

# Stoichiometry and Kinetics of Hydroxyl Radicals in Air Quality

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**Abstract**— *The environmental health that nature offers us every day is closely linked to the sanitization provided by atmospheric chemistry, due to the oxidative processes that occur under the powerful sunlight passing through the clouds and reaching the forests, oceans, and seas, performs the multiple reactions, recombinations, mineralizations, degradations etc. in the atmosphere. It is a chain reaction called Open Air Factor (OAF) that cleans and disinfects the environment in which all living beings live called the biosphere.*

*There are technologies and elements necessary to be able to imitate nature in this process of environmental sanitization for indoor environments based precisely on the Open Air Factor (OAF), and for this, for a question of safety and efficiency, it is necessary to measure the quantitative proportions or mass ratios of the chemical elements involved and that are involved in this natural chemical reaction, as well as to study the proportion of the various resulting elements and the composition of chemical mixtures of the components.*

*The comparison of this stoichiometry that nature provides us with similar artificial systems for interiors will give us a vision of how similar the processes and resultants are.*

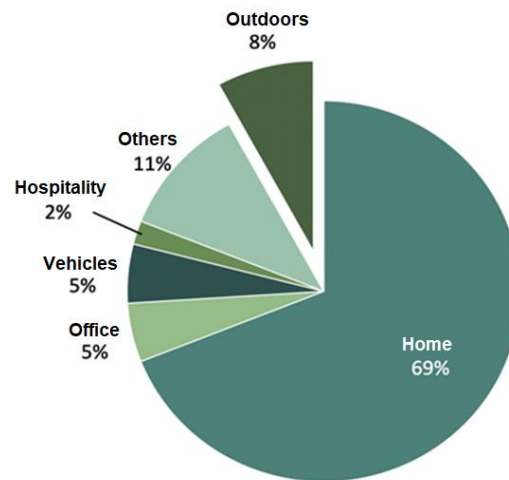
*This paper is based on the stoichiometry and kinetics of hydroxyl radicals emitted by a device technologically based on the Open Air Factor (OAF) aimed at controlling indoor air quality.*

*Specifically, it has been the analysis of the decay of the number of molecules of hydroxyl radicals ( $\text{OH}\cdot$ ) when reacting in the presence of typical air pollutants such as  $\text{CO}_2$ , hydrocarbons and bicarbonate ions. These amounts of hydroxyl radical molecules ( $\text{OH}\cdot$ ) under study, unlike the multiple reactants that exist in Nature, have been generated with only two reactants, hydrogen peroxide and ozone, following current international safety regulations regarding their emissions in the presence of people.*

**Keywords**— *Hydroxyl radicals ( $\text{OH}\cdot$ ); Volatile Organic Compounds (VOC's), Advanced Oxidation Process (AOP's), Indoor Air Quality (IAQ), Indoor Air Pollution (IAP), Open Air Factor (OAF), reactive oxygen species (ROS's).*

## I. INTRODUCTION

Air quality is closely related to good health. Although in general terms more importance has been given to outdoors air quality, due to urbanization, humans now spend more than 90% of their time indoors (**Figure 1**), which corresponds to more than 10,000 liters of air breathed per day.



**FIGURE 1: Fraction of average time spent in each space in a day according to US Environmental Protection Agency data [1]**

Indoor air can be up to ten times more polluted than outdoors resulting in poor Indoor Air Quality (IAQ), which poses a risk for the development or worsening of diseases as well as decreased productivity (resulting in economic charges) [1] [2]. Nearly 4 million people die each year from illnesses attributed to indoor air pollutants (IAP), which can exacerbate pre-existing acute allergy-type diseases such as dermatitis or rhinitis, and play a role in the development of respiratory diseases such as pneumonia, asthma or chronic obstructive pulmonary disease (COPD) and non-respiratory diseases such as heart attacks or cancer [3] [4]. IAPs include biological agents (viruses, bacteria, and fungi), as well as chemical agents and combustion products, the most relevant being particulate matter (PM) (e.g. smoke), volatile organic compounds (VOCs), carbon oxides (CO<sub>x</sub>), nitrogen (NO<sub>x</sub>) or sulfur (SO<sub>x</sub>), radon and ROS (Reactive Oxygen Species).

Ozone is one of the ROS and this gas can be emitted from any type of household appliance or device (e.g. microwave, television, photocopier, oven, discharge lamps such as tubular fluorescent lamps) by means of the so-called corona effect. This effect is an electrical phenomenon produced by the ionization of the gas surrounding a charged conductor. It occurs spontaneously on high-voltage lines and manifests itself in the form of a luminous halo [5] [6].

Due to the oxidation reactions generated by ozone in organic compounds (especially terpenes, present in perfumes and cleaning products), secondary non-volatile organic compounds are produced in aerosols (SOA) even more dangerous than the primary ones [2] [7] [8] [9].

Although air does not contain indigenous microbiota, it acts as a dispersal medium for a large number of microorganisms such as may be the cause of the recent Sars-CoV2 pandemic. Most microorganisms (including bacteria, viruses and fungi) are transmitted by bioaerosols, airborne particles that are dispersed in the air and when expelled (e.g. by talking, coughing, sneezing, etc.) contain more than 90% water, which evaporates according to the temperature and relative humidity of the environment until it is reduced in size and consists of microorganisms or parts of microorganisms and inorganic ions [10].

The IAQ is highly dependent on three factors [8] [11]:

- (1) the activities carried out by the occupants (e.g. emission of tobacco smoke, fragrances, cleaning products, cooking odors). Individually, we can contribute to improving the IAQ at home by reducing the source of pollutants, i.e., controlling the activities we carry out to minimize their emissions, although this is not always possible.
- (2) the intrinsic characteristics of the building (e.g. building materials, furnishings, ventilation capacity, presence of air conditioners). There is a set of symptoms and diseases attributed to poor IAQ called "building related illnesses", which are divided into Building related illness (BRI) if the causative agent can be identified, usually biological (e.g. legionellosis) but can also be chemical (e.g. hypersensitivity pneumonitis) or, in Building related illness (BRI) if the causative agent can be identified, usually biological (e.g. legionellosis) but can also be chemical (e.g. hypersensitivity pneumonitis). Sick Building Syndrome (SBB) if general environmental contamination is the trigger for the symptoms, which include irritation of mucous membranes (e.g. eye), neurotoxic effects (e.g. fatigue), asthma and the like (e.g. chest tightness) among others.



In the 60s it was determined that rural air had powerful germicidal properties, termed Open Air Factor (OAF). Druett et al. attributed this ability to the ozone-olefin complex, an organic compound previously identified in the composition of air that we now refer to as an alkene (hydrocarbon with double bonds) [21]. A couple of years later, Dark et al. verified that peroxide hybrid ions (now known as Criegee biradicals) formed in the ozonolysis of various alkenes were responsible for the significant but variable inactivation of two microorganisms and thus the active agent of OAF [22]. Very little work has been done on AOF since then, and although the disinfection capacity of AOF (greater than that of ozone) has been confirmed, no further information on the identity of the active agent has been provided [23] [24] [25].

According to current information, the cycle addition of ozone to an alkene (both in the gas phase) attacks the double bond and forms an unstable primary ozonide, which evolves generating radical intermediates called Criegee biradicals [26]. Although biradicals can theoretically decompose via three pathways, evidence rules out two of them occurring naturally in the environment: the removal of an oxygen atom from their structure is not feasible at room temperature and pressure, and radical formation, a consequence of the rearrangement of the biradical into an unstable ester, has not been detected [27] [28]. The decomposition of the biradical by the remaining pathway, through its rearrangement into a hydroperoxide, is considered an important source of generation of hydroxyl radicals ( $\text{OH}\cdot$ ), the major natural oxidant in the troposphere [29]. Could  $\text{OH}\cdot$  then be the active agent of OAF?

