Process Optimization of UV-Based Advanced Oxidation Processes in VOC Removal Applications

Francesco Montecchio

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KTH Royal Institute of Technology
School of Engineering Sciences in Chemistry, Biotechnology and Health
Department of Chemical Engineering
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FRANCESCO MONTECCHIO

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Fakultetsopponent: Professor Ernest R. Blatchley III, Purdue University, West Lafayette, IN, United States
To Alba,

You are my muse and source of joy

For Amanda,

I hope it may inspire you
Abstract

Air pollution is a major concern in developed countries due to its hazardous health effects. Recent studies by the WHO (World Health Organization) estimate that urban air pollution causes a number of diseases of the respiratory tract and is associated with 150,000 deaths each year. Volatile organic compounds (VOCs) are among the major pollutants affecting the outdoor air quality. Given that industrial processes are the main source of atmospheric VOC emissions, national and international authorities have issued regulations to limit such emissions. However, traditional removal technologies such as incineration, have low energy efficiency and high investment costs. AOPs (advanced oxidation processes) offer a promising alternative in which very reactive conditions can be achieved at room temperature, thus greatly increasing energy efficiency. However, this is still not a mature technology due to challenges that limit the range of applications.

This thesis focuses on two types of UV-based AOP: photocatalysis and UV-ozone. The goal is to improve VOC conversion and achieve a process that is competitive with traditional technologies. The research on photocatalysis presents an innovative UV reactor design that is closer to industrial conditions and has the ability to effectively screen different samples. Effort was put into finding a metallic support for the photocatalyst without using additional adhesives. Several electrochemical treatments were performed on metals to restructure the surface. One treatment proved to be superior when it came to stabilizing the TiO$_2$ coating, especially when compared with the traditional ceramic support.

Research on UV-ozone AOPs focused on reactor modelling, developing a numerical and a fluid dynamics model. The goal was to gain a deep understanding of the governing phenomena of UV-ozone reactors so as to optimize the reactor configuration. The numerical model created described
the UV irradiation and the reaction kinetics accurately, while a computational fluid dynamics (CFD) simulator modelled the fluid a larger scale, simulating two prototypes. The work resulted in general guidelines for the design of UV-ozone UV reactors as well as for full-scale units.

**Keywords:** AOP, UV, photocatalysis, ozone, air pollution, VOC abatement, reactor design, reactor modelling, photocatalyst support, electrochemical treatment, electrochemical etching, irradiation modelling, kinetics modelling, fluid dynamics simulation, prototype, full-scale, CFD simulation
Sammanfattning

Luftföroreningar är idag ett stort problem, särskilt i industriländerna, med allvarliga påföljder på befolkningen. I WHO:s (Världshälsoorganisationen) senaste undersökning beräknas att luftföroreningar i städerna orsakar 150000 dödsfall per år, vilket är en effekt av ett flertal sjukdomar i människans andningsorgan. VOC (lättflyktiga organiska ämnen) är bland andra en av de viktigaste typerna av luftföroreningar, som avsevärt påverkar uteluftens kvalitet negativt. Huvudkällan för VOC-utsläpp till atmosfären är industriella processer och därför har internationella och nationella myndigheter infört åtgärder särskilt riktade mot industriella utsläpp av VOC. Traditionell teknik för att rena denna typ av utsläpp är förenade med betydande begränsningar, som exempelvis låg energieffektivitet och höga investeringskostnader. Ett lovande alternativ är teknik, baserad på AOP (avancerade oxidationsprocesser), som möjliggör mycket reaktiva förhållanden vid rumstemperatur, vilket kraftigt ökar energieffektiviteten. Processer baserade på AOP-teknik är dock inte ännu en mogen teknik, vilket beror på ett flertal utmaningar, som begränsar användningsområdet.

Denna avhandling fokuserar i huvudsak på två typer av AOP med UV-ljus som bas, fotokatalys och UV-ozon, i syfte att förbättra VOC-omvandlingen och på så sätt uppnå en komplett process, som är konkurrenskraftig, jämfört med traditionell teknik. Inom fotokatalys utfördes forskning med en innovativ UV-reaktordesign, som slutresultat. Reaktorn möjliggör tester vid förhållanden som ligger närmare industriella tillämpningar och kan även användas i metoder för att effektivt salla olika katalysatorprover. En annaniktig del av arbetet berörde fotokatalysatorers bärarmaterial, där ytbehandling av metalliska material undersöktes som ett alternativ till bindemedel för ytor. Flera elektrokemiska ytbehandlingsmetoder undersöktes rörande deras effekter omstrukturering av metallytan. Ett fall
visade sig vara överlägset vid stabilisering av en beläggning av TiO$_2$-
katalytor i jämförelse med ett traditionellt keramiskt bärarmaterial.
Forskningen inom AOP med UV-ozon fokuserade utveckling av en
numerisk och en fluiddynamikmodell för reaktormodellering. Arbetet
syftade till att öka förståelsen av de processer som styr optimeringen av
den geometriska designen UV-ozonreaktorer. Den numeriska modellen
ger en beskrivning av UV-bestrålningen och reaktionskinetiken, medan en
CFD-simulator modellerar strömningsdynamiken i reaktorn. En
kombination av de två modellerna implementerades i större skala och
användes för simulering av två reaktor prototyper. Arbetet resulterade i
allmänna riktlinjer för utformningen av UV-ozonreaktorer för små till
fullskaliga AOP enheter.

**Nyckelord:** AOP, UV, fotokatalys, ozon, luftförreningar, VOC-
reduktion, reaktorteknik, reaktormodellering, bärare för fotokatalysator,
elektrokemisk ytbehandling, elektrokemisk etsning, bestrålningsmodellering, kinetikmodellering, simulering av fluiddynamik,
prototyp, fullskalig CFD-simulering
List of Publications

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Paper I

Montecchio F., Persson H., Engvall K., Delin J., Lanza R.
Development of a stagnation-point flow system to screen and test TiO$_2$-based photocatalysts in air purification applications
Chemical Engineering Journal 306 (2016) 734–744

Paper II

Montecchio F., Chinungi D., Lanza R., Engvall K.
Surface treatments of metal supports for photocatalysis applications

Paper III

Montecchio F., Bäbler M. U., Engvall K.
Development of an irradiation and kinetic model for UV processes in volatile organic compounds abatement applications
Chemical Engineering Journal 348 (2018) 569–582

Paper IV

Montecchio F., Altimira M., Andersson A., Engvall K.,
Fluid dynamics model development for scaling up UV reactors in VOC abatement applications
Submitted to Chemical Engineering Journal (2018)
Contribution to the appended papers

Paper I
I am the main author of the paper, responsible for writing the text. I was also responsible for the system design and setup and for modelling the reactor. Most of the photocatalyst synthesis, characterization, and tests were carried out by H. Persson under my supervision. I performed the surface characterization using a SEM microscope.

Paper II
I am the main author of the paper, responsible for writing the text. I planned and supervised the experimental tests, carried out by D. Chinungi. I was responsible for analyzing the particle size distribution and surface morphology with a SEM microscope. The surface analysis with the confocal microscope was performed at Swerea KIMAB.

Paper III
I am the main author of the paper, responsible for writing the text. I was also responsible for the design and setup of the experimental part, carrying out all the experiments. I developed the numerical model using a numerical computing environment, with insights and contributions from Associate Professor M. U. Bäbler.

Paper IV
I am the main author of the paper, responsible for writing the text. I was also responsible for the design and setup of the experimental part, carrying out all the experiments. Researcher M. Altimira contributed significantly to the development of the CFD cases. I performed the model verification
and the CFD simulations for the laboratory reactors. A. Andersson performed the CFD simulations for the prototype reactors under my supervision.
Related Contributions

Conference proceedings

Montecchio F., Delin J., Mills J., Engvall K., Lanza R., Effect of different UV lamp configurations and reactor geometries in a bench scale UV and ozone system for VOC abatement in air streams
Proceedings of the conference: IOA 22nd World Congress and Exhibition

Oral presentations

Montecchio F., Persson H., Trento D., Engvall K., Delin J., Lanza R.
Synthesis, characterization and screening of TiO$_2$-based photocatalysts in an innovative stagnation-point reactor for VOCs removal applications
9th International Conference on Environmental Catalysis
Newcastle, Australia, July 10–14 2016

Montecchio F., Persson H., Trento D., Engvall K., Delin J., Lanza R.
An innovative stagnation-point reactor for screening of TiO$_2$-based photocatalysts used for VOCs removal applications
17th Nordic Symposium on Catalysis 2016
Lund, Sweden, June 14–16 2016

UV / ozone oxidation of air emissions from wastewater treatment plants
2016 IUVA World Congress & Exhibition
Vancouver, Canada, January 31–February 03 2016

Montecchio F., Delin J., Mills J., Engvall K., Lanza R.
Effect of different UV lamp configurations and reactor geometries in a bench scale UV and ozone system for VOC abatement in air streams
Poster presentations

Montecchio F., Bäbler M. U., Altimira M., Engvall K.
Fluid dynamics and reaction modelling of UV reactors for odor and VOCs abatement applications
5th European Conference on Environmental Applications of Advanced Oxidation Processes
Prague, Czech Republic
June 25–29, 2017

Montecchio F., Lanza R., Engvall K.
Advanced oxidation processes for air purification
KTH Energy Dialogue
Stockholm, Sweden, November 24 2016

Montecchio F., Persson H., Delin J., Mills J., Canu P., Engvall K., Lanza R.
Photocatalytic abatement of VOCs: System design and catalysts screening
24th North American Meeting (NAM) of the Catalysis Society
Pittsburgh, Pennsylvania, USA , June 14–19 2015

Montecchio F., Delin J., Kaijser P., Mills J., van Rij C., Engvall K., Lanza R.
Photodegradation of VOCs in air streams derived from frying processes
Resultatdag – Mistra Innovation 2014
Lerum, Sweden, May 22 2014
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PART A: INTRODUCTION
1 Setting the scene

Urban air pollution is one of the most important environmental hazards faced by developed countries in recent decades. Despite numerous regulations aimed at improving air quality, it still poses a major threat. The WHO (World Health Organization) estimates that urban air pollution is the environmental risk with the highest impact on the population of developed countries, causing 150,000 deaths per year [1-3]. Several chemical species are responsible for air pollution [4, 5], including nitrogen oxides, particulate matter, ozone and VOCs (volatile organic compounds). This work focuses on VOCs as they represent an important category of pollutants. The term VOC refers to a broad range of compounds [6, 7], including all organic compounds with a high vapor pressure at room temperature. EU Directive 2004/42/CE provides a precise definition of the term VOC as “any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa” [8]. VOCs such as formaldehyde [9, 10] or benzene [11, 12] may be toxic even at very low concentrations. If inhaled, these compounds have acute and chronic effects on human health. Acute effects include eye irritation, coughs, and dizziness, while chronic effects are related to cancers and misfunctions of the bone marrow. Besides the toxicity due to direct exposure, VOCs contribute to the formation of ozone at ground level when emitted in combination with NOx in the presence of sunlight [13-15]. When inhaled, ozone has severe effects on the human body, worse than those of most VOCs. Measurements show that more than 95% of the EU-28 population has been breathing ozone concentrations that are too high for at least the last 13 years [16]. Therefore,
there is an urgent need for technologies to reduce VOC emissions, which
will also reduce the formation of ground-levels ozone.
This thesis focuses on the significant fraction of the total VOC emissions
that originate from industrial processes [4]. Several types of industries
(e.g. paint [17] and food processing [18]) use organic compounds such as
solvents, which often result in VOC issues. Technologies such as catalytic
oxidizers and RTO (regenerative thermal oxidizers) [19] have been
implemented to abate VOC emissions from industrial plants. However,
despite achieving very high VOC removal, close to complete abatement,
these technologies have important limitations. The main limitation is low
energy efficiency, for the process air needs to be heated to several hundred
degrees for oxidation to take place [20]. Furthermore, oxidizers often need
a continuous feed of fuel to maintain the necessary high temperatures. This
fuel is still frequently fossil-based, resulting in the emission of fossil CO₂.
Even if this species is not toxic, fossil CO₂ contributes significantly to the
greenhouse effect.
Other types of technologies such as biofiltration and adsorption have
recently been developed to replace traditional oxidizers [19]. Of these,
AOPs (advanced oxidation processes) show great potential to abate VOC
[21-23]. An AOP is defined as any process capable of producing hydroxyl
radicals with high energy efficiency, often at low temperatures [24]. These
radicals are very reactive species, also present in RTO, that attack and
oxidize VOCs. In many AOPs UV light is used to excite either a
photocatalyst [25-29] or other chemical species such as ozone [30, 31]. The
consequent excitation produces the hydroxyl radicals needed to oxidize the
VOCs.
Despite promising results, UV-based AOP is still not a mature and robust
technology with a broad range of applications. It currently has two major
limitations: lower performance compared to traditional technologies [19]
and the difficulty of scaling up laboratory results in a consistent way. The
latter limitation is due to the wide range of conditions found in the real world [18, 32], leading to difficulties in engineering a tailor-made solution for each full-scale case. In conclusion, the performance of AOP needs to be improved so that it can become a mature technology capable of replacing traditional technologies based on RTO.

