpaired valence electron. This unpaired electron is placed in the HOMO, which is at an uncomfortably high energy level, and the desire of the molecule to reach a lower energy state is strong. A reaction with another species will create a new set of molecular orbitals, which will be at a lower energy level than the current HOMO. Consequently, radicals are highly reactive. There are of course differences in reactivity between different radicals. The more reactive they are, the less selective they are about what they react with. The hydroxyl radical, shown below in Figure 5, is one of the most reactive radicals. [42]

![Hydroxyl Radical](image)

Figure 5 – Illustration of the hydroxyl radical, the lone electron coloured in red

The OH- radical is formed through the reaction shown below [43], where water is considered a reactant in excess.

\[
O(1D) + H_2O \rightarrow 2OH^-
\]

Reaction 6

Possible reactants and products of the VOC decomposition initially thought to be relevant are HO₂ and RO₂, which are commonly formed in the oxidation of hydrocarbons in the atmosphere. There, in the presence of NO, they have been known to act as reservoirs and secondary sources of OH, while the NO₂ acts as an OH sink. However, in the case at hand, the only possible source of NO would be from the ozone generator, and this NO amount is assumed to be low enough to neglect any NOx effects on the system. Therefore, since HO₂ and RO₂ in such case would only be some of the many reaction products of the VOC conversion, they will not be further discussed and the hydroxyl radical is assumed to only react with the pollutant. [44]

OXIDATION END PRODUCTS

Assuming that only photooxidation occurs in the reactor, the complete decomposition of acetaldehyde is given by Reaction 7 below. [7] The reaction shows acetaldehyde being oxidized by oxygen, but other oxidants will be present in the case at hand.

\[
CH_3CHO + \frac{5}{2}O_2 \rightarrow 2CO_2 + 2H_2O
\]

Reaction 7

This project will not be concerned with exactly what products and possible intermediaries are formed as the VOC reacts with the hydroxyl radicals (as explained above), only with the reaction rate of the VOC itself.

Assuming negligible photolysis for the H₂S also, the decomposition reactions were presented by Gilardi [20] as:
There is, as mentioned before, also formation of intermediaries in the process, but these will not be further dealt with here. It should be noted that the end products are not safe for inhalation.

THE ACTIVATED CARBON

AC functions by acting as adsorbate for passing pollutant molecules. As such, there is a limited number of adsorption sites that can be filled, giving the activated carbon a certain loading capacity, commonly given as the mass of pollutant that one kg of AC can adsorb.

The reason AC is so often and successfully used is in equal parts due to its comparatively low cost, easy installation, and its very high surface area per mass. This is a result of the internal structure of the carbon; a labyrinth of pores and micropores and more micropores. [2]

It was long believed that only the physical characteristics of the surface played a role in its adsorption capacity, but during recent decades it has come to light that also the chemical surface properties are highly significant. [45]

Different molecules have different affinities for the AC surface. One molecule of import is the water molecule, which has a relatively high affinity. Thus, if the gas stream is very humid and the pollutant has a lower affinity than water, an AC bed might simply dry the stream, not clean it. The VOC will compete with water vapour for adsorption spots, which is why it is important to both control the humidity and to have a VOC representative that does not give undue precedence to the water molecule.

OZONE INJECTION

Given that Ozonetech commonly uses ozone to aid in the cleaning of air and water streams and AC beds are widely known as efficient options for air cleaning, it is quite possible that ozone and AC beds will be used in conjunction. Therefore, the effect that ozone has on the lifetime of the AC bed is of great interest.

There are two schools of thought, both supported by literature. The first considers the surface of the AC, where multiple pollutants are adsorbed. As ozone arrives on site, it will react with the trapped pollutants, oxidize them, and thus generate the AC by increasing the number of empty sites. In this case, the ozone would have a positive effect on the life time of the AC, perhaps even creating a simultaneous adsorption and regeneration process, provided it does not harm the AC. However, this has mostly been investigated for reactions in water, not air. [46] [47] The suspected mechanism is shown in Figure 6 below.
The other scenario is that the ozone will have a detrimental effect on the AC surface, changing the surface properties to create a much more acidic surface with a decline in surface area. The acidic properties are developed due to the surface being covered in acidic oxygen-containing functional groups such as lactone, or carboxylic acid; the result of oxidation by the ozone. It should be kept in mind that this transforms the surface from a non-polar environment to a polar one, with the expected resulting effect on the adsorption capacity of organic pollutants. Professor Valdés Morales et. al. explains in their article on the subject that the oxygen containing functional groups on the surface influence the surface properties of activated carbons more than many other surface groups.

This effect is shown Figure 7 in below.

All things considered, evidence suggests that injection of ozone just prior to the AC bed inlet might prove detrimental rather than regenerative. To reach a conclusive decision on whether ozone in reasonably low dosages might have a positive impact on the bed, Professor Héctor Valdés Morales was contacted. His recommendation would be to not inject ozone due to both the risk of explosion in the AC bed and the effect ozone has been shown to have on the AC surface.

While a simultaneous adsorption and regenerative process might be out of the question, there is still potential for investigating the regeneration of a fully loaded AC bed using ozone injection, which is the recommended next step in the utilization of the system albeit not in the scope of this project.
METHOD - DESIGN

There was a very large amount of back and forth between suppliers and the metaphorical drawing table, but here below the process will be described in a more comprehensible manner than in chronological order.

The system design started off as is appropriate with a block flow diagram. The diagram from the very first day of the project is shown below. Of course, as the project proceeded, goals became solid or changed, and expectations were made clearer, the design evolved with the circumstances.

![Block Flow Diagram](image)

**Figure 8 – The very first block flow diagram is shown**

Questions such as ‘What flow rate should there be?’, ‘What size ozone generators are available?’ and ‘How to control the process?’ were asked and iteratively answered. New expectations appeared as the system became more defined, and it was finally settled that the rig would be designed to both test the life time of the adsorption materials (AC and GMO) and to test the efficacy of the UV reactor and its response to changing process parameters. This entails constructing a system with two very different sections. The final PFD and a clarification is shown below in Figure 9. This section will describe in more detail how this system configuration came to be.

![PFD Diagram](image)

**Figure 9 - The final PFD is shown**

In the life time subsystem, there will be absorption beds to investigate the GMO and the AC, while the efficacy subsystem will be used to investigate the efficacy of a UV reactor.

The risk of contaminating the system with sulphur when using H₂S as pollutant was considered, resulting in two separate lines leading to the same units wherever it was possible.
The whole system needed a fan to push the air, and a humidifier with hygrostat to reach an appropriate level of humidity. As mentioned previously, if the pollutant has a significantly lower affinity for the activated carbon than water, a polluted air stream passed over an AC bed might not clean the stream, only dry it. Whether or not this becomes an issue is of course dependent on the pollution and humidity of each separate case. The recommended upper limit of 60%RH was found in literature. Provided that the test rig remains indoors in Sweden, humidity levels will likely be between 40%RH and 50%RH.[48] Of course, the humidity suitable for the UV reactor need not be the same as for the AC bed since the two subsystems are never run simultaneously. For the efficacy tests, 60% RH is considered adequate humidity to assume that water vapour is a reactant in excess. Work had already been done on the effect of the humidity on the UV reactors' performance. Consequently, the humidity was set to a constant value for this project.