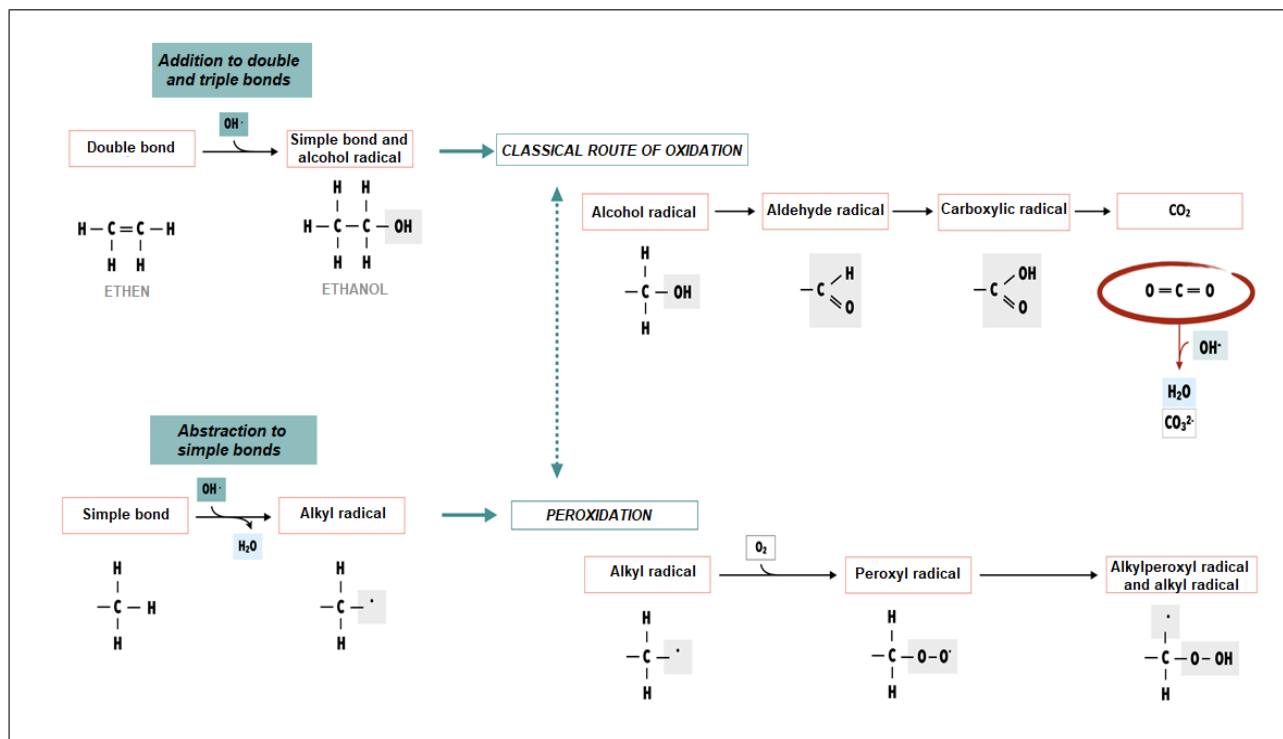
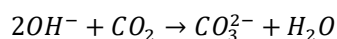
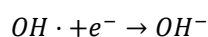
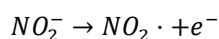
## 1.2 THE OXIDATION

Chemically  $\text{OH}\cdot$  is a free radical, which together with ions are the two main sources of chemical instability. Both species present anomalies in electrons and to return to equilibrium they need to react with others, which generates a cascade of instability in which other species, called instability precursors, participate. Ions present charge imbalance in their chemical structure, they have either an excess or a deficit of electrons: those species that have lost electrons (the cations) are electropositively charged (oxidized), while those that have gained electrons (the anions) are electronegatively charged (reduced). It is a dynamic and compensated system: due to the theft of an electron, one species is in the reduced (-) state when it leaves another in the oxidized (+) state. On the other hand, free radicals have a spin imbalance in their structure, i.e. they have some unpaired electrons, so they are much more reactive than ions. Radicals are electrically neutral by itself, so they do not seek to compensate their charge, but quickly steal an electron to compensate their spin, oxidizing without selectivity.

$\text{OH}\cdot$  react with organic compounds in 3 different ways:

- (1) by electron transfer, generating charge imbalance in the molecule with which it reacts and allowing the formation of new bonds and links. Finally, these structures lose their conformation and three-dimensional structure.
- (2) by addition to aromatic rings or double or triple bonds in unsaturated hydrocarbons, which breaks these bonds and generates an alcohol radical ( $-\text{OH}$ ) in the chain. These unstable radicals in organic compounds are incorporated in the classical oxidation pathway, until they become mineralized: the structures lose organic matter in the form of carbon dioxide ( $\text{CO}_2$ ) (**Figure 3**) [30].
- (3) by abstraction of a hydrogen in saturated hydrocarbons, resulting in a water molecule and a free alkyl radical ( $\text{R}\cdot$ ) in the organic compound [31]. The presence of an alkyl radical initiates the peroxidation process, where by incorporation and interaction of species a positive feedback of irreversible damage is generated in the molecule. Other radicals can also form in the chain (e.g. alkoxy radicals ( $\text{RO}\cdot$ )) that are transformed by decomposition, isomerization or hydrolysis, leading to the formation of oxygenated compounds (e.g. alcohols, carbonyls (aldehydes or ketones), carboxylic acids) that are incorporated into the classical oxidation pathway (**Figure 3**) [9] [32].

The remaining  $\text{CO}_2$  present at the end of these mineralizations is eventually transformed into carbonate or bicarbonate, oxygen and water, depending on the ambient humidity. This degradation is related to an indirect reaction between  $\text{OH}\cdot$  and  $\text{CO}_2$ , which occurs by the instantaneous uptake of an electron by the radical (part of the Fenton process) in an environment contaminated with  $\text{NO}_2$ . The resulting hydroxyl anion ( $\text{OH}^-$ ) is responsible for the formation of carbonate ions upon reaction with  $\text{CO}_2$  [33].



**FIGURE 3. The incorporation of an oxygen molecule ( $O_2$ ) into the alkyl radical ( $R \cdot$ ) gives rise to the peroxy radical ( $ROO \cdot$ ) in the organic compound, which can subsequently isomerize by stealing the hydrogen from a nearby carbon, transforming it into a hydroperoxide radical ( $ROOH$ ) and generating another alkyl radical in the chain ( $R \cdot$ ). [Own source]**

### 1.2.1 Mineralization, transformation, and precipitation of pollutant compounds

Due to the relevance of IAQ control, WHO developed guidelines recommending safe exposure limits for selected HAPs: formaldehyde and other VOCs (benzene, naphthalene, benzo[a]pyrene, trichloroethylene and tetrachloroethylene), radon, particulate matter (PM), carbon monoxide and nitrogen dioxide [4].