The work in this thesis deeply considers the Sustainable Development Goals set by the United Nations (UN). The research is aimed at facing three specific Goals: number 7, 11 and 13 dealing with Energy, Cities and Climate Change respectively. The Goal 7 promotes the development and share of reliable and sustainable energy across the planet. This work focuses on enhancing the share of green energy. Traditional technologies, such as RTO, often operate using fossil fuel, while AOP depends only on electrical energy which can be produced from renewable sources. The Goal number 11, about Cities, strengthens the importance of developing modern cities where people thrive with safety and no pollution. This thesis contributes to improve the air quality by reducing an important air pollutant, the VOCs. As industrial processes are the highest emission source, the work of this thesis becomes particularly relevant, also considering the continuous increase of the size of several cities, approaching the emission sites. Finally, the UN Goal 13 about Climate Change sets targets to minimize the climate change, with attention to the CO₂ emissions and global warming. By replacing RTO with green electricity, the results of this Thesis significantly contribute to reduce the greenhouse gas emissions, resulting in a reduction of the detrimental effects of the global warming.

1.1 Scope of the thesis

The goal of this thesis is to enhance the performance and robustness of UV-based AOPs, enabling them to overcome the limitations presented in section 1. Even though AOPs are a very efficient technology, the VOC
conversion rate needs to be increased to reach values close to complete abatement if AOPs are to replace traditional technologies. Therefore, all activities were aimed at increasing VOC removal without significantly affecting the power input to the system, thus increasing process efficiency. Throughout the research work, an applied approach has been considered, both during the design of the experiments and the reactor modelling, with final full-scale application in mind.

The thesis investigates both photocatalysis and reactor modelling. As regards the former, it seeks to develop an innovative setup for testing and screening photocatalysts. One of the main features of this setup is the relatively high airflow rate and low UV power applied on the photocatalyst. This represents a significant modification of current setups found in the literature [30, 33-35], making the developed version more relevant to industrial cases. Additional features of the test setup are optimized irradiation of the photocatalyst and controlled fluid dynamics, which is useful for developing a model of the results to describe the reaction kinetics.

Assessing the performance of various photocatalysts for reducing VOCs confirmed the great potential of this technology. Therefore, the possibilities of implementing a photocatalyst in large full-scale applications were evaluated. Issues arising during the scale-up process were analyzed. Due to the high flow rates at full-scale, the photocatalyst needs to be firmly bonded to the support, minimizing the abrasion while still maximizing the light exposure. Therefore, several electrochemical treatments were applied to the surface of metals used as photocatalyst support, to firmly immobilize the coating without using glues or adhesives. The first part of the thesis concludes with the identification of photocatalysts and coating methods suitable for full-scale applications in the industrial cases considered.
In the second part of the thesis, both laboratory- and prototype-scale reactors were modelled to study the scale-up process of UV-based AOP. The model is meant to be a tool for designing and optimizing the configuration of UV reactors for various scales and applications. First, a numerical model was developed to analyze the UV radiation and the consequent photochemical reactions. In the reaction mechanism, the reactions of ozone generation and depletion are described using a detailed approach to calculate the production of hydroxyl radicals. The reaction of VOC oxidation was modelled based on the radicals available.

The last part of this thesis combines the numerical reactor model with a fluid dynamics description using a CFD simulator. The tool significantly contributes to the scale-up process of UV reactors, since several configurations, both laboratory-scale and full-scale, may be simulated and screened before experimental evaluation. The features of several reactors configurations were analyzed, identifying the strengths and weaknesses of each configuration.

1.2 Thesis outline

This thesis is based on the four appended papers and this document. The results are summarized and presented in a broader perspective, highlighting the contribution to UV-based AOPs. The introduction continues in chapter 2 where the environmental hazards of air pollution due to VOC are presented. Chapter 3 presents an overview of the AOP, focusing on photocatalysis and UV-ozone processes. The materials and methods used for the present work are summarized in chapters 4–6. The results and discussion sections are divided into two topics. Chapters 7 and 8 focus on photocatalysis, presenting the insights concerning reactor development and material coating. Chapters 9–11 describe the reactor modelling, with remarks about the scaling up of UV-ozone reactors. Chapters 12 and 13 provide the conclusions and outlook.
2 Air pollution from VOCs

2.1 Hazards of VOC emission

As stated in Section 1, VOC emissions represent an important environmental hazard, significantly contributing to urban air pollution. Despite mitigation technologies implemented recently, the number of deaths associated with urban air pollution increased by 8% from 1990 to 2010 [5]. Based on the WHO analysis presented in 2002 [1], air pollution caused the death of 150,000 people in developed countries. The effect of air pollution is particularly remarkable in the countries of East Asia and the Pacific, with the death of approximately 400,000 people in the years 2000 [2] and 2001 [3].

The term VOCs refers to a broad range of organic compounds with high volatility as defined in Directive 2004/42/CE [8]. These pollutants are composed of organic chemicals such as aromatics, hydrocarbons, aldehydes and ketones. Aromatic compounds are particularly hazardous in terms of human health. For instance, benzene, widely used as a solvent in the past, has been studied for several years [11, 12] and has been shown to have a direct correlation to acute forms of leukemia and genetic damage such as chromosomal aberration [11, 36]. According to the WHO, the effects on the human body are so strong that no guidelines were issued for benzene exposure, given that it should be minimized as much as possible. Aldehydes are another type of compound with hazardous effects on human health, with formaldehyde as a typical example. Since 1905, the inhalation of this compound has been associated with bronchitis and pneumonia [9]. Recent studies have confirmed the acute effects of formaldehyde on eyes and the respiratory tract [10]. The same compound is also linked to chronic effects such as cancers due to the formation of protein cross-links and the promotion of cell proliferation [37]. Lastly, formaldehyde is also a severe
neurotoxin since it quickly diffuses in the body tissues and enhances the presence of ROS (reactive oxygen species) which damage brain cells [38]. Besides the toxicity issue, the emission of VOCs causes another severe environmental hazard: the generation of ozone at ground level. The organic compounds react with nitrogen oxides in the presence of sunlight, creating a complex cyclic mechanism leading to ozone formation [13-15].

![Graph showing calculated peak O₃ concentrations generated from various initial concentrations of NOₓ and a specified VOC mixture using the US EPA empirical kinetic modelling approach.](image)

**Fig. 1.** Example of an isopleth diagram illustrating calculated peak O₃ concentrations generated from various initial concentrations of NOₓ and a specified VOC mixture using the US EPA empirical kinetic modelling approach. Reprinted from [15] with permission from Elsevier.

As shown in Fig. 1, ozone can be generated even from very low concentrations of NOₓ and VOC, reaching hazardous levels [39] while NOₓ and VOC values are still in the ppb range. Ozone is a strong oxidant with very harmful effects on health [40], directly attacking proteins and lipids or activating intracellular oxidation mechanisms [41]. The effects on the population are so hazardous that ozone concentration limits are often lower than those for most VOCs [4, 39]. In order to reduce the hazardous
effects of air pollution, the WHO and the European Environment Agency (EEA) have set limits and guidelines (Air Quality Guidelines, AQG) for the concentration of the main pollutants, continuously monitoring the overall air quality in the whole EU area. As expected, ozone is one of the most important pollutants analyzed. The limits are set at 100 and 120 µg/m³ by the WHO AQG and EU reference values, respectively. Using these limits, the European Union has been monitoring the situation in the EU area year over year, modelling pollutant dispersion and human exposure. It has been found that a high percentage of the population are exposed to ozone values exceeding the recommended limits [4]. Based on the WHO AQG, more than 95 % of the population in the EU-27 area has been exposed to ozone concentration above the limits since the year 2002, without exposure showing any signs of decreasing [16]. Since the guidelines of the WHO are more stringent than the targets of the EU, the percentage of population exposed to higher than acceptable pollution levels is higher when the WHO guidelines are considered. The percentage of the EU population exposed to hazardous ozone concentration decreases to 12.5 % using the EU reference values [4]. The present situation in Europe was mapped by the EEA, which identifies the most problematic areas. The map is reprinted in Fig. 2.
As shown in Fig. 2, northern Italy is the most problematic area as the concentration exceeds the recommendation in every city [4]. The ozone problem tends to decrease as one moves away from this central area. The surrounding countries are the second most problematic, especially Austria and Croatia, while the ozone concentration is not problematic in the northern parts of Germany, UK or Scandinavia.

Apart from the toxicity and the formation of ozone, VOCs are correlated with another environmental issue: odorous emissions in the atmosphere. Organic compounds often have a very low odor threshold, even in the ppb
range [42-44]. Even if this issue does not pose an immediate threat to human health, the population has become more aware of the problem over the years, leading to a growing number of odor complaints to local authorities [45].

2.2 Emission sources

VOCs are emitted by a broad range of sources that can be grouped in sectors according to the EEA. The distribution is presented in Fig. 3 [4].

![VOC emission sources](image)

**Fig. 3.** Main VOC emission sectors in 2015 for the EU-28 area. Reproduced from [4].

The figure shows that the sector “industrial processes and product use” is dominant, with half of the total emissions. There are two main categories in this sector: the first one is stationary industries emitting VOC from their internal processes. To purify the indoor air, the volatiles are collected in the ventilation system and released in the outer atmosphere [18]. A treatment step of the ventilation exhaust may be performed if the VOCs
concentration exceed limits legislated by the local authorities. The second
category involves the use of certain goods that emit VOCs during use. A
typical example is painting, for the paint pigments are dissolved in solvents
that evaporate during the painting process and drying [17].
Significant VOC emissions are released by the transportation sector,
consisting of road and non-road transportation categories. The former
releases a higher portion of pollutants, due to the high number of private
cars and trucks in all parts of the continent. On the other hand, the low
number of non-road transportation vehicles limits the emission for that
category. Emissions from the transportation sector have been taken
seriously and regulated in the past, leading to significant reductions over
the years [4].
Sixteen percent of the total VOCs are emitted by commercial and
institutional organizations and by household equipment. Compared to
other sectors, it is difficult to clearly define the original source of the
emissions since this sector involves the everyday life of a large portion of
the population.
Out of all these different emission sources, this thesis focuses on the
industrial processes since these are an important part of the sector emitting
the highest amount of VOCs. They are also easier to categorize than others,
since various reference cases can be identified and characterized to clearly
understand the composition and concentration of emissions [17, 32].
Industrial processes are responsible for the emissions of a broad range of
types of VOC. One of the most important types is aldehydes, especially
formaldehyde and acetaldehyde. These chemicals are emitted during the
processing and production of food [18], wood resins, paints and adhesives
[46].
2.3 Legislation on VOC emissions

Due to the hazardous health effects of air pollution from VOCs, several organizations have issued legislation to reduce emissions and atmospheric concentrations. Before analyzing current legislation, it is important to note the difference between guidelines and legislation. Guidelines set concentration limits to minimize consequences for the population and environment. They may be issued by non-governmental organizations such as the WHO and they do not represent a strict rule for any single country or activity. Legislation normally seeks a compromise between the hazardous effects of pollutants and the current situation, trying to minimize emissions without significantly affecting the economic situation of countries and activities. Legislation is normally issued by local or national authorities and must be strictly respected by all parties involved at all levels.