No temperature control was setup for the system as ambient air would be used for the project, but for all calculation purposes, NTP was assumed.

**LIFE TIME INVESTIGATION**

Life time refers to how long the adsorption bed will remain efficient. Normally, this is given as a fraction upon acquiring the adsorption material; an adsorption capacity of 35% would mean 1kg of adsorption material could adsorb 0.35 kg of pollutant. The number of adsorption sites are limited, and therefore the total capacity is a constant value.

In the case of the GMO bed on the other hand, there is a set amount of metal hydroxide to react with the H₂S, but the metal hydroxide is then simultaneously regenerated. Chemically, this process could continue for an almost unlimited time. Practically though, the final product of the absorption and regeneration reaction is solid sulphur ($S_8$) which will clog the pores of the GMOs once enough sulphur has been produced. Questions that would need answers are for example “Is regeneration as fast as absorption?” and also “How much H₂S has been absorbed by the time the sulphur starts clogging the pores?”

For the AC bed the point of interest is the effect that ozone has on the AC bed; if it will ultimately increase or decrease the capacity (and thus life time). Knowing this would make it possible to predict how long a bed will survive in an industrial setting.

Practically the life time experiments consist of waiting until the bed becomes inefficient (aka breakthrough time) and calculating the mass of eliminated pollutant. The higher the pollutant concentration the faster the bed will become full. However, having a very high flowrate and a high concentration presents a safety risk for the operator should the system leak or an error be made. Therefore, the flow rate through the beds will be low but pollutant concentration high. Furthermore, purchased H₂S and acetaldehyde is not delivered pure, but in a mix with N₂. In order to properly simulate real life conditions so that the results would be representative and scalable, appropriately humid air was mixed with the pollutant gas. Note that at no point would both pollutants be tested simultaneously; the tests will always be done with H₂S OR with acetaldehyde.

Appropriate residence times are known from previous work at the company and were used to decide bed sizes. Bed properties are summarized in Table 4 below.

In the design of a packed bed reactor, some of the most important parameters to be considered are the height-to-diameter ratio (to reduce the risk of channelling), the pressure drop over the bed and of course also the particle size compared to the bed diameter. All those were considered for the construction of the beds. Since the life time system could also be used to test what residence times would be sufficient for i.e.
the H₂S absorption, it was preferable to build the system modularly, so that the total residence time could be easily varied by adding several small packed bed reactors in series.

Upon considering the type of AC needed for the bed, it was decided that it would preferably be able to adsorb both H₂S and VOCs.

### Table 4 – Properties of the packed bed reactors in the life time system. The X and Y represent confidential information.

<table>
<thead>
<tr>
<th></th>
<th>GMO BEDS</th>
<th>AC BED</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density [kg/m³]</strong></td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>GMO S K</td>
<td>GMO S K</td>
</tr>
<tr>
<td><strong>Residence time, t, [s]</strong></td>
<td>X s</td>
<td>X s</td>
</tr>
<tr>
<td><strong>Pressure drop [Pa]</strong></td>
<td>Negligible</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

### EFFICACY INVESTIGATION

The UV reactor will be used in conjunction with ozone injections to attempt to chemically remove the pollutant by converting it into harmless products. The efficacy of the UV reactor is dependent on several factors, of which three have been chosen for further investigation. The UV power used in relation to the pollutant flow rate, the total volumetric flow rate in the reactor, and the amount of injected ozone.

The efficacy investigation will consist of the development of a semi-empirical model for the pollutant reaction rate, and an experimental plan to validate the model, find model constants, and to investigate the interaction and importance of the different parameters through factorial design.

Previous work by supervisor Francesco Montecchio had yielded an optimal relationship between the UV lamp power used, and the volumetric flow rate of pollutant (dm³/min). This relationship was used to decide the flowrate of the efficacy system; several times higher than in the life time system. More about lamp power and its relation to the flowrate will be presented in UV Reactor Design. Concentrations of pollutant were decided to represent industrial cases and are shown below. Of course, during the course of the experiments they will be varied somewhat.

### Table 5 - Properties of the efficacy system

<table>
<thead>
<tr>
<th></th>
<th>EFFICACY SYSTEM [PPM]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conc. Of VOC</strong></td>
<td>Up to 20</td>
</tr>
<tr>
<td><strong>Conc. Of H₂S</strong></td>
<td>Up to 50</td>
</tr>
</tbody>
</table>

### LINES & TURBULENCE

The two subsystems have different purposes and different flowrates. The lines thus have different diameters. In the life time system a suitable inner diameter is 6mm and in the efficacy system it’s between 50 and 60mm. This was decided in order to attain sufficient superficial gas velocities (s.g.v.) in the lines, while avoiding a too high s.g.v. which could result in damage to the equipment. The UV lamps, for example,
are known to break at s.g.v. above a certain limit. Also, a laminar flow will behave quite differently from a turbulent flow. The Reynolds number is often used to determine if a fluid flow is turbulent or laminar which might have an impact on the system integrity and fluid mixing.

\[ Re = \frac{(VD\rho)}{\mu} \]

Equation 6

Where V is the mean velocity in the pipe (m/s), D is the pipe diameter (m), ρ is the density of the flowing fluid (kg/m³) and \( \mu \) is the dynamic viscosity (Ns/m²). Calculating the Reynolds number for pipes as defined above, this yields Re sufficiently high to ensure good mixing and appropriate s.g.v., but low enough that the system will not rattle.

Note also that only part of the system will need to be corrosion resistant, since not all of the system will be in contact with the corrosive species.

UV REACTOR DESIGN

The UV reactor should expose the gas to as much UV light as possible, which means having the lamps inside the reactor. The first requirement of the UV reactor was therefore that it should be built to accommodate the slim, cylindrical UV lamps and provide as close to an even light distribution as possible. The second requirement was to also create a flow profile that was turbulent enough to provide good mixing for the reaction. One thought was to try to simulate the industrial scale, but due to the known difficulties in scaling a process properly, it was decided to not attempt it. Instead, the fluid dynamics would only be considered to see if they ensured sufficient mixing of the reactants. A third criterion was to have a s.g.v. of at least 3 m/s in the reactor to avoid stagnation.

Initially, the configuration of a cylindrical reactor with one lamp inside was investigated. Using simple graphical tools, Figure 10 was created to illustrate the idea. It should be noted that it is customary to enclose the UV lamp in a quartz glass sleeve for protection, but the sleeve will not be included in the images displayed in the report. For any calculations, the diameter of the quartz sleeves is considered, not the diameters of the lamps themselves.

Since the reason for turbulence in a cylindrical reactor would be different molecules travelling at different speeds, an idea was to expose the gas flow to a fairly thin section of for example random metal packings, thus creating suitable drag for the molecules close to the wall, resulting in more turbulence.
It was then discovered that solution of ‘random packings to create turbulence’ had already been investigated and developed, and the updated version was known as a perforated plate or two set up at the reactor inlet. Thus, the creation of turbulence at the start of the reactor was no longer the main criteria; even light distribution was. The design tools were upgraded to a 3D modelling program known as Autodesk Inventor. Some further examples were sketched, modelled and presented for discussion, see Figure 11 below.