VOCs include all those hydrocarbons ("organic compounds") that occur in a gaseous state ("volatile") at room temperature.  $OH \cdot$  reacts with them by abstraction and addition, mineralizing them and decreasing their concentration indoors. Among the VOCs, the most important are **alkenes**, due to the danger that their accumulation poses to health, as well as the SOAs generated by their reaction with ozone, which is attacked by  $OH \cdot$  through addition or abstraction of a hydrogen, initiating its mineralization; **formaldehyde**, one of the SOAs generated by ozonolysis, especially of terpenes and highly flammable, with a strong and penetrating odor, soluble in water and very volatile, which is incorporated in phase 3 of the oxidation cascade of organic compounds (**Figure 3**); and **odoriferous molecules**, lipophilic and small chemical compounds perceptible by our sense of smell that usually contain nitrogen in addition to hydrogen and carbon, which due to the presence of nitrogen we will also obtain ammonia or another similar compound as a product of mineralization [34]. Due to its high reactivity, the reaction time of  $OH \cdot$  for the mineralization of most VOCs is generally shorter than the corresponding time for other oxidizing agents such as  $NO_3$  radicals and ozone, reducing the mineralization time of some organic compounds from years to days, even hours (**Table 1**).

**TABLE 1**  
**HALF-LIFE OF SOME VOCs WHEN REACTING WITH OH<sup>•</sup>, NO<sub>3</sub><sup>-</sup> AND O<sub>3</sub> IN THE GASEOUS STATE [35].**

VOC	Lifetime due to reaction with:		
	OH <sup>•</sup> radicals	NO <sub>3</sub> radicals	O <sub>3</sub>
Acetaldehyde	8.8 hr	17 d	>4.5 yr
Acrolein	6.9 hr	4.2 d	57 d
Benzene	9.4 d	>4 yr	>4.5 yr
Ethane	47 d	>12 yr	>4500 yr
Ethanol	3.6 d	23 d	--
Ethene	1.4 d	225 d	10 d
Formaldehyde	1.2 d	80 d	>4.5 yr
n-Octane	1.3 d	240 d	>4500 yr
Phenol	5.1 hr	9 min	~50 d
Propane	10 d	7 yr	>4500 yr
Propene	5.3 hr	4.9 d	1.6 d
Styrene	2.4 hr	22 min	1.0 d
Toluene	1.9 d	1.9 yr	>4.5 yr

On the other hand, OH<sup>•</sup> interacts with rhodon gas and PM (suspended volatile particles generally of undetermined composition of sulfates, nitrates, ammonia, sodium chloride, elemental carbon, mineral dust, water and even inorganic compounds such as dust or sand) by electron transfer, being electrostatically captured and agglomerated by its strong electrostatic charge, and subsequently precipitated to the ground with a sufficient size to be collected. In addition, the accumulation of carbon, nitrogen and sulfur oxides is prevented by promoting their natural cyclic oxidation [34].

### 1.2.2 Inactivation of microorganisms

Microorganisms, as well as all living matter, are made up of organic molecules (mainly hydrocarbon chains (H-C)) that are mineralized by a sequence of free oxidative reactions to obtain mainly CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. Although OH<sup>•</sup> acts non-selectively on all microorganisms present in water, air and surface, the morbid effect of OH<sup>•</sup> on each of them is due to their sensitivity to oxidation [36]. This sensitivity depends on which organic macromolecules make up its outermost structures and which, therefore, interact with the environmental OH<sup>•</sup>. There are 4 groups of macromolecules: the nucleic acids that make up the genetic material and the glucids, lipids and proteins that make up the structures that surround it. Of these last three, lipids and proteins are the macromolecules sensitive to oxidation.

According to their outermost layer, viruses can be non-enveloped (they present a protein capsid) or enveloped (over the capsid there is a lipid bilayer with glycoproteins); bacteria are classified as gram-positive (they present a thick proteoglycan wall) and gram-negative (over the wall there is a lipid bilayer with lipopolysaccharides); while fungi and yeasts (unicellular fungi) present in their outermost layer a wall formed by chitin and glucans from which glycoproteins protrude (**Figure 4**) [37].

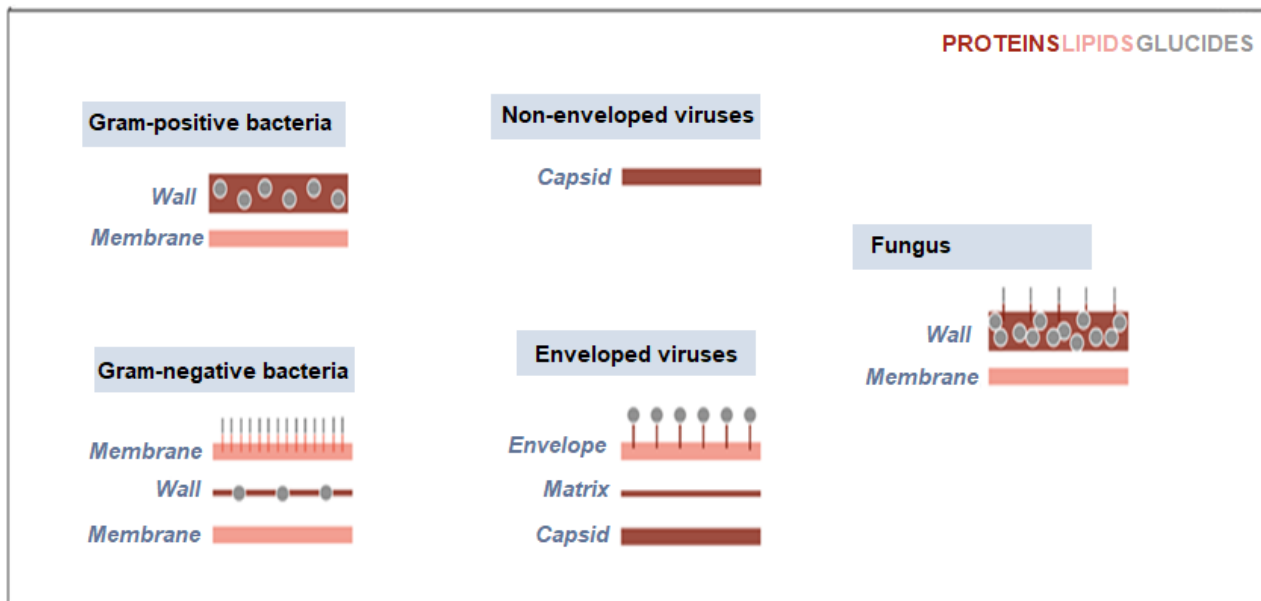


FIGURE 4: Structural composition of pathogens. [Own source]

**Lipids** are mainly composed of unsaturated hydrocarbon chains that react with  $\text{OH}\cdot$  either by addition breaking the double and triple bonds generating alcohol radicals ( $-\text{OH}$ ) that will be incorporated into the oxidation pathway or by abstraction of a hydrogen generating alkyl, peroxy and finally hydroperoxides radicals. Mineralization and peroxidation of lipid membranes modify their spatial distribution and consequently their structure. On the other hand, **proteins** are composed of amino acids and  $\text{OH}\cdot$  can alter their charges by electron transfer. This modifies their 3D structure and leads to protein fragmentation and can form disulfide (covalent) bonds between amino acids, resulting in intra- and interprotein bonds, so that the protein loses its conformation. In both cases, proteins form aggregates and lose their correct structure.

These irreversible structural alterations created in lipids and proteins through  $\text{OH}\cdot$  promoted oxidation lead to the loss of the integrity of the structures that envelop the microorganisms, and consequently the loss of their viability and functionality.