On the basis of the WHO and EEA guidelines and targets, the European Parliament issued several environmental directives aimed at reducing the air pollution. One of the first steps was the adoption of the Gothenburg Protocol in 1999, aimed at abating acidification, eutrophication and ground-level ozone. To reduce these hazards, the United Nations Economic Commission for Europe (UNECE) targeted the emissions of SO_2, nitrogen oxides, VOC and NH_3 since they are directly connected to environmental effects. All the adopting parties were committed to significantly reduce the VOC emissions, with a reduction of 57% from year 1990 to 2010 in whole Europe. Annex VI of the protocol sets specific limits on VOC emissions from stationary sources. These limits are divided into sectors, with specific threshold values defined for each sector. Once the EU member states had signed the Gothenburg Protocol, the European Parliament quickly took action, issuing Directive 2001/81/EC [47]. This directive confirmed the aims and the national emission ceilings signed
within the UNECE and introduced important indicators such as AOT 40. According to the directive, AOT 40 is defined as: “the sum of the difference between hourly concentrations of ground-level ozone greater than 80 µg/m³ (= 40 ppb) and 80 µg/m³ during daylight hours accumulated from May to July each year” [47]. These indicators are still used today and accurately represent the targeted environmental issues. The 2001 directive was followed by Directive 2008/50/EC [48], which compelled national authorities to designate specific bodies for air pollution measurements that were standardized by specifying methods and sampling points.

The European Parliament has continued to work year after year to ensure that the environmental targets are respected. Directive 2016/2284 [49] set another milestone for reducing air emissions. This document starts by summarizing the results of previous legislation, taking into account the targets set in the Gothenburg Protocol. In terms of VOCs, the results were positive, since emissions were reduced by 56 % between 1990 and 2010, in line with the targets of the protocol. The directive emphasizes the importance of further action to further reduce risks and impacts on human health and environment. Therefore, new reduction goals were set for 2020 and 2030, compared to 2005. According to the directive, VOC emissions in the EU28 area will be reduced by a further 28 % and 40 % by 2020 and 2030 respectively [49].

Besides the directives regarding overall VOC reduction, specific actions were taken to limit emissions from certain industries. One example is Directive 2010/75/EU regulating combustion plants, incineration plants, production of titanium dioxide, and the use of organic solvents. The industrial sector is relevant to this study, due to its high contribution to emissions (Fig. 3). The directive sets several limits for emission concentrations in waste gases, according to the type and size of the industry using solvents. Most of these limits vary between 20 and 100 mg C/Nm³ [50].
3 AOP for VOC removal

Several technologies have been developed to reduce VOC emissions [19]. As stated in section 1, AOPs have great potential to improve energy efficiency but still have some limitations as regards robust and widespread industrial application. In this thesis, two AOP technologies used in industry are considered: photocatalysis and UV-ozone. Both of these technologies may be incorporated in a single process for treating VOCs in industrial emissions.

3.1 Description of layout of AOPs

A typical treatment process is composed of several steps, each targeting a specific type of pollutant. Fig. 4 shows a typical flow diagram of a complete AOP for VOC removal.

The sources of VOC emissions in this diagram are industrial plants such as paint and food processing industries, which have a significant impact on total VOC emissions (see 2.2). These emissions often contain solid or liquid particles, so the first step in the treatment process is to separate these particles. Bag filtration is a traditional technology used for this purpose, since fine particles can be effectively removed with tailor-made solutions. However, excessive pressure drops may limit bag filter applications because they decrease overall process efficiency. Therefore, separation by
centrifugation is a viable alternative, especially for liquid droplets, as it minimizes the pressure drops. The aim of the particle filtration stage is to separate out all particles larger than approximately 1 µm. These particles would reduce the lifetime of the downstream stages, which are highly sensitive to particles.

After the first stage, the process air may be ozonated by an external ozone generator. Ozone is necessary for the production in air phase of hydroxyl radicals—essential in an AOP [51]—but an external ozone generator is not the only method of generating ozone. Therefore, the implementation of this step is based on process and economic considerations.

The core step for treating VOCs is the UV reactor. The hydroxyl radicals for oxidizing the air pollutants are generated in this stage. Three main options for radical generation are presented in this thesis. In the first option, ozone previously added by the generator is decomposed by the UV light, reacting with humidity in the air to form hydroxyl radicals. The second option is similar, with the radicals formed by ozone decomposition. However, in this case ozone is generated by the light from UV lamps (see 3.4.1 for details on reaction kinetics). Both these options generate radicals in the homogenous air phase, and thus the whole reactor volume is active in oxidizing the VOC.

The third option involves the use of a photocatalyst, which will be presented in 3.3. The catalytic material coats the inner parts of the UV reactor, so that hydroxyl radicals are generated on the surface. Therefore, the reaction of VOC removal is heterogeneous, occurring only on the surface of the photocatalyst.

There are several considerations to be taken into account when a photocatalyst is implemented in a reactor. The first is that the ratio between the power of the UV lamps and the airflow rate should be representative of industrial conditions. If a relatively high power is chosen, the results of the experimental tests may not be relevant to full-scale applications. However, most of the work reported in the literature uses a
relatively high power [30, 33-35], mainly to investigate features of the photocatalyst regardless of the light irradiation. In addition, the fluid dynamics of the airflow inside the reactor needs to be evaluated and controlled, so that eventual mass transfer limitations may be identified. Despite the efficiency of the UV reactor for removing VOCs, complete conversion is often not reached in this stage. Therefore, an optional polishing step may be added to maximize the removal. Activated carbons are often used due to their affinity to VOCs. The remaining pollutants are adsorbed on the carbon surface with potentially no organic compound leakage. However, this stage is not catalytic and so the carbon bed is consumed over time, due to the saturation of its active sites by adsorbed VOCs. Therefore, the material bed needs to be regularly replaced, resulting in higher operational costs for the whole process. Out of all the stages for treating the process air emitted by industrial emissions, this thesis focuses only on the UV reactor stage, investigating potential improvements for photocatalytic and UV-ozone reactors.

3.2 Scale-up process for UV reactors in AOPs

This research covers part of a scale-up process for UV reactors used for AOP applications. Traditionally, scaling up a reactor begins by investigating fundamental properties at the laboratory scale. The current research focuses on the two main processes for generating hydroxyl radicals: photocatalysis and UV-ozone. Both may be studied in a laboratory, as prototypes, and full-scale. Laboratory scale studies focus on fundamental properties, highlighting relevant features while operating in conditions far different to those in an industrial application. Studies of prototypes combine features relevant to a full-scale system in a more controllable environment due to the smaller scale. The prototype investigation serves to validate the laboratory indications while moving toward the final application. Lastly, the full-scale investigation is
representative of industrial applications and provides the ultimate verification of the results from the experimental research, considering the goal set in the early stage. Fig. 5 shows a flow diagram with the main activities potentially involved in scaling up a UV reactor.

![Flow diagram](image)

**Fig. 5.** Block flow diagram of the activities involved in the scale-up of UV reactors for AOP applications. The blocks / arrows are color-coded: green if covered in the scope of this thesis, blue if not covered, yellow for the feedback loops, and orange for the final activities.

The first activities in the photocatalysis system begin in the laboratory. The synthesis method, together with the eventual presence of dopants, is important for photocatalytic activity. Since these aspects have been widely covered in the literature [52-55], the current study does not focus on them. Instead it uses previous results and adapts them to the current case. The adhesion of the photocatalyst to the support is also fundamental to proper reactor scale-up, since it may be an important issue at full-scale, where the air velocity exceeds 10 m/s inside the reactor. This thesis presents the use
of electrochemical treatments on the support surface so that the material is functionally restructured to enhance binding with the photocatalyst. Since this possibility has not been covered in the literature, major experimental effort was dedicated to this activity. However, prototype and full-scale investigation of a photocatalytic reactor are not included in the thesis. Both would involve design stages combined with experimental tests to validate the design. Furthermore, the full-scale investigation would also include a modelling step (full-scale modelling in Fig. 5) to develop methods for implementing the photocatalyst in full-scale reactors under many conditions. The modelling also needs to provide guidelines for quick adaptation from one case to another.

Scaling up an UV-ozone reactor involves modelling very early in the process, while still working at the laboratory scale. For an accurate reactor description, the developed model needs to combine the reaction mechanism already established in the literature with the UV irradiation and fluid dynamics. Since not all the phenomena can be modelled a priori, experimental tests are necessary to provide relevant values and to address the radical chemistry of the VOC conversion. When the model is completed, it can be used at the prototype level to design optimized reactors on larger scales.

An important difference between a laboratory model and a prototype is that the flow regime is laminar/transitional at the laboratory scale, while the prototype presents a fully developed turbulent regime. Experimental tests are necessary to validate the model results at the larger scale. In addition, a full-scale UV-ozone reactor may integrate a photocatalytic stage, resulting in enhanced performance. The current thesis includes the scale-up steps up to the experimental test of the prototypes developed based on the model. The scale-up process of both the photocatalytic and the UV-ozone reactor ends with experimental tests at full-scale to confirm the expected results from engineering or modelling steps.
The following sub-sections of section 3 focus first on photocatalysis, especially synthesis and doping methods, which are well described in the literature. Thereafter the UV-ozone reactor modelling is presented, focusing mainly on three fundamental aspects of the modelling: the reaction mechanism, UV irradiation, and fluid dynamics.

### 3.3 Photocatalysis

Photocatalysis is an AOP technology based on a catalytic material called a photocatalyst. This material has some similarities to traditional catalysts, but also has significant differences. As with traditional catalysts, a photocatalyst lowers the activation energy of specific reactions (VOC oxidation in the present case); however, it needs the presence of a light source to be activated. The light source is usually in the UV range, since the energy needed is relatively high [29]. When a light photon reaches the surface of the photocatalyst, it creates a charge separation producing a free electron ($e^{-}$) and a hole ($h^{+}$) [26]. These two species react with oxygen, humidity, and directly with a VOC, initiating or propagating oxidation reactions. The reaction ultimately leads to the formation of CO$_2$ and water vapor (Fig. 6) [26, 28, 29].

![Figure 6](image-url)

**Fig. 6.** Processes on bare TiO$_2$ particles after UV light excitation.
Reprinted from [26] with permission from Elsevier.
In this reaction mechanism, the hydroxyl radicals are generated when water vapor reacts with the free hole. As presented in section 1, this species is very reactive, enhancing the rate of the oxidation reaction. The most common photocatalyst is TiO$_2$ due to its low cost, inertness, non-toxicity, and efficiency in oxidation reactions [56].

Some features of a photocatalyst are of particular interest for an efficient air treatment process. For instance, the activity of the photocatalyst should be as high as possible, so that VOCs are converted at a higher reaction rate. Surface area is a property strongly correlated with the catalytic activity. Traditional catalysts normally show higher activities for larger surface areas, since there is a larger surface available for the adsorption of the reagents and a higher number of active sites. However, a photocatalyst presents different behavior, since the deeper areas of the pores may be less irradiated than the outer surface. Therefore, a larger surface area may not correspond to higher activity [57, 58]. Crystallinity is another feature influencing the activity of a photocatalyst. When calcined at high temperatures, the material undergoes a phase transition from amorphous to crystalline. This phase transition is beneficial for photocatalytic activity since the structure organization of the crystals inhibits electron-hole recombination [35, 59]. However, all studies agree that the further crystalline phase transition from anatase to rutile, occurring at 600 °C, should be avoided [35]. Rutile has a much lower surface area and larger crystal sizes, resulting in reduced catalytic activity [59].

Photocatalysis is a broad discipline and has been continuously studied since the 1960s [29]. Therefore, this section will cover only applications and recently published papers. In recent years, there have been no significant improvements in the synthesis of TiO$_2$ as a pure compound suggesting that the synthesizing of pure TiO$_2$ is a mature technology. A significant portion of the literature focuses on surface restructuring in
order to alter the morphology of the photocatalyst, resulting in enhanced performance. TiO$_2$ nanorods/nanotubes are an example of surface modification for the present application. However, even more literature was oriented toward the introduction of dopants in the TiO$_2$ structure for three main purposes: to reduce electron-hole recombination, to selectively oxidize VOCs, and to enhance activity under visible light. A selection of the literature is presented in 3.3.1 and 3.3.2.