A UV reactor with only one lamp setting – ON or OFF – would hardly be suitable for an air cleaning rig at lab scale designed for testing parameters such as "lamp power"; there had to be a way to make the lamp power variable. The UV lamps considered for the project cannot be dimmed, which meant the only option would be to have several lamps of lower power that can be turned on or off individually. Of course, some thought also had to be given to where and how the cables would run.

The optimal ratio between lamp power and pollutant concentration given a flowrate was known, but the exact calculation process was classified.

It would not be reasonable to make the theoretically optimal lamp power correspond to the minimum lamp power. That is, if the lamps were for example only available at powers as low as 15W, to design the system flow rate so that 15W yielded the optimal ratio would make it impossible to investigate lower lamp powers. It was decided that one level higher and a few levels below the optimal lamp power was of interest. Reasonably, more UV light in the reactor would almost definitely move the conversion towards 100% (unsurprisingly) but the interesting part was whether one could decrease the lamp power and still yield a satisfactory conversion.

Further designs were thus variations on a multi lamp reactor where the lamps were placed so that any number of lamps would yield a suitable light distribution. Using four to six lamps in the examples below, some final sketches are shown in Figure 11.
Figure 11 - Illustrating some UV reactor design ideas. A) was designed according to a common model on the market, B) and C) was designed to provide a high gas speed through the reactor and D) was designed as a Lid-Box setup but otherwise similar to B) and C).

The reactor design chosen is not displayed in Figure 12 due to confidentiality issues. The decision was made giving more weight to the requirement of good light distribution rather than turbulent conditions inside the reactor, since the inlet was to be equipped with perforated plats for just that purpose. Note that it is not likely that the reactor achieves full turbulence, but attempts are made none the less to improve the mixing of reactants.

Following this decision, the design moved on to the details of appropriate volume (residence time), distance between the lamps, ratio between the inlet and outlet s.g.v., the practical details of how to fasten the lamps etc. etc. The result of this work was done in the 3D modelling programme, where also the transitional parts from pipe to reactor were modelled before finally sending the model off to a professional CAD engineer to finalize it for construction, applying standard measurements for stainless steel and gaskets etc. It was also agreed upon that all space inside the reactor should be utilized and any non-light emitting part of the lamp would be housed outside of the reactor volume. Final details on the reactor are shown in Table 6 below.

Table 6 - Properties of the UV reactor, where the volume inhabited by the lamps are accounted for.

<table>
<thead>
<tr>
<th>Technical specifications of the UV reactor</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>tr</td>
<td>0,18 s</td>
</tr>
<tr>
<td>Ratio of inlet s.g.v. to outlet s.g.v.</td>
<td>1:4</td>
</tr>
</tbody>
</table>
Fluid dynamics concerns the way in which a gas or a liquid moves. Today it is a discipline that is primarily governed by a large number of numerical methods, solved with a computer using Computational Fluid Dynamics software (CFD). Very briefly put, the reason why all molecules in a fluid does not move coherently as one large unit is due to differences in their velocities. These differences in turn might stem from any number of sources such as a physical obstacle, collisions with other molecules, drag along a surface or a temporary difference in density, pressure or temperature in the bulk fluid.

In the project at hand, fluid dynamics are of interest since they will be affecting the distribution of the gaseous reactant in the UV reactor, and thus also the conversion. For example, if the reactor design causes a stagnation of the flow in one dark corner of the reactor, it cannot be reliably assumed that all reactants are reached by the UV light.

Unfortunately, a CFD analysis of even a relatively simple case (consider a cylindrical lamp in a cylindrical reactor) is a fairly large project in and of itself. Therefore, no CFD analysis can be done within the scope of the project.

However, to completely ignore all fluid dynamics is not a viable strategy either. Some assumptions, however broad, have to be made and those assumptions need some basis.

It shall be assumed that the reactor is perfectly mixed, applying the model of a Continually Stirred Tank Reactor (CSTR). The design of the reactor yields the case of a flow of polluted air at NTP colliding orthogonally with multiple smooth glass cylinders (the lamps) at a certain ‘wind speed’. Obviously no case exactly like this was found in literature. [49] However, one article treating a similar case was found, written by Miller et. al. The expected air flow pattern around a tree in ‘slow wind’ was predicted using fluid mechanics, as a step to investigate pheromone distribution around the trees. The tree were modelled as a smooth cylinder. [49]

The mentioned air flow pattern is shown below. Since the article discusses the tree as a smooth cylinder, there is in this model no difference between the quartz sleeves the process flow will meet and the tree that the wind will meet other than the diameters.
The article further discusses the Reynolds number for the airflow at different wind speeds, colliding with cylinders of different diameters. The graph used by the authors is shown in the references. 

Figure 12 – Shown above is the first figure from the article by Miller et. Al. [49] illustrating the same flow case as process air flowing around a lamp in the UV reactor. As explained in their article, the lines are known as *pathlines* and longer pathlines indicate a faster flow. 

Figure 13 – Also as shown by Miller et. Al, a diagram showing the Reynolds number for the fluid case in
The red area marks approximately the present 'wind speed' and diameters of the quartz tubes, resulting in a Reynolds number indicative of a turbulent flow. It should also be noted that even though indicates that there might be stagnant regions behind each lamp, it is believed that due to the number of lamps, shape of the reactor and the velocity increase occurring in the reactor, the fluid dynamics can be neglected, and the flow labelled as turbulent. A turbulent flow results in good mixing, which is why the assumption of perfect mixing is acceptable for the case at hand.

REACTOR CHAMBER

Another point of interest that was expressed later in the project was to investigate only the ozone injection, without the UV light. One might think that it could be easily done by simply turning all the lamps off, but that would result in a residence time far too short for the ozone-pollutant reaction. Therefore, a reaction chamber would be required.

Since the residence time would be investigated, there would need to be a way to choose to run the system with different residence times. Preferably, to keep other parameters constant, the shape of the reactor would remain similar in order to maintain close to the same fluid dynamics. Difficulties with controlling the fan made it necessary to make the reactor chamber volume variable, since residence time is proportional to volume. Therefore, the approach would be to find a way to build a reactor chamber that could easily be added to.

PROCESS CONTROL

It was decided that process control would aim at being intuitive but fairly simple since the author of this report had no prior experience with automation, Programmable Logic Controllers or even electronics. This resulted in all valves being manually opened and closed, and the humidification control, the fan control and the lamp control all being separately controlled units. A control system, or perhaps even a Graphical User Interface is a project for the future.
RESULT & DISCUSSION – CONSTRUCTION

Once the design criteria were set, it was time to look to suppliers on the market and their available products.

THE LINES

A vital aspect of the choice of line material was whether it would be exposed to corrosive species. Also, since the design of the system resulted in different flow rates for the separate subsystems (the life time part, and the efficacy part), they will be treated in different sections below.

At the start of the system the fan and the connection to the two different subsystems would not be exposed to any corrosive species. A number of presently used systems of pipes and tubes were available on the market, but to avoid unnecessary difficulties a well-known system was chosen known as ‘spiro ducts’. This ensured a wide array of parts and compatible equipment, which is relevant since the system had to be air tight. Spiro ducts are commonly used as ventilation ducts and were available in several different sizes with dimension changing adapters in between each size. The size of 80mm diameter was chosen for the system’s initial parts.