## II. MATERIALS Y METHODS

### 2.1 Selection of Items

The literature review was carried out using the PubMed website, aiming to answer the question formulated at the beginning of this study: **What are the main atmospheric reactions involved in the formation of hydroxyl radicals from advanced oxidation processes, and how do they evolve over time?**

The search strategy for scientific articles on the use of  $\text{OH}\cdot$  as a participating agent in advanced oxidation processes, both for the mineralization of volatile organic compounds and the inactivation of microorganisms, was divided into two main criteria in order to find scientific evidence for the guarantee of a high indoor air quality.

The first criterion was based on focusing the search on atmospheric oxidation processes involving ozone, since it is one of the main pathways for reactions between ROS that occur in air, with the intervention of  $\text{OH}\cdot$  as an atmospheric detergent. This search could provide information on the proportion of reactants that optimizes the degree of environmental oxidation, as well as the speed of the reaction and information about the reaction products. It is also expected to find a medical device that uses ozone as the initiator of the chain of environmental reactions produced by  $\text{OH}\cdot$ . Thus, the MeSH Terms used in PubMed were as follows: {atmosphere AND ozone} AND {oxidation reduction}. A total of 91 papers were found.

The second criterion tried to narrow down the atmospheric reactions in the analysis of reactive oxygen species in general, in such a way that the transient evolution and steady-state concentration of  $\text{OH}\cdot$  against all reagents and organic compounds present in the air could be estimated, using both stochastic models and real experiments. The outcome of this second search would define the current conception of  $\text{OH}\cdot$  as a harmless agent and mineralizer of volatile organic compounds, with the aim of guaranteeing environmental quality. In this case, the MeSH Terms used in PubMed were as follows: {atmosphere/chemistry OR atmosphere/metabolism OR atmosphere/analysis} AND {reactive oxygen species}. A total of 38 papers were found.

In both search strategies, the scientific production was also limited to the last 5 years of publication in order to avoid the existence of determinant changes within the field of advanced oxidation processes, in addition to filtering the results by *Abstract*, in order to speed up the analysis of inclusion or exclusion of the paper in the final selection of publications.

In general terms, out of a total of 129 papers, all those following the criteria detailed below were included. The papers should include reactions as close as possible to those found in nature, where  $\text{OH}\cdot$  arises from the reaction between ozone and hydrogen peroxide, both naturally and photocatalytically initiated. Likewise, reactions of  $\text{OH}\cdot$  with various common environmental pollutants should also be collected, describing the rate of reaction development. Therefore, any publication that did not include the above information was not considered.

Complementary to the inclusion criteria, the exclusion criteria considered that the study of mineralization of some very particular and rare volatile organic component in the atmosphere was excluded. Finally, the titles referring to oxidation processes in liquid water media were also discarded, since the behavior of the reactions in liquid media is not analogous for the guarantee of a high level of environmental quality.

Once the articles were filtered according to the inclusion and exclusion criteria previously indicated, 37 of the 129 papers were finally selected and classified into the categories shown in Table 2.

**TABLE 2**  
**SUMMARY OF THE SELECTION OF SCIENTIFIC ARTICLES PUBLISHED DURING THE LAST 5 YEARS.**

Branch of study	Number of selected papers
Stoichiometric study of the reaction of ozone with hydrogen peroxide for the generation of $\text{OH}\cdot$ radicals.	7
Kinetic study of $\text{OH}\cdot$ concentration versus environmental reactions for the mineralization of volatile organic compounds and hydrocarbons.	11
Other items of general interest for the study.	19

In order to reduce the *risk of bias* and avoid distortion of the outcome of the *systematic review* process, the inclusion/exclusion criteria applied to the papers were obtained from a double parallel review of the entire set of articles, providing titles that had been discarded in the first instance. Likewise, the search of the *papers* aimed to collect the amounts of  $\text{OH}\cdot$  emitted, thus resulting in a numerical question. The articles found and selected according to the 3 criteria mentioned above reflect the diversity of both natural and laboratory-tested reactions, and provide us with the quantification of the  $\text{OH}\cdot$  emission, which will be used to give comparative values to the stoichiometric and kinetic calculations proposed in this article.

## 2.2 Objectives and Hypotheses of Mathematical Formulation

The generic purpose of the present study is to validate two theoretical models about the generation of hydroxyl radicals (hereinafter,  $\text{OH}\cdot$ ), produced by an OAF generator device, and subsequently emitted to the environment. For this purpose, two studies of maximum  $\text{OH}\cdot$  generation will be carried out in parallel, one stoichiometric in gas phase (study of the reactions produced in the device) and the other kinetic without air renewal (with and without device) only subject to the environmental chain reactions present (study external to the device). The hydroxyl radical emission results of the theoretical model will also be compared with the results of other publications, which report  $\text{OH}\cdot$  radical emissions.

In both stoichiometric and kinetic studies, mathematical formulas have been used, as well as physical constants and chemical reactions, subject to certain assumptions that will be detailed below.

Specifically, for the stoichiometric study, the three specific objectives consist of: 1° the calculation of the concentration of  $\text{OH}\cdot$  emitted according to the concentration of the reactants involved, 2° the study of the theoretical efficiency of the reaction and 3° the analysis of the theoretical residues of the reaction. In this stoichiometric study the capacity of the reaction between ozone ( $\text{O}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) both in gas phase will be analyzed, which will allow to calculate in a theoretical way the concentration of  $\text{OH}\cdot$  emitted, as well as the presence of the excess quantities of ozone and hydrogen peroxide. This will make it possible to verify compliance with the legal emission limits for these reagents after 8h, whose values are established by international organizations as 1 ppm and 0,05 ppm for hydrogen peroxide and ozone, respectively. Therefore, it is assumed



that both reagents will only participate in this reaction, without the intervention of any parallel or parasitic reaction, both in gas phase, to produce hydroxyl radicals in addition to the environmental ones that are always artificially present by default.

Hydrogen peroxide and ozone are present in gas phase. The amount of ozone is controlled by a generator that produces a fixed amount of 0,04 mg/h, while the peroxide has been obtained in gas phase by convective evaporation of a peroxide solution of known purity, by capillarity through a polyester wick that will be responsible for the evaporation. With a volume of 35 mL of solution, a constant evaporation of 0,39 mL/day is measured, based on calculations obtained in previous experiences with the OAF generator device, resulting in a total evaporation time of 90 days. During the stoichiometric calculation process, the density of both reactants in gas phase corresponding to room temperature is considered. Also, the reaction efficiency will be considered as the theoretical yield at stoichiometric level.

On the other hand, the specific objectives for the kinetic study consist of the analysis of the temporal evolution of the concentration of OH· in an environment, starting from the concentration of the usual components of nature. The evolution of the OH· concentration will be estimated over a time period of 30 minutes, starting from the ambient concentrations of the reagents, in a space of 300 m<sup>3</sup> volume occupied by 1 and 50 people and without air renewal, in order to check that the calculation of the artificial generation of OH· is in accordance with its natural generation. This evolution will be compared with an analogous case, where there is an external source of OH· by means of an OAF generating device, where, on the basis of previous experiences, an additional contribution of OH· by the device of  $2,84 \cdot 10^7 \text{ molec} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$  is assumed. In this kinetic study, the volume is considered to be completely isolated from the outside, and as indicated above, it will be 300 m<sup>3</sup>.

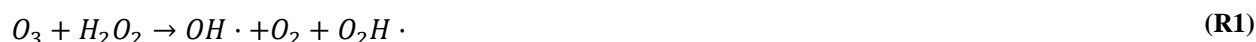
The concentration inside the 300 m<sup>3</sup> isolated volume will be based on standard ambient levels of CO<sub>2</sub>, VOCs, HC, etc. outdoors. The involvement of OH· with volatile organic compounds, viruses, bacteria, water, hydrocarbons, carbon dioxide, carbonates, bicarbonates, carbon monoxide, oxygen, hydrogen peroxide and ozone, which are involved is considered. Also, the oxidation of carbon dioxide to carbonates and bicarbonates is assumed by the presence of NO<sub>2</sub><sup>-</sup> ions in the environment, facilitating the production of the Fenton process.