3.3.1 Morphology restructuring

The main purpose of morphology restructuring is to enhance the activity of the photocatalyst by increasing the surface area and the number of active sites available. Starting from 1D structures, the most common restructured photocatalysts are nanorods (or fibers) and nanotubes. These configurations showed a high surface-to-volume ratio, enhancing the charge mobility on the photocatalyst’s surface and reducing the electron-hole recombination rate [26].

Nanotubes can be produced by various methods, often involving the use of electrical current to influence synthesis [60]. When the material undergoes no electrochemical treatment, the produced nanotubes have no ordered structure, since they are produced by mere elongation of the titania crystals. In addition, it is often not possible to synthesize only tubes due to the difficulty of controlling the mechanism at the nanoscale level. Therefore, a mixture of tubes and rods is often present. One route to synthesize nanotubes without electrochemical treatment is using alternate treatments of NaOH and HCl, with cycles repeated various times [61].

Despite the promising results obtained with this treatment, most publications discuss nanotubes produced using electrochemical treatments [60]. This process is similar to aluminum anodization, producing highly-ordered structures with properties directly related to the treatment variables. When electrochemical treatments are used, it is
possible to obtain complex hybrid structures, enhancing the activity even further. For instance, in the work of Müller and Shmuki [62], a hybrid structure of nanotubes and mesoporous titania is obtained. The authors start by synthesizing a layer of nanotubes by anodizing a thin sheet of pure Ti. This step is followed by the synthesis of mesoporous titania crystallizing inside the nanotubes, resulting in the enhanced hybrid structure shown in Fig. 7.

![Fig. 7. SEM micrographs of hierarchically structured TiO2 nanotubes with mesoporous particles. Reprinted from [62] with permission from Elsevier.](image)

### 3.3.2 TiO₂ doping

Photocatalyst doping offers a great opportunity to improve the properties of the material, tailoring the features to the targeted applications.
Therefore, TiO$_2$ doping has been widely investigated in recent years, with significant enhancements related to the topics described below.

Several elements have been reported as enhancing the electronic properties by reducing the recombination rate of the electron-hole pair. Iron is one of the most studied elements [63-66], since it showed superior properties compared to others. Silicon is also a dopant widely used combined with a photocatalyst. However, silicon has a very deep iteration with TiO$_2$ that is not limited to inhibition of the electron-hole recombination. For instance, Si can be used at high concentrations as support for the TiO$_2$. Several papers [67-69] present an improvement in photocatalytic activity when titania nanoparticles are synthesized on SiO$_2$ structures such as beads.

Another way to improve the potential of a photocatalytic application is to target only the compounds that need to be oxidized. In the present case, the photocatalyst should preferentially oxidize the VOCs. Since photocatalysis is a superficial reaction, a large number of references [70-75] report combining the photocatalyst with activated carbons. With this solution, the targeted VOCs are naturally directed toward the surface of the photocatalyst due to the adsorption properties of the activated carbons. The enhanced mass transfer potentially leads to a higher conversion of pollutants. Furthermore, since activated carbons are often used as the final stage in industrial purification processes, the combination of photocatalysis and adsorption may potentially greatly increase the efficiency of the overall process.

Interesting work is presented by Gao et al. in 2011 [70]. They used traditional commercial activated carbons (AC) from Darco and Norit and deposited the photocatalyst on the carbon surface (Fig. 8). The samples showed a high synergy between the carbon and the titania for an enhanced VOC removal. In the produced materials, the titania nanoparticles still
have a very small crystal size and a high crystallinity. Furthermore, the hybrid composite inherited the high values of Brunauer-Emmett-Teller surface area and pore volume from the AC. As a result, the photocatalytic activity greatly increased.

**Fig. 8.** SEM images and element maps of TiO$_2$/AC samples: TiO$_2$/AC-Darco (a–c) and TiO$_2$/AC-Norit (d–f). Carbon element maps: b and e; titanium element maps: c and f. Reprinted from [70] with permission from Elsevier.
The last type of dopants widely studied in the literature are those that enhance photocatalyst activity under visible light. However, the presentation of this category is excluded from this section, as it is beyond the scope of this thesis.

3.4 UV-ozone reactor modelling

The thesis also deals with the modelling of UV reactors for scaling up applications. Therefore, relevant modelling research is reported in this section. The literature published on this topic is limited, especially in comparison to photocatalysis, which indicates the novelty of the field.

A proper model for UV reactors in VOC removal applications is composed of three parts: the reaction mechanism, the UV irradiation description, and the fluid dynamics evaluation. This last part is particularly relevant when scaling up from laboratory models to prototypes or full-scale models.

3.4.1 Reaction mechanisms in UV-ozone reactors

The reaction mechanism considered in this part of the thesis is the UV-ozone oxidation mechanism without the presence of a photocatalyst. Unlike many oxidation applications, UV-ozone oxidation is a homogeneous reaction mechanism taking place in the air phase. Only UV Hg low-pressure lamps can be used to produce hydroxyl radicals as emission of the 254 nm wavelength is required. The reaction mechanism of the UV-ozone oxidation begins with the generation of ozone \([76, 77]\). This compound can be generated either by the 185 nm emitted wavelength from the Hg UV lamps (Eq. 1 and 2) or by an external ozone generator. Ozone is then decomposed by the 254 nm wavelength, resulting in an O(\(^{1}\)D) oxygen singlet (Eq. 3). This intermediate reacts with the air humidity, generating hydroxyl radicals in the homogeneous air phase (4). As for the photocatalyst, the radicals attack the VOCs, oxidizing them (Eq. 5). The whole reaction mechanism can be summarized as follows:
\[ O_2 + h\nu_{(185 \text{ nm})} \rightarrow 2O(^3P) \]  (1)
\[ O(^3P) + O_2 \rightarrow O_3 \]  (2)
\[ O_3 + h\nu_{(254 \text{ nm})} \rightarrow O(^1D) + O_2(^1\Sigma^+_g) \]  (3)
\[ O(^1D) + H_2O \rightarrow 2\text{HO} \cdot \]  (4)
\[ \text{HO} \cdot + \text{VOC} \rightarrow \text{CO}_2 + H_2O \]  (5)

The reaction mechanism between the hydroxyl radicals and the VOC is more complex than presented in the simplified version of Eq. 5, as it potentially leads to intermediates and by-products. However, the investigation of this branch of radical chemistry is very extensive, due to the high number of reactions involved [76]. Therefore, this topic falls outside the scope of this thesis and is not described in detail.

### 3.4.2 UV irradiation description

The driving mechanism for every photochemical reaction is light absorption according to the Grotthuss–Draper law [78], with a reaction rate proportional to the photons absorbed (Stark–Einstein law [79]). Starting from these laws, several models for describing the light emission from an Hg UV lamp have been developed, such as MPSS (multiple point source summation) [80] and LSI (line source integration) [81]. The former model describes the UV lamp as a series of spots emitting light in all directions, with the resulting UV irradiation in the reaction as the sum of the emissions from each spot. The LSI model extends the MPSS, so that the number of emitting spots is infinite, with the resulting UV irradiation calculated by integration. This latter model provides a formulation for the UV light propagation [81]:

\[
I_\lambda(r, z) = \int L_\lambda \frac{p_\lambda}{4\pi\rho(r, z)^2} \exp\left(-\sum_{i=1}^{N} \sigma_i n_i \rho(r, z)\right) dz
\]  (6)

where \( L_\lambda(r, z) \) [W cm\(^{-2}\)] is the fluence rate of wavelength \( \lambda \) [nm] reaching a receptor placed at the radial distance \( r \) [cm] from the UV lamp and at an
axial position \( z \) [cm]. The integral of Eq. 6 spans along the \( z \)-axis between \(-L/2\) and \( L/2\), where \( L \) is the length of the reactor. \( P_\lambda \) [W] is the power emitted at wavelength \( \lambda \) and \( \rho \) [cm] is the linear distance between the emitting light spot considered and the receptor. The exponential term of the integral considers the light absorption according to the Beer-Lambert law from the transmitting media, describing the total absorption as the sum of the absorption from each compound \( i \) present in the media. \( \sigma_i \) is the absorption cross-section coefficient \([\text{cm}^2 \text{molecules}^{-1}]\), \( n_i \) [molecules cm\(^{-2}\)] is the number of molecules of the compound \( i \), and \( N \) is the number of species considered in the model. Integrating Eq. 6 must be carried out numerically, since there is no analytical solution due to the exponential term.

When the propagating media are transparent, Eq. 6 can be simplified, resulting in [82]:

\[
I_\lambda(r,z) = \frac{P_\lambda}{4\pi Lr} \left[ \arctan\left(\frac{L/2+z}{r}\right) + \arctan\left(\frac{L/2-z}{r}\right) \right]
\]  

(7)

where \( I_\lambda(r,z) \) [W cm\(^{-2}\)] is the total fluence rate of wavelength \( \lambda \) [nm] at the radial distance \( r \) [cm] from the UV lamp and an axial position \( z \) [cm].

By calculating the light absorption in the reactor using Eq. 6, it is possible to calculate the energy and the rate of the UV-driven reactions, Eq. 1 and 3 in the reaction mechanism presented in 3.4.1.

### 3.4.3 Fluid dynamics evaluation

Since the reactions of an UV-ozone reactor take place in the homogeneous air phase, a deep understanding of the reactor fluid dynamics is necessary, because it influences VOC oxidation. This investigation may be performed using CFD simulation. The simulation discretizes the reactor domain into fine elements/volumes, calculating the chemical and physical properties for each element/volume. In this thesis, the CFD simulation is coupled with a numerical model describing the light propagation and absorption,
which also models the photochemical reactions. This approach is particularly useful when scaling up the reactor configuration, since a CFD simulation can properly evaluate the behavior of different configurations, including at a larger scale such as a prototype or full-scale.

Very little has been published on modelling UV-ozone reactors for VOC removal applications. A limited number of papers are available, targeting only the water sector with applications such as disinfection or pollutant removal [83-86]. However, water applications are significantly different from air applications due to the different purpose and the properties of the media. For instance, the driving force of water disinfection applications is the UV dose absorbed by the microorganisms, while the VOC abatement in air applications strongly depends on the production of hydroxyl radicals. The flow rates and the turbulence properties of air and water applications are significantly different, reducing even further the significance of a water study for an air application. A very limited number of publications have recently become available which analyze photocatalytic abatement of VOC in air [87]. However, as stated above, the present modelling does not consider a photocatalyst but is focused only on homogeneous VOC oxidation driven by ozone and UV. Since photocatalytic oxidation is a heterogeneous reaction, the models describing this technology cannot be directly applied to homogenous oxidation.
PART B: EXPERIMENTAL AND MODELLING
4 Photocatalytic reactor design

As stated in section 1.1, the first part of this thesis focuses on photocatalysis in order to design a test rig representative of the targeted industrial conditions. This work was covered in Paper I of this thesis. Further information about the experimental methods can be found there.