THE LIFE TIME SYSTEM

With injection points at the very start of this subsystem, the entire life time system would need to be made in corrosive resistant material. Since the company specialized in ozone production, such equipment were readily available. An inner diameter of 6mm as the design parameters required meant either a Teflon tube, or a stainless-steel pipe. To provide flexibility to the system as a whole, the option of Teflon tube was used. All valves and gas tube fittings were also available and in stock, all made in stainless steel.

THE EFFICACY SYSTEM

The flow rate was higher in the efficacy system, requiring a larger line. As mentioned above, the preferred diameter of around 60mm did not correspond to any available spiro duct sizes, as these are only available down to 80 mm in diameter. Since 80mm spiro ducts resulted in a slightly too low but acceptable s.g.v., the decision was made in order to facilitate the construction. While the first part of the efficacy system did not need to be corrosion resistant, the later parts containing the pollutant injection points did. Fortunately, spiro ducts are available in acid resistant stainless steel, which was used to construct the injection section.
The fan was placed at the beginning of the system and push air through the humidifier, and then through the chosen subsystem.

Searching for a suitable fan, the most important criterion was its ability to push the air with enough force to overcome any pressure drops. A high flow rate was required in the efficacy system which due to its line size had rather low pressure drops. The same fan also had to be able to create a much lower air flow through the lifetime system, a task much more gruelling considering the pressure drops caused first by the decreasing line size, and then the several valves before arriving at the beds.

For any given type of fan, a higher pressure drop means a lower flow rate through the system. The fan’s ability to create a certain flow rate while pushing against at certain pressure drop is shown in its fan curve. There are many types of fans, the majority suited to either higher airflows or smaller fans for systems with no pressure drop (i.e. computer fan). With guidance by the supplier a fan known as a side channel fan was chosen that suited the present conditions. The fan can be seen in Figure 15 to the right.

In order to lower the flow rate to the suitable to what was required in the lifetime system, an iris was installed at the entrance to the life time system and a flow meter measured the flow directly afterwards.

A side channel fan does not commonly have different output levels; the fan is simply ON or OFF. For a test rig where it might be of interest to vary the flow rate, this is a suboptimal setup.

The size of the airflow the fan can create is determined of course by the rotational speed of the fan, which in turn is proportional to the frequency of the alternate current supplied by its three-phase power source. It is however not recommended to run the fan at a higher frequency than it is built for. The standard frequency of the three-phase power supply is 50 Hz in Sweden. Lowering the frequency will subsequently decrease the
airflow. The frequency is manipulated using a frequency converter, installed between the power supply and the fan.

The fan should according to its suppliers not be run at a frequency below 20 Hz, providing the system with an interval for the flow rate. The frequency converter is operated manually and is equipped with a display and a number of programmable parameters. For a certain pressure drop the relationship between the frequency supplied and the resulting air flow is not necessarily linear, although the correlation is positive. A few experiments with the fan and a manometer over the iris yielded Frequency vs Flow rate – curves meant to aid the operator of the system in matching an input frequency to an expected flow rate.

An example test on only the fan with no pressure drop were done, and the resulting Frequency vs Flow rate – curve is shown below. The lack of an x-axis is due to confidentiality reasons.

![Graph showing Frequency vs Airflow](image)

**Figure 16** – Illustrating the relationship between frequency and flow rate, so that an operator can quickly read the flow rate given a frequency if a similar curve is created for the appropriate pressure drop.

**THE HUMIDIFIER**

The optimal humidity varied throughout the system. For the GMO beds there was a lower limit. For the AC beds there was an upper limit, and for the efficacy system there was an approximated a lower limit to be able to consider H₂O a reactant in excess.

Consequently, the humidifier had to have at least different modes if not a separate hygrostat to control the humidity. After much research, a humidifier was acquired that uses an ultrasound field to make liquid feed water into an aerosol, with an accompanying humidity sensor and hygrostat. The advantage with this technique as compared to the boil-water-and-inject-the-steam approach was both the lower cost and the smaller size. [50]

The suppliers were also able to provide a compatible hygrostat and a humidity sensor.

The humidifier had one inlet, but two outlets as can be seen in Figure 17 below. For some reason, the distance between the two outlets was such that no connections were available that could connect the two 40 mm outlets to one common line. Therefore, improvisations had to made using available VVS tubes, under
the assumption that the outgoing air from the right outlet would be enough that no air from the left outlet would be misdirected into the humidifier again.

**Figure 17 – Image of the humidifier unit. The inlet is the black rubber adapter to the left, and the outlet is the white tube.**

**THE UV REACTOR**

After the 3D modelling was done, the accompanying drawings were sent to a workshop for construction. The reactor was made in stainless steel according to instructions, and the supplier of the UV lamps also shipped the immersion lamp holders seen in the picture below, designed to allow a cable outlet for the lamps without causing a leakage.

![Image of the UV reactor's immersion lamp holder.](image)

Aside from the design criteria discussed in previous sections, the actual construction of the reactor had to also consider the exact dimensions of the lamps. The lamps chosen were of a standard model known as low-pressure mercury lamps. The glass bulb allows for the transmission of both 185nm and 254nm UV light, as does the quartz sleeves into which the lamps are inserted. Regardless, in practice there will be a slight decrease in the intensity as the light passes through the interfaces. This is accounted for when considering the lamp efficiencies later in the report. An illustration of the lamps used are shown below.
It was important to ensure that the reactor remain air tight, and at the same time having only the light-emitting section - the arc length - of the lamp inside the reactor volume. This led to encapsulating the reactor volume, and providing an outer box where the white ends of the lamps could rest. A schematic is shown below.

**Figure 19 – Illustration of the type of 4-pin UV lamp used in the reactor.**

In order to both protect the inside of the reactor and ensure no reactant would leak into the outer volume, a sheet of the corrosion resistant Viton (synthetic rubber) were glued onto the inside walls of the reactor. The holes in the Viton sheets were of the same dimension as the quartz tubes, creating an air tight seal upon insertion.

The choice of lamps was primarily based on their power. The design criteria of multiple levels, with the optimal power level corresponding to a mid-level meant the flow rate would need to be high if each individual lamp had a high effect. The lowest lamp power available thus solidified the flow rate for the efficacy system. Since the lamps did not desire 230V (normal outlet voltage in Sweden) suitable ballasts were also acquired.

**LAMP CONTROL**

As explained in previous sections, the reactor did not have the sole purpose of destroying pollutants, but also to investigate what lamp power was required to destroy a specific amount of pollutant at a specific flow rate. The lamps thus had to be individually controlled. Intuitively and in its simplest form, this might be done by connecting each lamp to its own outlet. Turning a lamp on and off would be done simply by pulling the plug. This is, however, impractical and not operator friendly.

Again, the author of this report had no experience with electrical work. Therefore, a qualified electrician was contacted and extensively consulted anytime electrical knowledge was required, but the practical work was done by the author. One such case was the construction of the control box. All ballasts were placed in the box, and the lid was equipped with light switches. The control box is shown in Figure 21 and Figure 22 below.
Figure 21 – Image of the control box under construction

Figure 22 – Image of the control box after construction
The main reaction chamber design criterion was for modularity, to be able to smoothly test a range of volumes. At first a setup consisting of one large volume divided into smaller sections was considered, where the sections would be opened according to the volume required. This would take significant time to build. The second approach was to find smaller units who could be easily fitted together to form a large reaction volume. Since the efficacy subsystem was already designed with spiro ducts, this option was investigated.