Finally, in the case studies where 1 or 50 people are considered inside the 300 m<sup>3</sup> isolated volume, an additional contribution of carbon dioxide will be considered only, due to the exhalation of the CO<sub>2</sub> people. This extra CO<sub>2</sub> input shall be defined by the average lung capacity of a human being, giving a magnitude to the exhaled volume of air, which includes a small portion of carbon dioxide. The human being shall be considered to be approximately 100 times the inhaled concentration of CO<sub>2</sub> in the instant immediately preceding exhalation.

## 2.3 Theoretical Model

### 2.3.1 Stechiometric Study

This section will analyze the ability of the following reaction at stoichiometric level to generate OH· radicals in compliance with the legal emission limits of the reactants both in gas phase. O<sub>3</sub> will be produced by a generator and H<sub>2</sub>O<sub>2</sub> will be obtained by convective evaporation of liquid hydrogen peroxide in contact with a polyester wick.



In this way, the following physical constants will be considered:

- Volume of liquid hydrogen peroxide: 35 mL.
- Evaporation of hydrogen peroxide: 0,39 mL/day.
- Duration of the hydrogen peroxide tank: 90 days.

In addition, the legal emission limits for each reagent are as follows:

- Maximum exposure time of hydrogen peroxide: 8h (1 ppm).
- Maximum O<sub>3</sub> exposure time: 8h (0,05 ppm).

On the other hand, the degrees of freedom to be used for the study of OH· generation are the following:

- Purity of liquid hydrogen peroxide  $p$ , in %.
- Volume of the enclosure area where the reaction takes place  $V$ , in m<sup>3</sup>.
- Initial O<sub>3</sub> concentration  $c$ , in ppm.

The steps carried out to calculate the concentration of OH· emitted according to the concentrations of the reagents, represented as degrees of freedom (c, p and V expressed in ppm, % and m<sup>3</sup>, respectively), are shown below, as well as the resulting formula that will allow the OH· concentration to be represented graphically by modifying these values at will.

#### A. Calculation of the [OH·] emitted according to the concentration of reagents

In order to calculate the concentration of the OH· radical emission, the ozone concentration (initially in parts per million) is first expressed as the concentration of the amount of substance per unit volume, in mol/cm<sup>3</sup>. This initial calculation is shown in the following equation, where the density of ozone at ambient temperature has been used:

$$c[\text{ppm}_{\text{O}_3}] \cdot \frac{1\text{m}^3\text{O}_3}{10^6\text{m}^3\text{air}} \cdot \frac{2,14[\text{kg}]}{1[\text{m}^3\text{O}_3]} \cdot \frac{1000[\text{g}]}{1[\text{kg}]} \cdot \frac{1[\text{mol}]}{48[\text{g}]} \cdot \frac{1[\text{m}^3]}{10^6[\text{cm}^3]} = 4,167c \cdot 10^{-11}[\text{mol}/\text{cm}^3] \quad (\text{R2})$$

Then, the previous value is also expressed per unit of time, using as a reference a value of 8h, representing the exposure time to a certain ppm of ozone:

$$c(\text{O}_3) = \frac{4,167c \cdot 10^{-11}[\text{mol}/\text{cm}^3]}{8 \cdot 3600[\text{s}]} = 1,447c \cdot 10^{-15}[\text{mol}/(\text{cm}^3 \cdot \text{s})] \quad (\text{R3})$$

On the other hand, starting from the initial volume of hydrogen peroxide, as well as the density (which, in general, is a function of the peroxide purity), this volume is converted into the amount of peroxide substance at the start of the reaction, as shown in the following equation. Despite conceiving density as a purity-dependent variable, it has been empirically determined that the value of the average or effective density for different purities was found to be approximately invariant, as follows  $\rho_{ef} \approx 1,08\text{g}/\text{ml}$ .

$$35[\text{ml}_{\text{H}_2\text{O}_2}] \cdot \rho(p) \left[ \frac{\text{g}}{\text{ml}_{\text{H}_2\text{O}_2}} \right] \cdot \left( \frac{p}{100} \right) \cdot \frac{1[\text{mol}]}{34[\text{g}]} \equiv 0,011p[\text{mol}] \quad (\text{R4})$$

The concentration of the peroxide involved in the reaction is then expressed per unit volume and time, analogous to the case of ozone. In this case, the volumetric concentration is expressed using the volume of the enclosure area where the reaction takes place. The reference time is the duration of a 35 mL tank of peroxide, which turns out to be 90 days, based on previous experience with the OAF generating device.

$$c(\text{H}_2\text{O}_2) = \frac{0,011p[\text{mol}]}{V \cdot 10^6[\text{cm}^3] \cdot 90 \cdot 24 \cdot 3600[\text{s}]} = 1,430 \frac{p}{V} \cdot 10^{-15}[\text{mol}/(\text{cm}^3 \cdot \text{s})] \quad (\text{R5})$$

The limiting reagent (LR) is the reagent that is used up first and, consequently, determines how much product can be obtained against the excess reagent (RE). Using the 1:1 stoichiometry between reactant-product of R1 and Avogadro's number to convert moles to molecules, the amount of OH· emitted can finally be expressed in terms of the limiting reagent:

$$c(\text{OH} \cdot) \left[ \frac{\text{mol}\cdot\text{c}}{\text{cm}^3 \cdot \text{s}} \right] = c^{RL} \left[ \frac{\text{mol}}{\text{cm}^3 \cdot \text{s}} \right] \cdot 6,022 \cdot 10^{23} \left[ \frac{\text{mol}\cdot\text{c}}{\text{mol}} \right] \quad (\text{R6})$$

#### B. Study of the theoretical efficiency of the reaction

The theoretical efficiency of a reaction is defined as the capacity of the reaction to consume all the reactants as far as possible and at stoichiometric level, without taking into account the other external factors that occur in reality (additional evaporations, impurities...). Therefore, it will only depend on the deviation of the ratio between the reactants, with respect to the ideal stoichiometric ratio.  $c_i^{RE}$ ,  $c_f^{RE}$ , represent the initial and final concentration, respectively, of the excess reagent, being the component with the highest concentration at the start of the reaction.

$$\eta_t = \frac{c_i^{RE} - c_f^{RE}}{c_i^{RE}} \cdot 100 \quad (\text{R7})$$

### C. Analysis of reaction residues

According to the theoretical efficiency, the residues of the reaction (or final mixture), the final concentration of each reagent have been calculated in order to justify the regulation on the concentration of these reagents. Both values shall be expressed in ppm and an exposure time of 8 hours.

$$r(O_3) = (c(O_3) - c^{RL}) \cdot 8 \cdot 3600[s] \cdot 48 \left[ \frac{g}{mol} \right] \cdot 10^6 \left[ \frac{cm^3}{m^3} \right] \cdot \frac{1[m^3 O_3]}{2140[g]} \cdot \frac{1[ppm]}{1m^3/10^6m^3} \quad (R8)$$

$$r(H_2O_2) = (c(H_2O_2) - c^{RL}) \cdot 8 \cdot 3600[s] \cdot 34 \left[ \frac{g}{mol} \right] \cdot 10^6 \left[ \frac{cm^3}{m^3} \right] \cdot \frac{1[m^3 H_2O_2]}{1386[g]} \cdot \frac{1[ppm]}{1m^3/10^6m^3} \quad (R9)$$

#### 2.3.2 Kinetic Study

In this section, the evolution over time of the concentration of hydroxyl radicals in a closed volume, starting from a concentration equal to the ambient concentration, will be estimated. Inside the enclosure area, one or more persons will be placed exhaling CO<sub>2</sub>, without air renewal. This evolution will also be compared with an analogous case where there is also an external source of hydroxyl radicals by means of an OAF generating device. In any case, the various environmental chain reactions will be taken into consideration.