Since the power of the UV lamps should not be so high to be unrepresentative (3.1), two lamps with very low power were chosen (5 W each) with a relatively high inlet airflow of 6 L/min. The UV lamps are low-pressure Hg lamps and emit a monochromatic 254 nm wavelength. Stagnation-point flow geometry was chosen for the flow pattern of the air inside the reactor to obtain a flow with a controlled air velocity on the photocatalyst surface, so that mass transfer and fluid dynamics can be modelled more effectively. With this geometry, the photocatalyst is coated on a square plate placed horizontally in the lower part of the reactor. The air enters the reactor vertically from the top, reaching the center of the photocatalyst plate. The air then diverts orthogonally, flowing along the surface of the photocatalyst toward the edges of the plate and the outlet of the reactor. The UV lamps are placed horizontally above the photocatalyst plate. A drawing of the reactor is shown in Fig. 9.
The position of the UV lamps was numerically optimized by adjusting sizes and proportions inside the reactor so that the UV irradiation on the photocatalyst was as homogeneous as possible. With the reactor design presented in this thesis, it was possible to quickly screen and test various photocatalysts. Each sample was coated on a different plate that was replaced at the end of the experimental tests, thus simplifying the experimental procedure once all plates were coated. Several samples could be quickly screened and the most active ones identified. Acetaldehyde was used to represent the VOC since it is often found in industrial air emissions [18, 43]. The temperature was set to 50 °C and the relative humidity to 20 %.
4.1 Photocatalyst synthesis

Both commercial and synthesized samples were tested during the screening of photocatalysts. The commercial samples used were Aeroxide® P25 and P90 from Evonik, CristalACTiV™ PC105 from Cristal, and M311 from Hombikat. The synthesized samples were prepared using the sol-gel method as set out in Zhang and Liu [88], calcined at 400 °C and 600 °C, using Ni as dopant. This metal was chosen due the reported higher activity of the photocatalyst when doped with Ni [88]. TiO$_2$ nanorods were also included in the study. On the basis of previous research [89, 90], commercial samples were alternatively treated with NaOH in an autoclave at 150 °C and washed with a solution of HCl and deionized water in order to modify the surface morphology so that nanorods could be produced.
5 Photocatalyst support

Stable coating of the photocatalyst on the support is an important issue to be addressed when scaling up photocatalytic reactors (see 3.2). Therefore, several methods for improving the binding between TiO$_2$ and metallic plates were tested (see Paper II). Aluminum and 304 stainless steel were used for the plates, as they are suitable candidates for use in a scaled-up UV reactor due to their chemical resistance and mechanical properties. Most of the methods for performing the treatments were adapted from the literature and involved chemical and electrochemical etching of the metals’ surface [91-95]. No important modifications from the literature were implemented in this work since the focus was the evaluation of the restructured surface for stabilizing the TiO$_2$ coating. The newly restructured surface was evaluated using a SEM and a confocal microscope to assess the degree and morphology of the restructuring. For the most promising surfaces, the stability of the coating was tested with X-cut tapes tests [96] in which the tape was stuck on the surface and then peeled off. The mass of photocatalyst adhering to the tape (i.e., removed from the surface) was then determined. For comparison, the mass loss from the restructured metal plates was compared to the loss from a cordierite ceramic plate, a support frequently used in catalysis applications. Lastly, the coated surfaces showing the highest TiO$_2$ stability were tested in the UV reactor developed (section 4) to evaluate the effect of the surface restructuring on the activity of the photocatalyst.
6 Reactor modelling

After analyzing the photocatalytic reactor design and the stability of the coating, the scale-up process continued with the modelling of a UV-ozone reactor. This task was divided into two parts: first, UV irradiation and reaction kinetics, and secondly, fluid dynamics.

6.1 UV irradiation and reaction kinetics model

The UV-ozone reactor was modelled numerically using MATLAB. A detailed description of the methods used can be found in Paper III. The main concept behind the model development was the implementation of the LSI model for describing light propagation, as described by Blatchley III [81] (see 3.4.2). Ozone generation and depletion were modelled according to Voronov [77]. In this thesis, the LSI model was expanded by also considering light reflection from the reactor walls. Even if the reflection of stainless steel is moderate [97], the UV reflection may become relevant, especially for reactors with small diameter. The UV reflection was approximated by modifying Eq. 6 to include the reactor walls as an emission source. The light source is obtained by multiplying the incident irradiation times the reflection coefficient presented by Li et al. [97]. The resulting model calculated the light propagation by also considering the absorption by oxygen and ozone, depending on the wavelength. Since it is not possible to describe the light absorption analytically, due to the exponential term of Eq. 6, approximate analytical expressions were developed to minimize the error. These expressions were developed to significantly reduce the computational workload of a workstation, as an analytical expression would be less demanding than a numerical expression. The solution of Eq. 6 for a cylindrical geometry (Eq. 7 in [82]) was taken as the starting point. Eq. 7 was then modified using empirical
parameters and an exponential term to consider the light absorption, resulting in:

\[ I_\lambda(r, z) = \frac{P_\lambda}{4\pi r L} \left[ \arctan\left( \frac{L/2+z}{r} \right) + \arctan\left( \frac{L/2-z}{r} \right) \right] \exp\left( \alpha_{1,i} \sigma_i n_ir \right) \alpha_{2,i} \]  

(8)

where \( I_\lambda(r, z) \) [W cm\(^{-2}\)] is the transmitted fluence rate of wavelength \( \lambda \) [nm] at the radial distance \( r \) [cm] from the UV lamp and an axial position \( z \) [cm]. In the exponential term, \( \sigma_i \) [cm\(^2\) molecules\(^{-1}\)] is the absorption cross-section coefficient and \( n_i \) [molecules cm\(^{-3}\)] is the molecular concentration of the compound \( i \). In the present investigation, air is the absorbing compound \((i)\) at the 185 nm wavelength, while ozone is the absorbing compound at the 254 nm wavelength. \( \alpha_{1,i} \) [-] and \( \alpha_{2,i} \) [-] are the empirical parameters/variables of the model for the absorbing compound \( i \). Since the concentration of air can be assumed constant in all cases, \( \alpha_{1,\text{air}} \) and \( \alpha_{2,\text{air}} \) are only numerical parameters, when air is the absorbing compound in Eq. 8. Empirical first-order equations were used to describe the variation of \( \alpha_{1,O3} \) and \( \alpha_{2,O3} \) with ozone concentration:

\[ \alpha_{1,O3} = \beta_1 + \beta_2 c_{O3} \]  

(9)

\[ \alpha_{2,O3} = \beta_3 + \beta_4 c_{O3} \]  

(10)

where \( c_{O3} \) [ppm] is the concentration of ozone and \( \beta_1 \) to \( \beta_4 \) [-] are numerical coefficients.

Starting from the irradiation model, the reaction model considers the local values of the absorbed fluence rate to calculate the amount of energy absorbed. Then the reaction rates of ozone generation and depletion are calculated in accordance with Voronov’s formulation [77]. These local values of the reaction rate were integrated to calculate the ozone production and depletion in the reactor volume. Assuming an excess of water vapor, it is possible to use the rate of ozone depletion to calculate the production of hydroxyl radicals according to Eq. 4. This chemical species is the only intermediate reacting with the VOC in this model, due to the low reactivity of the model compound (acetaldehyde) with other species such
as ozone [76, 98-100]. As a result, the local rate of VOC decomposition is a function of the reaction rate of ozone depletion, according to:

\[ r_{VOC}(r, z) = k \cdot r_{O3,dep}(r, z)[VOC(r, z)] \]

\[ \text{(11)} \]

where \( k \) [m^3 mol^{-1}] is an empirical kinetic constant, \( r_{O3,dep} \) [mol s^{-1} m^{-3}] is the local reaction rate of ozone depletion and \([VOC]\) [mol m^{-3}] is the local concentration of VOC. The final overall conversion was calculated using two simplified reactor models: traditional CSTR and S-PFR. Further information about the expressions developed for calculating the VOC conversion in each reactor can be found in Paper III. These values, together with the values of net ozone concentration at the outlet, were used to verify the model against experimental results, using the setup presented in Paper III.

### 6.2 Fluid dynamics model

The evaluation of the fluid dynamics in an UV-ozone reactor can be performed with a CFD simulator, as presented in Paper IV. The volume is discretized into fine elements and the relevant properties are calculated for each element. In this thesis, the CFD simulator used was COMSOL Multiphysics®, version 5.3. A CFD simulator calculates the solution for its case iteratively, minimizing the errors until certain convergence criteria are met. In this situation, the expressions developed previously in Eq. 8 are very relevant, since they avoid the numerical calculation of Eq. 6 at each iteration, resulting in shorter solution times. Thus the irradiation and kinetics models were adapted for use in the CFD simulator from the numerical work reported in Paper III. This simulation software was used to evaluate the performance of UV reactors with different geometries, so expanding the scope of the numerical model to prototype reactors. The presence of turbulence phenomena is expected to be the main difference between the laboratory scale (in the pseudo-laminar regime) and the prototype scale.
The geometry of the laboratory-scale reactors was cylindrical, with the UV lamp placed axially at the center of the reactor, as shown in Fig. 10.

The inlet and outlet are 6 mm in diameter and are placed at opposite ends of the reactor, oriented toward the center. The length of the UV reactor is 28 cm. Three diameters were simulated: 85, 135 and 164 mm. The UV lamp is a low-pressure Hg lamp with the same arc-length as the reactor body and a power of 17 W. A quartz sleeve encases the UV lamp for protection from external agents.

Two prototype reactors are included in the scope of this thesis. Both of them operate in a turbulent air regime due to the airflow rate tested – 100 m$^3$/h – approximately one order of magnitude higher than the laboratory reactors. As a consequence, more than ten lamps are required for results comparable to the laboratory scale. The geometry of the prototypes is presented in Fig. 11.
The inlet and outlet of the prototypes are much larger than those in the laboratory reactors, since they now occupy the entire left and right side of the reactor. The air flows from left to right (Fig. 11), orthogonally to the UV lamps placed vertically. Both the standard reactor (left reactor in Fig. 11) and the hexagonal reactor (right in Fig. 11) have the same size and volume, 40 x 40 x 28 cm along the x-, y-, and z-axis respectively. The main difference between the reactors is the lamp distribution. The standard reactor has ten lamps, arranged in two parallel rows. The lamp distribution of the hexagonal reactor starts from a central lamp at the center of the reactor. Around this lamp, six lamps are placed at the same distance, forming a hexagon. With this design, all seven lamps are at the same distance from each other. To reduce unreached areas, the reactor is completed with four lamps at the extremities, forming three rows in a 4–3–4 configuration. The hexagonal reactor has eleven lamps versus the ten lamps of the standard reactor. Therefore it is expected to have higher VOC conversion due to the higher UV power. The VOC conversion normalized by the number of UV lamps will be evaluated as a more relevant comparison.
The results of VOC conversion and ozone concentration from the CFD simulator were verified against experimental results, using the same setup presented in Paper III.
PART C: RESULTS AND DISCUSSION
This introductory paragraph of Part C summarizes how the work carried out in this thesis is located in and contributes to the research field. No significant effort was spent on synthesizing the photocatalyst due to the large number of existing papers on this topic. The focus was on the design of a photocatalytic reactor with features relevant to commercial VOC removal applications, such as a low ratio between the power of the UV lamps and the airflow. The reactor chosen made it possible to identify which of the previously developed photocatalysts is the most active for the chosen application. Based on the literature, several synthesized photocatalysts were screened, including nanorods and doped samples. An important part of scaling up photocatalytic systems is finding a good way to bind the photocatalyst to the metallic surface, which may be the reactor walls in a scaled-up application. For this study, electrochemical treatments for restructuring the metallic surfaces were taken from the literature. The core of the work was the evaluation of the most promising treatment for binding TiO$_2$ to the metallic surface. The result is an innovative application of an already existing electrochemical treatment, with insights on the effect of the surface restructuring on the photocatalyst’s activity. The modelling work, covering both numerical and CFD analysis, will significantly contribute to research in this field, since no similar models have been published. In particular, this thesis covers reactor geometry and lamp configuration, optimized for the model developed.

7 Reactor design for photocatalytic tests

This section presents the most important results in the development of the photocatalytic reactor, emphasizing the fluid dynamics, UV irradiation, and photocatalyst activity. More details can be found in Paper I.
7.1 Reactor development

One of the aims for the design of the photocatalytic reactor was obtaining a particular flow pattern, called stagnation-point flow, for the air inside the reactor. Therefore, the inlet of the air was orthogonal to the photocatalytic plate, placed in a central position. The fluid dynamics were evaluated using CFD simulations, with the results presented in Fig. 12.

Fig. 12. Velocity profile of the air inside the UV reactor in a vertical slice at the center of the reactor (a) and on the catalyst surface (b). Reprinted from Paper I.

Fig. 12.b shows the actual flow distribution following a stagnation-point flow. The air enters the reactor with a relatively high velocity, slowing down when approaching the photocatalytic plate. Close to the central – stagnation – point, the air velocity is close to zero, as expected in stagnation-point flow applications [101, 102]. After this point, the air deflects orthogonally, flowing radially on the plate surface, with decreasing velocity. Paper I presents more detailed insights about the air streamlines and the flow of the VOC toward the photocatalyst. Fig. 5 of Paper I shows that convection is the main driving mechanism for mass transfer of the VOC until the stagnation point, with diffusion becoming relevant after that point.
Another feature of the reactor design was homogeneous UV irradiation on the photocatalyst. This was obtained by optimizing the position of the UV lamps. The optimal placement strongly depends on the lateral position of the lamps, while the vertical height above the photocatalyst influences the homogeneity of the irradiation to a lesser extent. The results are presented in the supplementary material of Paper I (Fig. S1). The center of the UV lamps is almost vertically above the edge of the photocatalyst support and 13 mm from the lateral walls of the reactor. The vertical distance between the center of the lamp and the photocatalyst is 50 mm. The resulting average irradiation on the photocatalyst surface is $5 \pm 0.4 \text{ mW/cm}^2$, as shown in Fig. 13.