Neglecting the dimension changing units, each of the larger spiro elbows below correspond to a suitable unit of added residence time. The volume added by each unit – consequently also the residence time added – was calculated using the degree of the elbow, and the assumption that the units could be seen as parts of a larger torus. In the end, this led to the below units being acquired since they together can form a reactor with appropriate residence times.

![Image of spiro duct elbows with time details](image)

**Figure 23** – Illustration of how the degree of the spiro duct elbow results in a certain volume, which increases the reactor residence time with a corresponding unit of time. The different spiro elbows combined make up the reaction chamber.

The packed bed reactors (hereafter referred to as 'beds') were constructed following a previous design used by the company. The reactor bed body consisted of a transparent pipe, since in the case of the GMO the colour change from orange to black is the indication that the bed has become full. It was the intention to be able to compare the colour of the packing material to the actual break-through time. The inlet and outlet of the beds were identical, which is why only the inlet is shown in the picture below.

Only the inside of the reactor container and the metal mesh keeping the pellets inside the reactor would come into contact with the corrosive gases, and both the metal mesh and the PVC-U pipe were classed as sufficiently resistant. [51]
The inlet was supplied with an adapter connecting to a gas fitting. The beds were filled with the respective material, and the reactor body was cut into the appropriate length to yield the volumes specified in the design section. Below is an image of some of the beds after construction (Figure 25).

The bed body was made of PVC-U transparent plastic, so that any colour change could be observed in the GMO beds. The density of the GMO and the AC were similar, so as can be seen in Table 4 – Properties of the packed bed reactors in the life time system, the different volumes would yield very different heights if they had the same diameter. Unfortunately, the PVC-U pipe could only be acquired in lengths of 5m or more. Therefore, the same diameter was used for all beds. The height to diameter ratio of 4 was considered acceptable for the GMO beds, which rendered a height almost twice the size of the AC bed. For the significantly smaller AC bed, the ratio was only 1.2. The preferred ratio is 2, but no better solution was found. Therefore, as can be seen in Figure 25 – Image of the beds after construction, the beds look quite different.

The AC used in this project is in the shape of extruded particles with a diameter of 3 mm.[52] It is of a kind possessing unique catalytic properties to treat both H\textsubscript{2}S and VOCs. The particular type of GMO used was classified.
DETECTORS

In order to measure the conversion acquired by the system, there must be some means of detection installed at the outlet. After some research and consulting with the project supervisor, it was decided that a Flame Ionization Detector (FID) would be used to detect the acetaldehyde, and an Xam 5000 type sensor provided by Dräger to measure the H₂S.

THE MASS FLOW METERS

Dealing with toxic pollutants of high concentration, the outlet flow rate from the gas containers must be carefully controlled. Not only for health and safety reasons; the inlet pollutant concentration must be known in order to find the conversion upon measuring the outlet pollutant concentration.

There are mass flow meters, and mass flow controllers. A mass flow controller also regulates the flow, whereas a mass flow meter only measures the flow. The combination of a needle valve prior to the mass flow meter fulfills the same function as the mass flow controller, albeit relying on manual control by the operator, and this was the solution used in the project.

The pollutant gases were available at specific concentrations and pressures as shown in Table 7 below.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S + N₂</td>
<td>35 bar</td>
<td>10 vol%</td>
</tr>
<tr>
<td>Acetaldehyde + N₂</td>
<td>85 bar</td>
<td>1 vol%</td>
</tr>
</tbody>
</table>

Since the task of the Mass Flow Meter (MFM) is to measure the amount of gas passing through, it must be able to measure all the predicted flow rate sizes the system will test with acceptable accuracy. It must also be resistant to corrosion by the gases themselves, and be appropriately calibrated by the manufacturer.

Finally, two suitable MFMs were found and tested by the manufacturer to ensure that they would hold up to the gases. The MFMs are shown below. When ordered, no connections, cables or power cables were included. Therefore, the certified electrician was consulted for recommendations on what equipment was required to set up the MFMs.

Figure 26 – Images of the MFMs. A) Shows model 8701 for H₂S and B) shows model 8700 for acetaldehyde.
As can be observed in Figure 26, the MFMs have no displays. Obviously, the flow rate cannot be monitored if it is not made known to the operator. As can also be observed in Figure 26, there is a connection for a 15-pin D-sub plug. Each pin either receives or sends a specific signal, such as the flow rate measured by the MFM. A display was found that could receive and interpret the same type of signal that the MFM sent.

The MFMs also required a power supply. Since the datasheet specified a different voltage than given directly by the outlet, a transformer was acquired. All connections to and from the MFMs were installed in the control box, but unfortunately the transformer supplied the wrong type of power. The MFMs were rendered unusable, and as a result of the time-consuming repair, they would not be returned until after the end of the project. Due to the safety risk of not properly controlling the flowrate of the toxic gases, all experiments initially intended to be part of the project were cancelled.

**SETUP**

Once all units had been acquired and individually tested, the system of course had to be put together. While the planning and the acquisition of all parts were part of the project, the practical work was done by more qualified personnel.
RESULT & DISCUSSION – MODELLING

One way to complete this project would be to simply piece together the units, test a pre-determined set of parameters and report the result. This approach would however only be useful for the particular combination of conditions used for that one test, which would not suit the purpose of the air cleaning test rig.

One of the purposes of doing efficacy tests is to generate a better understanding of the events in the reactor and of the influence the different parameters have on the result. Therefore, a physical model based on reaction kinetics was set up to describe the process, with a few empirical parameters to be determined experimentally.

INTRODUCTION TO MODEL

The model is based on the chemical reactions that have a significant effect on the reaction rate of pollutant, as well as the chemical properties of the different species’ and the distribution of light in the reactor. The model is applicable to both pollutants, but the tabulated constants and the resulting model parameters will be different for different pollutants.

Below, lower case \( \dot{n} \) indicates a molar flow rate in moles per second.

Starting simply, there will be an inflow of the pollutant, reactant A, \( \dot{n}_{A}^{in} \), into the reactor and an outflow of reactant A, \( \dot{n}_{A}^{out} \), both expressed in moles per second. The inflow is known and set, while the outflow can be measured experimentally with a FID or Xam 5000.

The difference between the inflow and the outflow is the number of molecules that have reacted per second in the UV reactor. It shall be referred to as \( r_{A}V \) moles per second.

\[
\dot{n}_{A}^{in} - \dot{n}_{A}^{out} = r_{A}V \\
\text{Equation 7}
\]

The reaction rate in the reactor of volume V is dependent on several parameters, among them are

- The UV fluence rate in the reactor and its distribution
- The inflow of A
- The inflow of ozone
- The distribution of the gas inside the reactor
- The probability of a photoactive species absorbing the UV light
- Efficiency and power of the lamps

It is assumed that the flow distribution can be neglected, and the reactant concentration will be uniform in the reactor, just like a CSTR. As mentioned previously, this assumption is deemed valid since the flow will pass two perforated plates at the reactor entrance, and the multiple lamps in combination with a few other properties of the reactor likely results in a flow distribution similar to a turbulent case, as described in Fluid dynamics.[49]

Simple reasoning will provide a start, and will mathematically distinguish between products and terms:

- When there is zero UV light but still ozone, the reaction rate should \textit{not} be trivial.
- When there is zero ozone but still UV light, the UV light will produce ozone from the oxygen in the air, and the reaction rate should \textit{not} be trivial.
• When there is neither UV light nor ozone, the reaction rate should be trivial.
• When there is zero pollutant (A), the reaction rate should be trivial.