As a first approximation to the resolution of the time evolution of radicals in a closed and isolated volume, only those reactions involved in producing or eradicating radicals have been considered. These are those corresponding to carbon dioxide, hydrocarbons, bicarbonates, and carbon monoxide. It should be noted that the lifetime of OH· reactions with various volatile organic compounds is reduced in contrast to other reagents, such as O<sub>3</sub> and NO<sub>3</sub>, justifying the effectiveness of OH· for the speed of pollutant eradication [27] [38] [39].

The **chain reactions** that generate or consume OH· cover the compounds shown in section 1.3, in particular in Figure 3, where the whole oxidation process provided by the OAF-generating device is schematized.

The following situations are identified:

- Volatile organic compounds react with radicals to generate carbon dioxide.
- Viruses and bacteria react with radicals to generate water.
- Various hydrocarbons can react with the radicals to generate carbon dioxide.
- Bicarbonates react with radicals to produce carbonates.
- Carbon monoxide can react with radicals to produce carbon dioxide.
- Oxygen reacts with radicals to produce ozone and water.
- Hydrogen peroxide reacts with radicals to produce ozone and water.
- Water reacts with radicals to produce hydrogen peroxide.

With all the reactions to be simulated exposed, the initial atmosphere of the closed control volume (of 300 m<sup>3</sup>) is defined [40] [41] [42] [43].

First, equation R10 shows the initial or ambient concentration of hydroxyl radicals within the isolated volume of 300 m<sup>3</sup> (without air renewal), expressed in molec/cm<sup>3</sup>.

$$[OH \cdot]: 10^7 \frac{molec OH \cdot}{cm^3} \quad (R10)$$

Secondly, equation R11 shows the initial or ambient concentration of carbon dioxide inside the isolated volume of 300m<sup>3</sup> (without air renewal), expressed in ppm. Subsequently, this value is expressed in molec/cm<sup>3</sup> through the gas density.

$$[CO_2]: 412ppmCO_2 \cdot \frac{1m^3 CO_2}{10^6 m^3 air} \cdot \frac{1,98kg}{1m^3} \cdot \frac{1000g}{1kg} \cdot \frac{1mol}{44g} \cdot \frac{1m^3}{10^6 cm^3} \cdot \frac{6,022 \cdot 10^{23} molec}{1mol} \approx 10^{16} \frac{molec CO_2}{cm^3} \quad (R11)$$

Thirdly, equation R12 shows the average initial or ambient hydrocarbon concentration inside the 300 m<sup>3</sup> isolated volume (without air renewal), expressed in ppb.

$$[\text{Hydrocarbons}]_m: 26,9 \text{ppbHC} \quad (\text{R12})$$

Finally, equation R13 shows the initial or ambient concentration of carbon monoxide inside the isolated volume of  $300\text{m}^3$  (without air renewal), expressed in  $\text{mg}/\text{m}^3$ . Subsequently, this value is expressed in  $\text{molec}/\text{cm}^3$ .

$$[\text{CO}]: 0,115 \frac{\text{mgCO}}{\text{m}^3} \cdot \frac{1\text{g}}{1000\text{mg}} \cdot \frac{1\text{mol}}{28\text{g}} \cdot \frac{1\text{m}^3}{10^6\text{cm}^3} \cdot \frac{6,022 \cdot 10^{23}\text{molec}}{1\text{mol}} \approx 2,47 \cdot 10^{12} \frac{\text{molec CO}}{\text{cm}^3} \quad (\text{R13})$$

The  $\text{OH}^\cdot$  emission rate by the OAF generating device is that corresponding to a purity of 4.95%:

$$X = 2,84 \cdot 10^7 \frac{\text{molec}}{\text{cm}^3 \cdot \text{s}} \quad (\text{R14})$$

On the other hand, the **lung capacity of a human** being will be taken into account in order to give magnitude to the exhaled volume of air, which partly includes a small portion of carbon dioxide. In concrete terms, the total capacity of a person is 4,6 liters of air, of which 1,6 liters is exhaled. The 4% of the exhaled volume represents the fraction of carbon dioxide that has been emitted by the individual. Taking into consideration that the human being multiplies the inhaled concentration of  $\text{CO}_2$  approximately by 100, and considering the total volume of the room where he is, it will be possible to estimate the variation of carbon dioxide produced in the control volume, together with the chain reactions. Finally, an average of 16 exhalations per minute will be considered [44] [45] [46] [47].

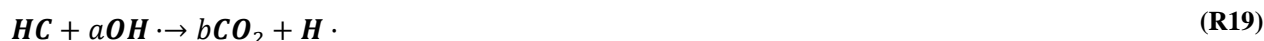
Firstly, an indirect reaction between hydroxyl radicals and carbon dioxide can occur by the instantaneous uptake of an electron in a heavily  $\text{NO}_2^\cdot$  polluted environment, such that carbonate ions are obtained from the reaction of carbon dioxide with hydroxyl ions [48] [49] [31].



The combination of the above reactions gives the following overall expression:



Thus, it should be noted that carbon dioxide represents the dominant reaction in the evolution of  $\text{OH}^\cdot$  over time. In fact, hydrocarbons and carbon monoxide react with radicals (separately) to produce the same carbon dioxide, and bicarbonates to produce carbonates. The higher the  $\text{CO}_2$  concentration, the higher the consumption of radicals compared to the production of radicals in other reactions. The theoretical reactions of the above process are as follows:[50]



The differential equations governing the kinetics of each reaction have been found to follow first and second order laws. In each expression the terms  $[\text{X}]$  indicate the concentration of the reactant or product X in  $\text{molec}\cdot\text{cm}^{-3}$ , and the chemical kinetic constants of the reaction k in  $\text{cm}^3\cdot\text{molec}^{-1}\cdot\text{s}^{-1}$ . [51]

The different theoretical reactions are shown in (R18) through (R21). The corresponding differential equations governing the kinetics for each case are those shown in (R22) to (R25).

$$\frac{d[\text{CO}_2]}{dt} = -k_A[\text{CO}_2][\text{OH}^\cdot] \quad [52] \quad (\text{R22})$$

$$\frac{d[\text{HC}]}{dt} = -k_B[\text{HC}][\text{OH}^\cdot] \quad [53] \quad (\text{R23})$$

$$\frac{d[\text{HCO}_3^-]}{dt} = -k_C[\text{OH}^\cdot][\text{HCO}_3^-] \quad [54] \quad (\text{R24})$$

$$\frac{d[\text{OH}^\cdot]}{dt} = -k_D[\text{OH}^\cdot] \quad [55] \quad (\text{R25})$$

With all this, we can obtain the global resolution of the system of differential equations that will allow us to calculate the  $[\text{OH}^\cdot]$  emitted (R26). The letters A-D refer to the different reactions considered (A corresponds to the variation of radicals referring

to the reaction with carbon dioxide, B to hydrocarbons, C to bicarbonates and D to carbon monoxide). In addition, the character  $i$  refers to the assessment of the magnitude in the  $i$  –ésimo instant of time, being  $i = 1$  the initial condition. The above expression is only valid in the absence of external  $\text{OH}\cdot$  sources.