![Fig. 13.](image)

Since the difference in irradiation across the reactor was less than 10 % of the average value, the UV irradiation was considered sufficiently homogeneous. To verify the calculations, the UV irradiation was experimentally measured at four points (as shown by the stems in Fig. 13),
confirming the homogeneity of the light intensity. The experimental values were significantly lower than those calculated due to the low sensitivity of the sensor used for non-orthogonal photons and the natural aging of the UV lamps.

7.2 Photocatalyst screening

A fundamental feature of the designed system is that it facilitates quick screening of different photocatalysts. Significant differences between different samples need to be observed to identify the most active sample suitable for the reactor design. Before testing the activity, each photocatalyst was characterized using traditional techniques, as presented in the supplementary material of Paper I. Since the characterization results confirmed the expectations from the literature, this section highlights only one specific case: the SEM micrograph of the sample with nanorods. This sample was a P25 photocatalyst, treated according to the process set out in 4.1 in order to elongate the titania crystals. Fig. 14 shows the results.
As expected, the basic/acid treatment deeply modified the surface morphology of the P25 photocatalyst, resulting in the formation of nanorods. The original nanocrystals of P25 observed in Fig. 14 (a) were clustered into larger crystals (Fig. 14.b), with evident superficial formation of nanorods. These nanorods have a length of hundreds of nanometers and a diameter of a few nanometers, as observed in previous work [89].

The activity of all the photocatalyst samples, both commercial and synthesized, was evaluated in the designed reactor, with the results presented in Fig. 15.

**Fig. 14.** SEM micrographs at 50k x and 200k x magnifications of (a) untreated P25 sample, and (b) nanorod P25 sample.
Fig. 15. VOC conversion for the photocatalysts screened. The error bars correspond to the standard deviation of the conversion during the last 4 h of testing after reaching steady state conditions.

Analyzing each sample in detail, the first two samples (sol-gel synthesized) on the left of Fig. 15 confirm previous results presenting VOC conversion that increases with calcination temperature \([35]\). Despite the consequent decrease in surface area (as presented in Fig. S4 of Paper I, supplementary material), a higher calcination temperature results in a higher degree of crystallinity, with a lower rate for electron-hole recombination \([55]\). On the other hand, the Ni-doped sample did not show the expected activity improvement \([88]\). This behavior may be due to the synergy with the Nitrogen doping that is observed under visible light. This literature work suggests that this synergy is relevant only for visible wavelengths, not under UV light as in the present case. However, this hypothesis needs to be
tested in future research. All the commercial samples outperformed the synthesized ones, with P90 showing the highest activity. Given that the synthesis techniques of the commercial samples are not described in as much detail as the techniques for the synthesized samples, it is difficult to present relevant reasons for the difference in activity of each sample. The results of the nanorod samples are contradictory. The surface restructuring of the P25 successfully increased the activity of the photocatalyst due to the increased charge transfer and surface area [103]. However, the nanorod sample of P90 showed lower activity than the untreated sample, even lower than the untreated P25 sample. The reasons for this particular behavior are beyond the scope of this thesis and thus were not explored in detail. However, since the P90 has a surface area higher than P25, the surface restructuring process may have significantly reduced this value, resulting in the low activity observed.

Analyzing the overall photocatalyst screening, significant activity differences were observed between the samples, confirming the suitability of the designed reactor for screening. Each sample was quickly evaluated due to the ease of replacing the coated photocatalytic support without stopping the reagent flow in the system.

Concluding the photocatalytic reactor study, this reactor design proved to be very suitable for efficiently testing various samples with controlled fluid dynamics and UV irradiation. These last two features are particularly relevant for later modelling. However, despite being an interesting development of the presented work, modelling of the UV reactor is beyond the scope of this work, as was stated in 1.1.
8 Photocatalyst support

Once the optimal photocatalyst has been identified, the next step in the scale-up process is implementation in the chosen UV reactor. As presented in 1.1, improvement of the binding of TiO$_2$ to metal without the use of organic adhesives was considered a priority for a successful scaled-up configuration.

Both stainless steel and aluminum were subjected to a wide range of electrochemical treatments. A detailed description of the results is presented in Paper II. The aim of these treatments was strategic surface restructuring to enhance the stability of a coating. Even though some treatments may involve high concentrations of mixed acids, their effect in terms of surface restructuring may be minor, and may not be correlated to the concentration of the chemicals. For instance, this is the case with the “$H_2SO_4$–$H_2O_2$” treatment for stainless steel (Paper II, Fig. 2) and with the anodization for aluminum (Paper II, Fig. 3). In other cases, the surface restructuring with some treatments was too intense, as the previous surface was completely erased and converted into a smooth surface. This effect was observed, for instance, when treating aluminum with sulfuric acid (Paper II, Fig. 3.c). Of all the treatments, two produced interesting surface structures when subjected to SEM analysis. The first is the DC etching of steel, which produced characteristic potholes. The second is the AC etching of aluminum, which resulted in terraces. Fig. 16 shows the results.
A hierarchical series of potholes was observed in the stainless steel sample, completely restructuring the surface, as has been observed elsewhere [93]. Even at low magnifications (Fig. 16.a.I) the surface looks completely restructured, presenting potholes a few µm in size. Inside these primary potholes, secondary and tertiary nano-potholes can be observed, highlighting the extent of hierarchy on the treated surface. The size of the nano- and micro-potholes is relevant given the size of the deposited titania powder. The tertiary nano-potholes have a size of about 50 nm, comparable to the thinner photocatalyst particles (Paper II, Fig. 1). However, the primary potholes, with a size of about 1 µm, can accommodate even the larger titania clusters. The correspondence between potholes and titania sizes suggests that this electrochemical treatment will exhibit high performance in terms of coating stability, since every titania grain might be accommodated effectively.

**Fig. 16.** SEM micrographs at various magnifications of treated metal samples. (a) DC etching on stainless steel and (b) AC etching on aluminum. Adapted from Paper II.

<table>
<thead>
<tr>
<th>Magnifications</th>
<th>3k x</th>
<th>20k x</th>
<th>100k x</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a.) DC etching, stainless steel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b.) AC etching, aluminum</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Unlike the stainless steel treatment, the AC etching on aluminum did not completely restructure the surface. As shown in previous research [95, 104, 105], the surface restructuring started at weak spots on the original surface where the aluminum was attacked, resulting in the nucleation of the first terrace. The surface restructuring propagates from these spots with a pit-on-pit propagation mechanism [105]. Several layers of hierarchical cubical terraces are observed inside each large primary pit, significantly increasing the surface area. The terraces produced have very smooth sides and very sharp edges due to the presence of the AC current. The size of the edge of the smallest nanoscale terraces is 100–500 nm (Fig. 16.b.II). Like the DC etching of stainless steel, this electrochemical treatment of aluminum was considered a good candidate for stabilizing the TiO$_2$ coating. Due to its hierarchical structure, it should be able to accommodate both large and fine catalyst grains. However, the large sections of unmodified surface may affect the total amount of stable coated photocatalyst.

These two electrochemical treatments, along with three other promising treatments, were chosen for tape tests to analyze the mechanical stability of the titania coating, as shown in Table 1.
Table 1. Treatments chosen for the titania tape tests, with their code and surface morphology. Adapted from Paper II.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Material</th>
<th>Treatment method</th>
<th>Surface morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS_1</td>
<td>Stainless steel</td>
<td>Chem. etching H₂SO₄</td>
<td>High number of pits at nanoscale and rougher surface</td>
</tr>
<tr>
<td>SS_2</td>
<td>Stainless steel</td>
<td>Electrochem. DC etching</td>
<td>Hierarchical potholes from micro to nanoscale</td>
</tr>
<tr>
<td>Al_1</td>
<td>Aluminum</td>
<td>Chem. etching H₂SO₄</td>
<td>Several nanoscale pits</td>
</tr>
<tr>
<td>Al_2</td>
<td>Aluminum</td>
<td>Anodization</td>
<td>Cylindrical and ordered nanopores</td>
</tr>
<tr>
<td>Al_3</td>
<td>Aluminum</td>
<td>Electrochem. AC etching</td>
<td>Localized cubical pits, with pit-on-pit propagation</td>
</tr>
</tbody>
</table>

The most important result from the tape tests was the improvement in coating stability observed for the treatments. The coating on a traditional ceramic support was completely removed after just three tape tests, leaving the support surface completely uncoated. On the other hand, all the treated metal surfaces still had titania on the surface after 12 tape tests; coating removal appeared to have leveled off during repeated tests (Fig. 17).
Any electrochemical treatment significantly restructures the support surface and has a direct effect on coating stability, increasing the stability. The potholes produced by the DC etching on stainless steel showed the best performance since only 25% of the titania was removed after 12 tape tests. This high performance is due to the complete surface restructuring (Fig. 16.a), resulting in a shape that effectively accommodates both coarse and fine grains of titania.

Finally, the photocatalytic activity of the TiO$_2$ coated on the DC etched steel was analyzed by comparing it to the activity of the same photocatalyst coated on a traditional cordierite support. The UV reactor previously developed in Paper I was used for the activity tests. The photocatalyst coated on the restructured metal surface had stable activity over time, confirming the stability of the coating. In addition, this photocatalyst had
higher activity than the photocatalyst on the ceramic support due to the higher surface area exposed to the UV light. The roughness resulting from the chemical etching almost doubled the surface area of metal used as photocatalyst support (Table 4, Paper II). The larger photocatalyst surface resulted in higher conversion.

Based on these results, it can be concluded that a stable titania coating can be obtained on a metal surface without using any adhesive. DC etching on stainless steel proved to be suitable both for stabilizing the photocatalyst and for increasing photocatalytic activity. This technique could be successfully adapted for use in commercial reactors, leading to firm photocatalytic binding to the support even in full-scale systems with high air velocities.
9 Reactor modelling

9.1 Irradiation and reaction modelling

The focus of the investigation now moved to modelling UV-ozone reactors in order to enhance understanding of the phenomena involved. The aim was to identify governing variables and potential weak points in UV reactors, resulting in optimized scaled-up units. The first step in this direction was the description of the UV irradiation and kinetic mechanism (Paper III), followed by a fluid dynamics implementation (Paper IV).

The UV irradiation assumes both the transparency and absorption of the irradiating media (i.e., air). In both cases, the results indicate a sharp decrease in the fluence rate when moving away from the UV lamps (Fig. 18).

![Fluence rate for the total 185 nm emitted light. The light source is a cylindrical 17 W UV lamp, 28 cm long, placed along the z-axis with a center at (0,0) coordinates in the zr-plane. Reproduced from Paper III.](image)

This behavior is expected due to the light-emitting principle of a low-pressure Hg-vapor UV lamp. In this lamp, the Hg vapor is inserted in the
space between the two ends, where the electrical current flows between the arcs. The UV light is emitted when the Hg vapor relaxes after being excited by the current, releasing the excess energy as UV light and radiating isotropically. Therefore, the fluence rate is strongly dependent on the distance from the emitting point, with a trend decreasing by the power of 2 from the source, as presented in the definition of the LSI model [81].

While the profile of the fluence rate has the same trend for both the emitted wavelengths (185 and 254 nm), the light absorption is very wavelength dependent. The results of the modelling show that the former wavelength is almost completely absorbed within the first centimeters of the reactor radius, while the latter wavelength penetrates the UV reactor almost unabsorbed (Fig. 19).

Fig. 19. Ratio between absorbed fluence rate and total fluence rate for (a) the 185 and (b) the 254 nm wavelength. The light source is a cylindrical 17 W UV lamp, 28 cm long, placed along the z-axis with a center at (0,0) coordinates in the zr-plane. Reproduced from Paper III.