Ozone is a strong oxidising agent itself, but since there is expected to be a large number of extremely reactive hydroxyl radicals, it is assumed that the reaction between radical and pollutant is so much faster than the oxidation by ozone that the oxidation by ozone is negligible. Therefore, ozone will mathematically be present only as a source of starting material for OH-radicals, according to Reaction 3. The OH-radical itself will be formed through Reaction 6 as described above:

\[ O'(1D) + H_2O \rightarrow 2OH \]  

Reaction 6

As discussed in Photolysis vs photooxidation, it shall be assumed that all 254nm-photons produced participate in the formation of the O(1D) radical.

It is also assumed that the photons are not absorbed on their way to the reactants. In reality, there is likely to be some cases of absorption by the media in the reactor, but this is neglected. It should be noted that these effects will be included into the semi empirical constants the experiments yield. Practically, it is insignificant since the pollutant degrades either way and the exact mechanism of how is of more academic interest. However, in the case of the model development this could be important if either the UV fluence rate is very low (few photons present), or the concentrations of oxygen and pollutant are similar (resulting in a competition for the photons available). Since neither is the case, it will not be included in the mathematical model.

The reactions initiated by the radicals in the reactor are likely to be complex (i.e. the formation of different types of hydrocarbon radicals \( R \) in the case of the VOC) and the model will therefore be simplified by assuming that only the hydroxyl radical will react to remove the pollutant. This assumption is validated by the high reactivity of the hydroxyl radical (i.e. no other reactant will have time to react with the pollutant first). Also, literature reports that the oxygen radicals in the system primarily react with other oxygen molecules, and do not react with hydroxyl radicals.\[53\] Expressed as briefly as possible, the reaction this project is interested in would be Reaction 11 below:

\[ A + OH \rightarrow \text{Photooxidation products} \]  

Reaction 11

If the radical turns out to react with other species more than the pollutant, this will be seen by the model since the production of OH will not be equal to a decrease in pollutant. In the case of the possible photolysis of the pollutants, this will contribute to the final conversion but not be distinguishable from the reaction with the hydroxyl radical. This would be a question for a possible future study.

ASSUMPTIONS

Most assumptions made to create the model are confidential.
Considering the reactions involved in producing the main reactant that removes the pollutant as well as the limiting conditions, the model takes the shape of Equation 8 below, where $\alpha$, $\beta$, $k_1$, and $k_2$ are so far unknown constants. While $k_1$ and $k_2$ could physically be interpreted as reaction constants for Reaction 11 and the formation of hydroxyl radicals, the exponents $\alpha$ and $\beta$ are purely empirical constants that will show the degree to which $rAV$ depends on the respective variables. The variables will be known only as X, Y and Z and are unfortunately confidential. In the further development of the model the abbreviation “CF” signifies that the information is confidential.

\[ rAV = k_1 \cdot X^\alpha \cdot (Y^\beta + k_2Z) \]

**Equation 8**

**EQUILIBRIUM OZONE**

Consider $\dot{n}_{O_3}$ to be the ozone production, and $\dot{n}_{O_3}^-$ to be the ozone destruction happening in the reactor volume $V$. In such case, the equilibrium ozone amount per second will be $n_{O_3}^{eq}$.

\[ n_{O_3}^{eq} = \dot{n}_{O_3}^+ - \dot{n}_{O_3}^- \]

**Equation 9**

The ozone decomposition term in Equation 9 is neglected, leaving only $\dot{n}_{O_3}^+$. This consists of two parts, since a certain amount of ozone is injected into the flow. The term $\dot{n}_{O_3}^+$ must consider this initial injected amount of ozone, $\dot{n}_{O_3,0}$ as well as the ozone that is formed in the reactor.

\[ \dot{n}_{O_3}^+ = \dot{n}_{O_3}^{gen} + \dot{n}_{O_3,0} \]

**Equation 10**

The term $\dot{n}_{O_3,0}$ is a known constant, while the generated ozone is produced in the chemical reactions Reaction 1 and Reaction 2, repeated below for clarity.

\[ O_2 + hv(185) \rightarrow 2O(3P) \quad \text{Reaction 1} \]

\[ O(3P) + O_2 \rightarrow O_3 \quad \text{Reaction 2} \]

It is assumed that the oxygen radical, product in Reaction 1 and reactant in Reaction 2, reacts immediately, and therefore 2 ozone molecules are created for each oxygen molecule that absorbs a photon in Reaction 1. The photon flow in moles per second is given as $\dot{n}_{185}$. $N_A$ is Avogadro’s number, $P$ is the power of the lamp reaching the specific spot at hand, $\eta_{185}$ is the lamp efficiency at 185 nm, and $E_{185}$ is the energy of a 185nm-photon.[22]

\[ \dot{n}_{185} = \frac{P \eta_{185} E_{185}}{N_A} \]

**Equation 11**

Then there’s the probability of an oxygen molecule absorbing the photon; a variation of Beer Lambert’s law. As defined by Voronov [22]:

\[ Pr(\text{absorption of photon by oxygen at 185nm}) = 1 - e^{-k_{O_2,185}O_2} \]

**Equation 12 [22]**
Probability will be abbreviated to $Pr$, where $Pr(185)$ signifies the probability of absorption of a photon at 185 nm. $L$ signifies the distance from the light source to the point at hand. $\kappa_{O_2}^{185}$ is the absorption coefficient, given in the unit cm$^{-1}$, in this case for oxygen at 185 nm. $x_{O_2}$ is the molar fraction of the species $O_2$. Together, the equations above form an expression for the equilibrium amount of ozone.

**HYDROXYL RADICAL FORMATION**

The hydroxyl radical is formed through Reaction 6, repeated below for clarity:

$$O\,(1D) + H_2O \rightarrow 2OH^- \quad \text{Reaction 6}$$

For each high energy oxygen radical two hydroxyl radicals are formed.