$$[\text{OH}\cdot]_{f,i} = [\text{OH}\cdot]_{f,i-1} + d[\text{OH}\cdot]_A + d[\text{OH}\cdot]_B + d[\text{OH}\cdot]_C + d[\text{OH}\cdot]_D \quad (\text{R26})$$

In the case of inclusion of an  $\text{OH}\cdot$  source, the  $[\text{OH}\cdot]$  emitted shall be calculated according to R27, where  $X$  is the rate of radical emission produced by the OAF generating device.

$$[\text{OH}\cdot]_{w,i} = [\text{OH}\cdot]_{f,i} + Xdt \quad (\text{R27})$$

Finally, it will also be necessary to define the numerical resolution of the rest of the compounds present in the air, since the infinitesimal variation of the  $\text{OH}\cdot$  radical at an instant of time  $i$  will depend on the concentration of the other compounds at the same instant. For example, in the case of carbon dioxide:

$$[\text{CO}_2]_i = [\text{CO}_2]_{i-1} + d[\text{CO}_2]_A + d[\text{CO}_2]_B + d[\text{CO}_2]_D + d[\text{CO}_2]_{\text{people},i} \quad (\text{R28})$$

In this case, the reaction linked to bicarbonates does not contribute, as it neither consumes nor produces  $\text{CO}_2$ . Note that the additional term is included  $d[\text{CO}_2]_{\text{people},i}$ , relating to the increase in carbon dioxide due to the exhalation of air by a group of people:

$$d[\text{CO}_2]_{\text{people},i} = [\text{CO}_2]_i - [\text{CO}_2]_{i-1} = \frac{N_p[\text{CO}_2]_{i-1}f_aV_{ex}^{CO_2} + [\text{CO}_2]_{i-1}(V - V_{ex}^{CO_2})}{V} - [\text{CO}_2]_{i-1} \quad (\text{R29})$$

$$d[\text{CO}_2]_{\text{people},i} = N_p[\text{CO}_2]_{i-1} \frac{(f_a - 1)V_{ex}(p_c/100)}{V} = N_p[\text{CO}_2]_{i-1} \cdot 2,112 \cdot 10^{-5} \quad (\text{R30})$$

In the previous expression,  $N_p$  is the number of persons present inside the enclosed volume,  $f_a$  the amplifying factor of the carbon dioxide concentration produced by a human being (it is considered  $f_a = 100$ ),  $V_{ex}$  the exhaled volume of air exhaled by a human being (it is considered  $V_{ex} = 1,6L$ ),  $p_c$  the percentage of  $\text{CO}_2$  in the exhaled volume of air (according to WHO,  $p_c = 4\%$ ) y  $V$  the volume of the enclosure area ( $V = 300000L$ ).

Once the time distribution of the  $\text{OH}\cdot$  has been obtained by evaluating the expressions from the instant  $i = 1$  to  $i = i_{max}$ , it is possible to obtain the rate of generation of these by means of the numerical derivative with respect to time. The instant  $i = i_{max}$  is linked to the final instant of time  $t = T$ .

To meaningfully compare the difference between the case of 1 and 50 persons, the average increase in  $\text{OH}\cdot$  concentration with the activated OAF generator device will be calculated. This is equivalent to the calculation of the area between the two curves on  $\text{OH}\cdot$  radical emission with the activated and non-activated OAF generator device, weighted over time (numerical integral):

$$\Delta[\text{OH}\cdot] = \frac{1}{T} \int_0^T ([\text{OH}\cdot]_w - [\text{OH}\cdot]_f) dt \quad (\text{R31})$$

$$\Delta[\text{OH}\cdot] \simeq \frac{\Delta t}{2T} \sum_{i=1}^{n_t-1} ([\text{OH}\cdot]_{w,i} + [\text{OH}\cdot]_{w,i+1} - [\text{OH}\cdot]_{f,i} - [\text{OH}\cdot]_{f,i+1}) \quad (\text{R32})$$

## 2.4 Results of the Theoretical Model (Data Analysis)

### 2.4.1 Stoichiometric Study

The results deduced for the stoichiometric study are given below. These have been obtained using the expressions R3, R5, R6, R7, R8 and R9, given in the previous section, altering the 3 degrees of freedom:  $c$  (initial ozone concentration),  $p$  (purity of the 35 mL hydrogen peroxide solution),  $V$  (volume of the enclosed area where the reaction takes place). A fixed volume study was carried out on the one hand, and a fixed ozone concentration study on the other hand.

Firstly, the results according to the fixed volume model ( $\text{OH}\cdot$  emission, theoretical efficiency, and residues) have been calculated for two magnitudes:  $300 \text{ m}^3$  and  $8 \text{ m}^3$ . These values represent the room where the reaction would take place (once the reaction starts, the volume is considered constant).

For each volume value, the remaining two degrees of freedom have been iteratively altered: the concentration of ozone inside (in ppm) and the purity of the 35 mL tank of hydrogen peroxide (in %). In general, those combinations of both degrees of freedom that result in an efficiency close to 100% would imply minimization of reaction residues and maximum OH· emission.

#### A. Calculation of the [OH·] emitted according to the reagent concentration

**Table 3** shows the concentration of hydroxyl radicals emitted for a fixed volume of 300 m<sup>3</sup> and 8 m<sup>3</sup> as a function of the alteration of the two remaining degrees of freedom: peroxide purity and initial ozone concentration. In general, it can be observed that the sensitivity of the emission to the change in peroxide purity or ozone concentration is always positive, until a constant emission value is reached. That is, if for example the evolution of the radical emission along a column of ozone concentration is analyzed, the radical emission would always increase with purity up to the point where ozone becomes the limiting reagent, where the radical emission would be constant for further changes in purity. The analysis would be completely analogous for each row of peroxide purity.

**TABLE 3**

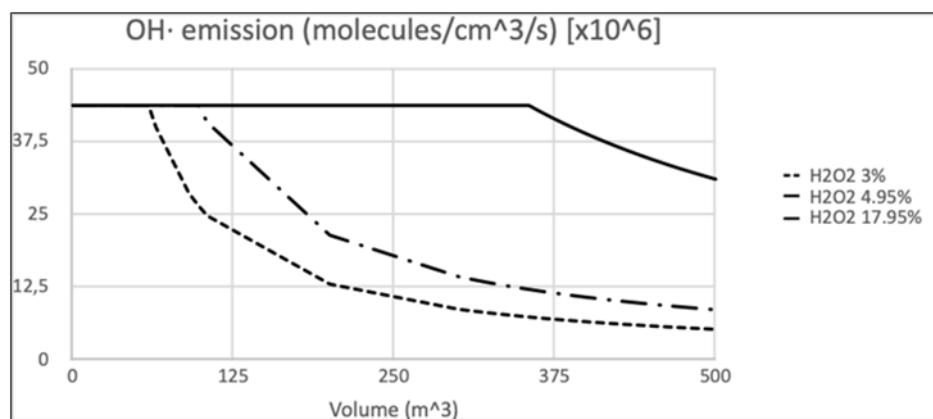
**Results of hydroxyl radical emission in the reaction of ozone with hydrogen peroxide (fixed volumes). Natural emissions measured according to absorption spectrum air-water/gas interface measurements report, spectroscopic signatures of ozone at air-water interface and photochemistry implications [56] – At cloudy day (air-water):  $0,21 \cdot 10^{10}$  molecules per cm<sup>3</sup> per second; at gas phase:  $(0,7 - 10) \cdot 10^6$  molecules per cm<sup>3</sup> per second.**