Fig. 19 shows a difference of one order of magnitude between the relative absorption of the 185 nm and 254 nm wavelengths. Therefore, assuming a reactor radius of 15 cm, most of the 185 nm light is used to generate ozone while only a small fraction of the 254 nm light is used to decompose ozone and generate hydroxyl radicals. This situation is far from the ideal in which all the UV light would be absorbed in the smallest volume possible.
Furthermore, considering the scale-up process of UV reactors, size is an important variable. Large reactors are more expensive than small ones, due to the higher material costs. In addition, space constraints may limit the use of large reactors. The remarkable difference in light absorption between the 185 and 254 nm wavelengths is due to the low concentration of ozone absorbing the 254 nm wavelength. Even though the absorption coefficient of ozone for 254 nm [106-108] is higher than the coefficient of oxygen for the 185 nm wavelength [107, 109], the high concentration difference between these two compounds counteracts the effect of the absorption coefficient, resulting in the higher absorption observed for the 185 nm wavelength.

When the 254 nm wavelength reaches the reactor walls, it is mostly absorbed by the material as the stainless steel of traditional walls is weakly reflective [97]. That is why the effect of reflection was investigated, as reported in 6.1. However, even if a high reflection coefficient was considered (typical of a material such as aluminum [97]), the effect of reflection appears negligible (Fig. 9, Paper III).

The results of light absorption are very relevant in terms of process efficiency. Even if the efficiency of a UV-based AOP is higher than that of traditional technologies for VOC abatement [19], further improvements are possible by maximizing the light absorption. Using a photocatalyst may be one way to improve a UV-ozone system, since the UV light not reacting with ozone is absorbed in the first 5 µm of the photocatalytic surface [110]. However, the design of a full-scale UV-ozone-TiO₂ reactor is very challenging since the fluid dynamics need to be carefully assessed, minimizing the mass transfer limitations and avoiding shadowed areas in the reactor.

The efficiency of a UV-ozone system may also be increased by implementing an external ozone generator. This unit produces ozone using a corona discharge mechanism, which is a more efficient process than the
185 nm ozone generation mechanism. Thus the concentration of ozone in the UV reactor can be increased, resulting in higher light absorption (Fig. 20)

![Graph showing relative absorption for different ozone concentrations](image)

**Fig. 20.** Ratio between absorbed fluence rate and total fluence rate (relative absorption) for the 254 nm wavelength at different concentrations of external ozone addition. The light source is a cylindrical 17 W UV lamp, 28 cm long, centered at \( r = 0 \) and axis orthogonal to the plot. The curves are calculated at a central axial position \( z = 0 \). Reprinted from Paper III.

When 100 ppm of ozone are injected into the system, the light absorption doubles, resulting in more effective use of the 254 nm wavelength. However, optimization of the overall process efficiency requires evaluation of the power consumption from the ozone generator. Therefore, even if the efficiency of the UV reactor increases, this may not directly correlate with the efficiency of the whole process for VOC decomposition. In addition, an ozone concentration of 100 ppm is relatively high in a full-scale reactor. The investment and operational costs for the ozone generators may become too high, despite the eventual gain in process efficiency. Furthermore, such a high concentration is 1000 times higher the limit for
working environments [111], so the process stream would require ozone destruction before emission.
The presented model for UV irradiation was coupled with the reaction mechanism in 6.1 describing ozone and VOC reactions. One of the most relevant results in terms of reactor modelling was the accuracy of the model for predicting the ozone concentration at the reactor outlet. This value derives from the net reaction rate ozone production, which is defined as the difference between the total production and depletion rate. Despite an offset of approximately 20% from the experimental values, the model predicted the ozone concentration accurately for all the tested cases (Fig. 21).

![Fig. 21. Experimental and calculated ozone net concentration for different reactor diameters and airflow rates. The UV lamp is a low-pressure Hg-vapor lamp with a power of 17 W. The inlet concentration of VOC is 15 ppm and the relative humidity is 20% at 25°C. Reprinted from Paper III.](image)

The modelling results are particularly meaningful due to the absence of empirical parameters, thus possibly resulting in a model that is also valid for cases very different from those experimentally tested. However, this
hypothesis needs to be confirmed by further experimental data under different conditions. These results are not invalidated by the offset of 20% since this difference was expected due to the natural aging of the lamp and the presence of the protective quartz sleeve. Traditional quartz sleeves absorb approximately 10% and 40% of the UV light at 254 and 185 nm respectively affecting the overall VOC conversion.

The reaction rate of VOC decomposition was simplified according to Eq. 11 due to the complexity of the radical chemistry mechanism. At first, this expression was implemented in simplified reactor models such as S-PFR and CSTR. Despite the latter having a more accurate prediction than the former in terms of VOC conversion, both the models showed limitations in their predictions. Since the reaction rate depends on the concentration of the compounds, fluid dynamics plays an important role, especially considering the low concentrations of ozone and VOC, which are strongly affected by the flow pattern during reactor operation. Therefore, the UV irradiation and reaction model were implemented in a CFD simulation to refine the results. The implementation was based on Eq. 8–11, resulting in analytical expressions accurately describing the UV propagation and absorption without using numerical expressions (Fig. 14, Paper III). The absence of numerical expressions simplified setting up the simulation and also greatly reduced the workload of the workstation. Therefore, more cases were evaluated in a shorter and more effective way.

9.2 Fluid dynamics modelling

The first step in the CFD investigation is fitting the model to the experimental data with regard to ozone concentration (Fig. 22) and VOC conversion (Fig. 23).
The CFD model showed the same degree of accuracy as the numerical model (CSTR). This was considered acceptable, especially given the absence of empirical parameters, as mentioned in 9.1. The consistent 20% offset from the experimental data observed in the numerical model is not present in the CFD model because the smallest reactor presented lower values of ozone concentration. Further investigation is needed to assess the reasons for this behavior, possibly including new experimental tests using different reactors and airflow patterns.
The modelling of the VOC conversion shows much the same pattern as the modelling of the ozone concentration. The CFD simulation is less accurate than the numerical model for the smallest reactor, for the experimental results are even more underestimated. This result may be related to the low ozone concentration observed for the CFD model in Fig. 22. The CSTR model shows an increase in conversion with diameter from 85 mm to 164 mm diameter. The experimental results first show an increase in conversion from 85 mm to 135 mm diameter, followed by a slight decrease in conversion from 135 to 164 mm reactor diameters (Fig. 23). This behavior is also seen in the CFD model, which means the CFD model is better than the numerical model for this case.

Analyzing the offset between the CFD and experimental results provides relevant insights regarding the accuracy of the reaction model for VOC
decomposition (Eq. 1–5). Because of the complexity of modelling the radical chemistry, this mechanism was simplified with the single-reaction model presented in Eq. 11. Fig. 22 and Fig. 23 present the same offset trend for both the ozone concentration and the VOC conversion. Therefore, it is reasonable to expect that refining the VOC oxidation reaction mechanism would not contribute significantly to improving the model accuracy, since the VOC reaction mechanism depends mainly on the offset already observed for the ozone concentration. A more promising way to improve the accuracy of the model is related to the refinement of the ozone reaction mechanism (Eq. 1–4), possibly considering the concentration profile of this species in the reactor. However, verifying this hypothesis will require further investigation, including expanding the present model and simulating different geometries.

In general, a CFD model is to be preferred to a numerical model due to its intrinsic flexibility. A CFD simulator already has a built-in structure for the user to insert relevant properties for irradiation and reaction kinetics. Thus geometry and lamp changes can quickly be implemented in the CFD simulator. A numerical model is less user-friendly. Furthermore, even if the fluid dynamics model does not improve the model accuracy, it still provides relevant indications regarding the flow properties of the reactor, which would be missed by the numerical model. This feature is particularly important when the system is scaled-up and the fluid flow begins to show turbulent phenomena and non-linear flow patterns. Therefore, including the numerical model in the CFD simulation is considered essential for the scale-up process, whether or not this results in potential improvements in the model accuracy.

9.2.1 Description of fluid dynamics for laboratory cases

After evaluating the accuracy of the CFD model, the fluid dynamics for one specific case (airflow rate: 32 L/min, reactor diameter: 135 mm) will be
described in this section to enhance understanding of the governing phenomena. Starting from this case, general considerations applicable to similar cases are presented. Paper IV gives more details regarding the flow behavior of this case and the others simulated.

As expected, the flow pattern is complex, due to the characteristic geometry of the reactor. In particular, the size difference between the inlet/outlet tube and the reactor body strongly affects the air velocity (Fig. 24).

**Fig. 24.** Streamlines of the velocity field for the 135 mm laboratory reactor with an airflow rate of 32 L/min. The color expression is the velocity magnitude (m/s). Reprinted from Paper IV.

Due to the relatively small size of the inlet, the incoming air enters the reactor domain as a jet oriented toward the UV lamp. When the streamlines reach the quartz sleeve, the flow splits into different directions, decreasing the velocity both surrounding the UV lamp and moving axially
along it. Fig. 24 presents different residence times for various VOC streamlines inside the UV reactor, depending on whether the flow enters a dead volume or a high velocity region, bypassing most of the reactor volume. In principle, an optimal reactor should have the opposite behavior, with all the streamlines being exposed to the same UV dose and ozone concentration so that all the VOC is equally converted. When there are large variations inside the reactor domain, the reactor is behaving sub-optimally, without accurate control of the VOC conversion. For instance, if a significant part of the flow bypasses irradiated areas, the ozone cannot be converted into hydroxyl radicals to trigger VOC oxidation. Therefore, even if the power of the UV lamp is increased, no additional VOC is converted from the bypassing streams, leading to low process efficiency. On the other hand, if all the streamlines are processed equally, changes in the reactor properties are directly related to VOC removal rates, accurately predictable with a reactor model.

The complex fluid dynamics pattern is converted into non-homogeneous reaction rates and concentration profiles (Fig. 25), as expected.
Fig. 25. Reaction rates and concentrations at a symmetrical cut plane. 
(a) Reaction rate of ozone depletion. (b) Ozone concentration. (c) Reaction rate of VOC decomposition. (d) VOC concentration. The velocity magnitude is the expression for the cone surface with a velocity-based color legend. Velocity values higher than 1 m/s were removed for clarity. The air inlet is at the bottom-left and the outlet at the top-right. The inlet flow rate is 32 L/min and the reactor diameter is 135 mm. Adapted from Paper IV.

Both the concentration of ozone and VOC are strongly affected by the fluid dynamics, especially considering their low average concentrations. For instance, the concentration of ozone increases in stagnation areas, since the reaction rate of ozone generation is higher than the reaction rate of ozone depletion (top-central part of Fig. 25.b). In the same areas, the VOC concentration is lower than in the surrounding areas, since acetaldehyde has a much longer residence time, so it will eventually react, regardless of the UV irradiation.

Another interesting consideration regards the relation between the plot of ozone depletion rate and VOC concentration. As shown in Fig. 25.a, the
depletion rate has different values in the reactor domain depending on the proximity of the UV lamp and the ozone concentration. When ozone decomposes, hydroxyl radicals are produced, so the highly ozone depleting areas are also very reactive with the VOC. Therefore, it is reasonable to have a sort of “specularity” between the ozone depletion and the VOC concentration plot. When the ozone depletion is at its highest, the VOC concentration is at its lowest and vice versa. This behavior is connected to the profile of the VOC oxidation rate (Fig. 25.c), since this variable is a linear combination of the ozone depletion rate and the VOC concentration (Eq. 11). Therefore, the differences between these two variables smooth the profile of the VOC oxidation rate, resulting in more homogeneous values in the reactor domain.

Based on the current results, it is possible to conclude that the CFD simulator presented properties of UV reactors relevant to increasing understanding of the governing phenomena. Even if the geometry of the reactor is apparently simple, the flow pattern is rather complex, with significant variations of the fluid dynamics properties between different areas of the reactor. The CFD simulator was confirmed to be a useful tool for assessing the properties of UV reactors.
10 Scale-up process for UV reactors

As presented in 3.4.3, the CFD model has two main aims: a deeper understanding of the governing variables of UV reactors and an effective scale-up process. Therefore, after analyzing the relevant properties in the laboratory reactors, the flow rate of the process air was increased to 100 m$^3$/h to design new, larger prototypes. As shown in 9.2.1, sub-optimal reactor regions need to be minimized and all the air streamlines treated equally. This goal does not necessarily correspond to a simple “box-shaped” reactor geometry, with the same size for the body and the inlet/outlet. The reactor body, lamp distribution, and flow pattern may be made more complex if this yields better performance and process efficiency. The following criteria need to be adopted, as much as possible:

- each streamline should receive the same treatment due to similar conditions such as residence time, average ozone concentration, and UV dose;
- stagnation zones and bypasses need to be minimized since they lead to unpredictable performance and low process efficiency;
- if the flow pattern is complex, the airflow should move as a plug, following the designed pattern in the reactor.