This can be expressed mathematically through the following equation, where the constant 2 originates in the quantum yield:

$$\dot{n}_{OH}^+ = -2 \cdot \frac{dn_{O_3}}{dt}$$

Equation 13

Only the 1D-oxygen radical ( $O(1D)$ ) can react to produce the hydroxyl radical, as seen in Reaction 6. The hydroxyl radical formation requires this oxygen radical’s higher energy state in order to occur. The only reaction that creates these oxygen radicals is the decomposition of ozone, Reaction 3.

$$O_3 + h\nu(254) \rightarrow O\,(1D) + O_2 \quad \text{Reaction 3}$$

This reaction of course depends on the probability that an ozone molecule absorbs the photon of 254 nm. In the same manner as before, the probability is given by

$$Pr\,(254\,nm) = 1 - e^{-\kappa_{O_3}^{254}x_{O_3}L}$$

Equation 14

Where the probability is dependent on the fraction of ozone present as seen in the exponent. This can be expressed as

$$x_{O_3} = \frac{\dot{n}_{O_3}^e}{\dot{n}_{air}}$$

Equation 15

Stoichiometrically, for each ozone decomposing, two hydroxyl radicals are formed as expressed in Equation 13. We can therefore express the hydroxyl radical formation as twice the ozone decomposition $\dot{n}_{O_3}$, where the quantum yield is 1.
**FINAL MODEL**

The model started at a very conceptual stage, where all probable relevant factors were included and their effect upon the output, reaction rate of A, was given by unknown exponents and constants, expressed in Equation 8.

\[
 r_A V = k_1 \cdot X^\alpha \cdot (Y^\beta + k_2 Z) \quad \text{Equation 8}
\]

After considering the equilibrium ozone, then the quantum yield and the hydroxyl formation, the final version of the model incorporates everything presented above. Unfortunately, due to the model’s confidential nature, it will here only be presented as slightly different versions of the confidential factors in Equation 8.

\[
 r_A V = k_1 \cdot X_{CF}^\alpha \cdot (Y_{CF}^\beta + k_2 Z_{CF}) \quad \text{Equation 16}
\]

Where the unknown constants are \( k_1, k_2, \alpha \) and \( \beta \).

The variables are \( X, Y \) and \( Z \), of which some also depend on the location in the reactor since light is not evenly distributed.

The tabulated constants are the absorption coefficients, the efficiency per wavelength of the lamp, the total power of the lamp, and the energy of a photon at \( \lambda \). Given a certain number of photons, this model will thus give the corresponding reaction rate.

**LIGHT DISTRIBUTION**

Simply put, there is primarily one factor having a major impact on the conversion of \( A \); how many of the pollutant molecules react. Once again considering the case in a highly conceptual manner, this is directly correlated to how many pollutant molecules are encountered by a hydroxyl radical, which due to their immediate reactivity and the assumptions is the same as being directly correlated to how many ozone molecules decompose.

The number of pollutant molecules that react thus depend on the number of ozone molecules that absorb a photon. Obviously, this depends on how many photons are available (lamp power in the reactor) and if the molecule is at a location where it’s likely to get hit by a photon. In short, two factors ought to affect the conversion; flow distribution and UV light distribution.

In order to make the problem more manageable, the fluid dynamics yielding the flow distribution were neglected, and there is assumed to be perfect mixing. With this assumption, the only factor of interest is how much light reaches the different corners of the reactor. This is not a problem solved by hand, but rather by a program such as MATLAB. In order to accurately design the program, the solution process first has to be thoroughly understood.

Consider the reactor cross area. Now, there are multiple circular lamps in the reactor, and this will be exemplified by 3 lamps configured in the shape of an equilateral triangle, see Figure 27a) below. Very intuitively it can be seen that where the lamps’ light overlap, the intensity is stronger, Figure 27b). This provides an indication of the direction this problem is going in.
Figure 27 – Figure A) illustrates a cross section of the reactor as seen orthogonally form the lamps. Figure B) illustrates how the overlapping light from multiple lamps lead to different light fluence rates [W/m²] in different areas of the reactor.

In an article by James R. Bolton [21], the author provides an equation for the fluence rate (FR) of UV light [W/m²] at a certain radial distance x and axial distance H from the midpoint of a cylindrical lamp of length C, based on the PSS model in Figure 4.

\[
FR(x, H) = \frac{\phi}{4\pi L x} \left[ \arctan \left( \frac{0.5L + H}{x} \right) + \arctan \left( \frac{0.5L - H}{x} \right) \right]
\]

Equation 17

It is important to understand the conception of “fluence rate”. While dimensionally similar to irradiation of a 2D area, this would not be sufficient in a 3D case. If one instead considered an infinitesimal sphere of volume dV and surface area dA, then the fluence rate through the sphere is the total fluence rate that passes through the sphere regardless of direction, divided by dA. [21]
Equation 17 is used in a MATLAB program to provide a fluence rate at a certain point given by the distances \( X \) and \( H \) from the lamp midpoint. Note that there is no reflection by the walls of the reactor. It was shown by Montecchio [4] that the fluence rate of the reflected light even under optimal conditions (maximum reflection efficiency, small cylindrical reactor) was negligibly small. Thus, this model shall not concern itself with the reflected UV light.

First, the cross section of the reactor is considered to be overlaid by a mesh such that any point in this 2D representation of the reactor can be defined using cartesian coordinates. Optimally this mesh would be infinitely small, but due to processing limitations the mesh calculates one point for each half millimetre of the real-world reactor. See Figure 29 for illustrative purposes.
Secondly, each lamp position is defined using cartesian coordinates and the program is designed to tell the difference between a point in the reactor volume and a point outside of the reactor, or a point colliding with a lamp.

Thirdly, Equation 17 is applied to consider the fluence rate contribution from each lamp in turn. The fact that some points are shielded by one lamp from being irradiated by some other lamps are taken into account.

For each point provided by the mesh, the combined fluence rate reaching that point from all relevant lamps is calculated. In this way, a topographical map of the light intensity at each point in the reactor is created.

Considering that each lamp midpoint (X=0) is inside a glass tube and also inside a quartz tube, there will be void areas where no UV light can come into contact with a reactant. Since each point in the 3D reactor volume will have a specific fluence rate, this would have to be illustrated in 4D. Due to obvious dimensional limitations, the case is instead considered by looking at cross sections one by one. First, starting at the cross section in the middle of the reactor the fluence rate at each point on this surface is calculated. Then, the model moves half a millimetre towards a wall to consider the cross-section surface at this point. This is illustrated in below (each cross-section surface depicted in orange), with the resulting fluence rate at the middle compared to at the wall are shown in Figure 31. The fluence rate is symmetrical around the midpoint, which is why it does not matter towards which wall the program moves.

The exact value and unit of the axis are not very relevant since the figures are intended only to illustrate the difference in fluence rate, and consequently also reaction rate, between the middle and the edges of the reactor.

Applying the mathematical model on each point results in a reaction rate for that point, which will also be depicted as a topological surface. Summarizing the reaction rate for every part in the reactor will give a complete reaction rate in the reactor, in turn providing us with the predicted conversion.

**Figure 30** - Illustration of the calculation method for the reactor fluence rate. A) shows an example reactor, where the pink cylinders are the lamps and the grey disks are the reactor inner walls. B) shows the midpoint cross section orthogonally to the lamps. The fluence rate is symmetrical around this cross-section plane. C) shows how each cross-section is considered in turn before stepping closer to the wall and considering the next cross section surface. The fluence rate of each surface is calculated.
Figure 31 – The topological graphs shows the fluence rate at different points on the surfaces considered in Figure 30. The lack of units and axes is due to the comparative nature of the image. Compare the high fluence rate at the midpoint (A) with the lower fluence rate at the wall, where the lamps end (B).
In order for the model to be useful, the empirical parameters must be found and tested. They are found using a first set of experiments, and the same constants are then assumed to produce reliable predictions even if some conditions are changed in the subsequent experiments. That is, the model will predict a certain conversion given a set of conditions. The predicted conversion can then be compared to the actual conversion reached under these conditions, which will show if the model is reliable. It could be the case that the empirical parameters calculated are only applicable within certain intervals. For example, lowering the flow rate too much might change the impact that the initial pollutant concentration has on the reaction rate, meaning a new beta would need to be found for flow rates that low. It will however only be observed as the model predicting incorrect results, and the cause would need to be found through more experiments.

To start with, the mathematical approach to finding the empirical parameters will be explained.

Consider the final model:

\[ r_A V = k_1 \cdot X_{CF}^a \cdot Y_{CF}^\beta + k_2 \cdot Z_{CF} \]

And expand the parentheses:

\[ r_A V = k_1 \cdot X_{CF}^a \cdot Y_{CF}^\beta + k_2 \cdot X_{CF}^a \cdot Z_{CF} \]

Set all variables except one, \( Y_{CF} \), to a constant value and vary \( Y_{CF} \) within a pre-determined interval for one and the same lamp configuration. Measuring the outlet concentration of pollutant will result in an array of \( Y_{CF} \) values with corresponding \( r_A V \)-values. Theoretically, they should fit a linear equation as shown below. Imagine the variable \( Y_{CF} = x \), \( r_A V = y \) and the rest as constants.
All the other potential variables are set and summarized with the constants as $K$. The shape of the curve formed by the two arrays will be:

$$y = K_1 x^\beta + K_2$$

Equation 18

If the correct $\beta$ was known, plotting $y$ vs $x^\beta$ would show a linear shape. Thus, plotting the measured or set $x$ and $y$ values for different constants $\beta$ should eventually reveal a linear shape. Once the plot is linear, we know the correct constant $\beta$ is found. This will of course be done mathematically by using linear regression on the different tested $\beta$s.

The parameters included in the constants such as the lamp power $P$, the length to the nearest light source $L$ and the photon flows are dependent on where in the reactor the point under consideration is located. In this case, there is no one point considered, but all of the reactor. Thus, the photon flow and the lamp power is the total lamp power input into the reactor. The length $L$ will be a characteristic length of half the distance between two lamps.

Let’s have a look at the constants.

$$K_1 = k_1 X_{CF}^\alpha$$

Equation 19

$$K_2 = K_1 k_2 Z_{CF}$$

Equation 20

In the equations above only $k_1$, $k_2$ and $\alpha$ are unknown constants, since $X_{CF}$ was set to a constant value during Exp.1. If plotting Equation 19 as $K_1$ vs different values of $X_{CF}$, $\alpha$ could be found in the same manner as $\beta$ above. After finding $\alpha$, $k_1$ is found as the slope of the line formed by plotting $K_1$ vs $X_{CF}$.

For each $K_1$, there is a corresponding $K_2$ and through Equation 20, $k_2$ could then be found.

Thus, the first experiment consists in varying $Y_{CF}$ only, and subsequent experiments are repetitions of the first but for different set values of $X_{CF}$. Since this will yield several opportunities of calculating $\beta$, it will provide some insight into the robustness of $\beta$. The experimental plan itself with parameter values is unfortunately confidential and will not be shown here.
PART I - FINDING EMPIRICAL PARAMETERS

The model shall be both validated and the empirical constants shall be found. Since it is a numerical problem, starting guesses for beta and alpha are derived through intuitive logic, explained below.

BETA

\( \beta \) indicates the relationship between reaction rate of A and \( Y_{CF} \). It is known that an increase in \( Y_{CF} \) should logically yield an increase in the reaction rate of A. Therefore, \( \beta \) is confined to non-negative values. If \( \beta \) were equal to zero, it would have the chemical interpretation that changing \( Y_{CF} \) would have no effect on the reaction rate of the pollutant. Thus, it can safely be said that \( \beta \) is above zero. Much more cannot be said with the same level of confidence due to the complex nature of the radical reactions taking place, which is why a value close to but above zero is a sufficient starting guess for \( \beta \), from which it is slowly increased until the appropriate \( \beta \) is found.

It is assumed that the dependence of \( rAV \) on \( \beta \) remains the same as other parameters in the experiment changes.

ALPHA

In an identical manner, since \( \alpha \) signifies the dependence of the reaction rate of A on \( X_{CF} \) it can be assumed that \( \alpha \) is above zero. Other than being larger than zero, not much can confidently be said about \( \alpha \), and it will thus have the same starting value as \( \beta \).

PART II – EFFECT AND INTERACTION

The interaction between the variables and their effect on the end result will be investigated in Part II of the experiments. To investigate the interaction and in a way the importance of the different parameters, the approach chosen is known as factorial design.

This allows us to choose three parameters, a high level, low level and a centre point for each. Given that the process is known by the company, the chosen levels are assumed to be representative of a high and low setting. There are alternative experiment designs where all three levels are used, but due to time constraints the two-level design is chosen. Three parameters, and two levels each result in \( 2^3 = 8 \) experiments.

The parameters chosen for investigation is the flow rate through the system, the UV power (the lamp power corresponding to a certain pollutant concentration), and the ozone concentration. The humidity was first also a possible parameter to investigate, but the variation of conversion with humidity is already fairly known by the company.

The centre point is chosen in order to control that the default value of each parameter yields a response in between the response to the high and low levels. Three separate centre point experiments will be run, at the start, middle and finish. These three points will be used to find and represent the standard deviation in the measurements. Thus, Part II of the experiments will consist of 11 experiments in total.

There will be no repetition of experiments. Instead, each experiment will be longer than the actual time it takes to measure the response in order for the system to reach a steady output, as opposed to normally reading a number of instantaneous outputs and calculating an error.
The experimental plan cannot be explained further due to its confidential nature.

**PART III – LIFE TIME TESTS**

The original intention was to include the testing of bed life times within the scope of this project. The ozone injection effect on the activated carbon bed, the type of activated carbon and more was discussed for investigation. Similarly in the case of the GMO, the most important parameters affecting the life time were discussed to be the regeneration rate, whether the regeneration efficiency diminished after several cycles of absorption and regeneration and in such case how much pollutant could be absorbed per cycle and how long a cycle was. However, the life time tests had to be removed from the time plan already after two thirds of the project.

**CONCLUSION**

The design criteria of a system and the real-world construction of said system does not always agree, and a lot of work must be spent on the things that are rarely thought of. The things that just are. Most simple questions such as ‘how efficient is the system?’ do not have a simple answer, and when attempting to answer them yield exponentially more questions that all have to be considered for the answer to carry any merit.

The air cleaning test rig was built as modularly as possible to allow for changes and updates in experimental design as well as in the selection and number of units used. The possible hypotheses that can be tested on the system are numerous, both from a business perspective and from an academic one.

In conclusion, design, construction and modelling of the air cleaning rig has been a highly iterative process relying heavily on the cooperation between all persons involved more than one individual. The future testing of the rig is thus handed over to the next ambitious thesis project worker.

**ACKNOWLEDGEMENTS**

This project would not have been possible without the support of supervisor Francesco Montecchio. Neither would it have yielded any useful results without the good advice from Ozonetech’s process engineer Axel Forsgren and all the practical help from production engineers Andy and Amir. Thank you all!


[52] Norit Nederland BV. Norit RST 3 [Online].
APPENDIX A

Confidential.

APPENDIX B

The below picture will give an overview of how the programs are interconnected. Each name ending with two parentheses is a program.

The programs themselves are confidential.