If all the criteria above are applied, the performance of the resulting reactor configuration will most likely be a very predictable function of the process variables.

Two simple prototype geometries are presented in this thesis. Due to the higher airflow rate, the power of the UV lamps needs to be proportionally increased. Therefore, 10–12 lamps were used, each equal to the one used in the laboratory reactor. The first prototype, called “standard,” is a standard configuration with ten lamps arranged in two frames, while the second, “hexagonal” reactor has a lamp distribution aimed at having an equal distance between each lamp (see 6.2 and Fig. 11).
Despite being simpler than in the laboratory cases, the fluid dynamics are also important for the prototypes. Following the criteria presented above, the streamlines in the simulated reactors are linear, moving as a plug with a simple pattern and no stagnation zones. As regards the homogeneity of the treatment, eventual differences between streamlines need to be investigated, since each streamline has a different distance from the UV lamps.

In the UV reactors, the reaction rate of ozone generation depends only on the power and distance from the UV lamps, regardless of the fluid dynamics, since the concentration of oxygen can be considered constant (Fig. 7 and Fig. 19, Paper IV). However, the movement of the airflow pushes the first ozone molecules generated before the first row of UV lamps toward the outlet. Therefore, both reactors show no significant ozone concentration until the first row of UV lamps (Fig. 26).

![Fig. 26. Ozone concentrations at a central cut plane for (a) the “standard” reactor and (b) the “hexagonal” reactor.](image)

If no ozone is present, no hydroxyl radicals can be generated; therefore there is no VOC oxidation before the first UV lamps (Fig. 20 and 21, Paper IV). The oxidation is also limited after the last row of UV lamps, due to the low concentration of remaining VOC and quick decay of UV irradiation as the air moves away from the lamps. Therefore, most of the acetaldehyde
conversion takes places in the reactor area confined between the UV lamps (Fig. 27).

![Image](image.jpg)

**Fig. 27.** VOC oxidation reaction rates at a central cut plane for (a) the “standard” reactor and (b) the “hexagonal” reactor.

As presented in Fig. 27, the order of magnitude of the oxidation rate is the same for both the reactors. The main reason for the higher conversion for the “hexagonal” reactor is the larger active reactor volume included within the UV lamps. However, this is mostly due the greater number of lamps for this prototype, twelve instead of ten. This result is confirmed by the values of VOC conversion normalized by the number of UV lamps, showing no significant difference between the two reactors. In any case, no important differences in terms of rate of VOC oxidation are observed inside the active reactor region defined by the UV lamps. Therefore, the treatment for each streamline can be considered sufficiently homogeneous, in accordance with the first design criterion.

In conclusion, two simple reactor geometries were simulated following the criteria presented above. No significant differences in terms of process efficiency were observed between the two prototypes. However, even if the study presented in this thesis does not result in a reactor design with higher performance, it still provides relevant considerations for scaling up. The importance of the CFD investigation for evaluating different reactor
configurations is confirmed, given the greater understanding derived from the results of the simulations. By simulating and testing various reactors, it is possible to obtain great savings in terms of the resources needed to scale-up UV reactors. Many ideas can be simulated relatively quickly, especially when compared to performing field tests. Configurations showing fluid dynamic issues or poor performance can be screened out at an earlier stage, without testing them. In addition, the design chosen for a reactor can be fine-tuned using CFD simulation as the air and reactor variables can be modified and controlled very efficiently.
11 Contribution to AOP for VOC abatement

As presented in 1.1, the aim of this thesis is to improve the efficiency of AOP processes for VOC abatement, focusing on the core of the process: the UV reactor (see 3.1). The research work was application-oriented, focusing on the optimization and scale-up of the UV unit, especially by developing modelling tools to enhance understanding of the most relevant features (see Fig. 5 for a more detailed description). The results can be divided into two areas: photocatalysis and modelling of UV-ozone reactors.

The main targeted improvements in terms of photocatalysts were to identify an optimal photocatalyst and a suitable coating method on metals. The results presented in section 7 show that commercial P90 is the most active photocatalyst for the current industrial application. Despite the synthesis of several other photocatalysts, including various synthesis techniques and dopants, none were more active than P90; this is the preferred photocatalyst in both laboratory- and full-scale photocatalytic reactors.

Section 8 investigates several electrochemical treatments to modify surface morphology for a more stable photocatalyst coating. Of all the tested treatments, DC etching on stainless steel was found to be the best at stabilizing the coated TiO$_2$ due to the potholes formed the surface. Tape tests showed that the photocatalyst is strongly bonded to the metal without any additional adhesive, since only 25 % of the coated TiO$_2$ was removed after 12 tape tests. This coating method may thus be implemented for coating P90 in a full-scale reactor, as the mechanical stresses due to the air speed are considered to be less than the stress of the tape tests.

Considering UV-ozone reactors, where the radicals are generated by ozone decomposition, the research was firstly geared to enhancing the understanding of the phenomena governing UV reactors, both on the laboratory scale and prototypes. One highlights from the results is the low
CONTRIBUTION TO AOP FOR VOC ABATEMENT

Absorbance by ozone of the 254 nm wavelength, which limits the efficiency of the UV stage. Including reflected UV light in the reactor when the reactor walls are reflective did not show a significant improvement in terms of VOC conversion. Lastly, the fluid dynamics of the reactors play an important role, especially affecting the local concentrations of ozone and VOC, which have a direct effect on the VOC conversion.

These insights on UV reactors were converted into criteria for optimally designing laboratory- and full-scale reactors. As a first step, the absorbance of the low 254 nm wavelength may be improved by adding an external ozone generator or by using a photocatalytic coating on the reactor walls. However, these options need to be carefully assessed. The former increases both the installation and operational costs, and may thus be detrimental to the overall process efficiency, despite improving performance at the UV stage. The latter needs to consider the mass transfer limitations between the bulk air and the photocatalytic surface before going to a full-scale implementation. In addition, a full-scale reactor needs to optimize the fluid dynamics by ensuring that each streamline has the same intensity and that the airflow moves as a plug, without dead volumes. Lastly, the “reactive area” (section 10) of an UV reactor needs to be assessed and maximized at the design stage.
PART D: CONCLUDING REMARKS
12 Conclusions

This thesis focuses on reducing VOC emissions from industrial plants by using UV-based AOPs. Traditional technologies have significant limitations, and AOPs represent a promising alternative due to the production of hydroxyl radicals at room temperature, resulting in highly reactive conditions. Therefore, AOPs have higher energy efficiency with a lower footprint and costs. However, these technologies still have limitations that prevent widespread application. For instance, the VOC conversion is lower than with traditional technologies, which can achieve complete removal.

The purpose of this work is to improve the overall efficiency of AOPs, resulting in higher VOC conversion without significantly increasing installation and operating costs. As presented in section 1.1, this thesis focuses only on one step in the whole VOC treatment process: the UV reactor. This thesis analyzes two types of UV reactors in order to improve their performance: a photocatalytic reactor and a UV-ozone reactor (see 3.1 for more details about features and differences).

12.1 Photocatalytic reactor design

The first concept for enhancing the performance of a photocatalytic reactor was the identification of an optimal photocatalyst. Many previous studies of photocatalytic VOC abatement [30, 34, 35] were designed to address specific aspects of this technology, and thus the reactor conditions were far from industrial applications. An innovative reactor was therefore designed to reproduce the conditions in real full-scale applications and determine the cost effectiveness of reactors. One of its most important features is a low ratio between the power of the UV lamps and the airflow rate. In addition, the UV irradiation on the photocatalytic surface was homogenized so that
the process could be modelled. Lastly, the reactor allows test samples to be quickly replaced, so that different samples can be easily screened. Significant differences in terms of activity were observed between the tested samples, confirming the suitability of the reactor design for screening photocatalysts. The results showed that commercial P90 is the most active photocatalyst, although other samples were synthesized with dopants and different techniques. Therefore, this type of photocatalyst should be implemented in photocatalytic applications for VOC removal, regardless of the size of the UV reactor.

For a successful industrial application, the photocatalyst needs to be firmly coated on the support, without being removed by abrasion due to the high air speed. Metallic parts such as the reactor walls may be the suitable candidates to support the photocatalyst, and so aluminum and stainless steel were chosen for testing. Several electrochemical treatments were tested on these metals to determine the best method of restructuring the surface morphology and increasing the stability of the coated TiO₂. Of all the tested treatments, DC etching on stainless steel showed the highest coating stabilization, due to the potholes produced on the surface. The coating proved to be stable after several stress tape tests without using any additional adhesive. The activity of the coated photocatalyst is also increased by the higher surface area exposed to the UV light. In conclusion, for a successful industrial application, the P90 photocatalyst can be coated on stainless steel parts of the UV reactor using the DC etching technique, without risking eventual removal of the photocatalyst.

12.2 UV-ozone reactor design

The governing features of UV-ozone reactors were investigated in order to enhance understanding of the phenomena involved. A numerical model was developed to describe the propagation of UV light, including light absorption and light reflection. A kinetic mechanism was developed to
describe ozone generation, depletion, and VOC conversion based on the light absorption rate. This numerical model was then coupled with a fluid dynamics model to investigate the relationship between fluid flow and reactions at a prototype scale. These models were verified against experimental results, showing good agreement, based on the considerations in 9.2. The results highlight some limitations of UV-ozone reactors, such as weak absorption of the 254 nm wavelength, with no significant contribution by the UV light reflected by the reactor walls. This situation may be improved by adding an external ozone generator or by coupling a photocatalytic reactor with a UV-ozone reactor. The fluid dynamics modelling proved to be fundamental for scaling up UV reactors, since the flow pattern strongly affects the ozone and VOC concentration, which has an effect on the VOC conversion. In addition, by investigating the fluid dynamics of prototypes that could be used in full-scale applications, it is possible to obtain a good estimate of their performance. Thus weaker configurations can be weeded out and only the most promising candidates need to be tested experimentally. Even if the work in this thesis does not lead to a particular reactor configuration, it provides criteria relevant for the design of optimal UV reactors for full-scale applications. These criteria can be summarized as follows (see section 10 for more details):

- all the process streamlines should undergo the same treatment;
- stagnation zones and bypasses should be minimized;
- even when there are complex flow patterns, plug flow for the air streamlines is desirable.
13 Outlook

Since AOP-based technologies for VOC abatement are relatively young, there is much to be done in the future. The most relevant suggestions, with regard to overall process efficiency are reported below.

A large part of future research should be devoted to modelling and scaling up UV-ozone reactors. The design criteria and model from this thesis should be implemented to design new prototypes for higher VOC conversion. These reactor configurations should be experimentally tested in order to further verify model accuracy. If the model validity is confirmed, the design process should be repeated at full-scale.

A similar modelling approach should be applied to photocatalytic reactors. However, more fundamental work will be required as the modelling of this type of reactor was not dealt with in this thesis. The phenomena governing photocatalytic reactors at laboratory scale should be elucidated, especially as regards the mass transfer limitations between the bulk air and the photocatalytic surface. The assessment of the catalytic area exposed to the UV irradiation also requires special attention.

Once photocatalytic laboratory reactors have been modelled, implementation of this knowledge in a UV-ozone reactor should also be considered. A scaling-up process similar to that for UV-ozone reactors, should be carried out using the photocatalytic model developed, screening prototypes and full-scale configurations prior to the experimental tests. If the photocatalyst is implemented in a UV-ozone reactor, the aim of this scaling-up process should be the evaluation of the benefits in terms of VOC conversion derived from using the photocatalyst in full-scale reactors. If the photocatalyst is not used, the photocatalytic and UV-ozone reactors should be compared at full-scale to determine their performance and cost effectiveness.
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15 References