$x10^6 \frac{\text{molec OH} \cdot}{\text{cm}^3 \cdot \text{s}}$	O <sub>3</sub>	300 m <sup>3</sup>					8 m <sup>3</sup>				
		0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm	0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm
H <sub>2</sub> O <sub>2</sub>											
0,25%		0,72	0,72	0,72	0,72	0,72	26,91	26,91	26,91	26,91	26,91
0,50%		1,43	1,43	1,43	1,43	1,43	43,56	53,81	53,81	53,81	53,81
0,75%		2,15	2,15	2,15	2,15	2,15	43,56	80,72	80,72	80,72	80,72
3,00%		8,61	8,61	8,61	8,61	8,61	43,56	130,69	261,37	322,87	322,87
4,95%		14,21	14,21	14,21	14,21	14,21	43,56	130,69	261,37	532,74	532,74
17,95%		43,56	51,52	51,52	51,52	51,52	43,56	130,69	261,37	609,87	784,11

The graph in **Figure 5** shows the evolution of the OH· radical emission for an ozone concentration of 0,05 ppm, as a function of the alteration of the two remaining degrees of freedom: the peroxide purity and the volume where the reaction takes place. It can be seen that the radical emission (per unit volume) is constant for small space enclosures, defining ozone as the limiting reagent.

However, as the volume where the reaction takes place increases, there comes a point where the specific radical emission starts to decrease, as hydrogen peroxide becomes the limiting reagent. The explanation for this decay rate lies in the fact that the peroxide reagent figure is given in absolute terms, as opposed to the ozone specification as a volumetric concentration, implying the generation of the same number of OH· molecules, but in an increasing volume.

Finally, as the peroxide purity increases, the onset of the specific emission drop is delayed in proportion to the magnitude of the increase in reacted H<sub>2</sub>O<sub>2</sub>.



**FIGURE 5: Results of the emission of hydroxyl radicals in the reaction of ozone with hydrogen peroxide using the previously justified formulation. Emission as a function of volume for different values of hydrogen peroxide purity and constant ozone concentration at 0,05 ppm (legal maximum for 8 hours)**

On the other hand, it can be observed that for all volume values, there is always an emission of radicals of the order of  $10^6$  both measured and calculated [56].

#### B. Study of the theoretical efficiency of the reaction

**Table 4** shows the theoretical efficiency of the reaction for a fixed volume of  $300 \text{ m}^3$  and  $8 \text{ m}^3$ , depending on the alteration of the two remaining degrees of freedom: peroxide purity and initial ozone concentration. In line with the results of the radical emission, the maximum theoretical efficiency is obtained for those combinations of reagents that provide the maximum possible emission value, with the minimum residual of ozone and hydrogen peroxide.

Thus, a low efficiency value may imply that the radical emission is very low, and the presence of reagent residues is notorious. However, it is also possible that a low efficiency value is associated with a maximum emission, but not optimized by the large amount of residues present.

**TABLE 4**

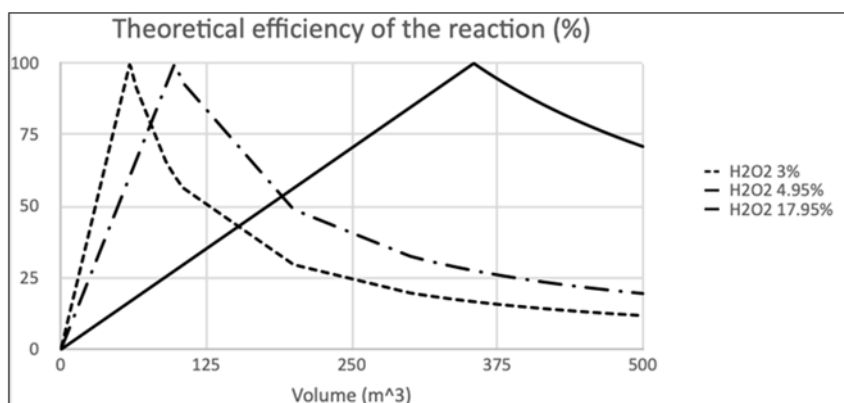
**THEORETICAL REACTION EFFICIENCY AS A FUNCTION OF VOLUME AND FOR DIFFERENT PURITY VALUES (FIXED VOLUMES).**

%	$\text{O}_3$	$300 \text{ m}^3$					$8 \text{ m}^3$				
		0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm	0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm
$\text{H}_2\text{O}_2$											
0,25%		1,65	0,55	0,27	0,12	0,09	61,76	20,59	10,29	4,41	3,43
0,50%		3,29	1,10	0,55	0,24	0,18	80,95	41,18	20,59	8,82	6,86
0,75%		4,94	1,65	0,82	0,35	0,27	53,97	61,76	30,88	13,24	10,29
3,00%		8,61	6,59	3,29	1,41	1,10	13,49	40,48	80,95	52,94	41,38
4,95%		32,61	10,97	5,44	2,33	1,81	8,18	24,53	49,06	87,35	67,94
17,95%		84,56	39,42	19,71	8,45	6,57	2,25	6,76	13,52	31,57	40,59

The graph in **figure 6** shows the evolution of the theoretical efficiency of the reaction between ozone and hydrogen peroxide for an ozone concentration of 0,05 ppm, as a function of the alteration of the two remaining degrees of freedom: the purity of the peroxide and the volume where the reaction takes place. A maximum theoretical efficiency at a given volume can be observed in each curve. On the other hand, in the volumetric range where ozone is the limiting reagent (below the respective optimum volume) the efficiency starts to grow until it reaches 100% theoretical, when it then decreases, defining peroxide as the new limiting reagent. In this way, and linking the present graph with the previous one, an efficiency of 100% would indicate a maximum emission of  $\text{OH}\cdot$ , while minimizing the final reaction mixture. For a volume lower than each optimum value

( $V < V_{opt}$ ) the specific radical emission is still the maximum, but this is not optimized in terms of the amount of peroxide left over after the reaction.

Setting the ozone concentration value at 0,05 ppm (legal limit), it can be seen that a larger volume of the enclosure is required to obtain optimum efficiency as the purity of the hydrogen peroxide used increases. In other words, for each purity value there is an optimum volume where the reaction takes place. Likewise, the possible use of 17,95% peroxide is justified for enclosures with a large volume (around 350 m<sup>3</sup>).



**FIGURE 6: Results of the theoretical efficiency of the ozone reaction with hydrogen peroxide. Value as a function of volume for different values of hydrogen peroxide purity and constant ozone concentration at 0.05 ppm (legal maximum for 8 hours)**

### C. Residues analysis of the reaction

**Table 5** shows the results for ozone and hydrogen peroxide residuals for a fixed volume of 300 m<sup>3</sup> and 8 m<sup>3</sup>, expressed in ppm per 8h, as a function of the alteration of the two remaining degrees of freedom: peroxide purity and initial ozone concentration. Note how the highest efficiency values coincide with the respective lowest residual values. Also, the presence of residual defines which of the two reagents corresponds to the excess part, whose value depends on the extent to which the initial mixture of reagents departs from the ideal stoichiometric ratio.

It is important to identify which regions of the theoretical reaction efficiency are associated with ppm residues above a certain reference value, which could be the legal limit set by the competent bodies at international level.

**TABLE 5**

**Results of the residues, or final mixture, in the reaction of ozone with hydrogen peroxide (fixed volumes). Ozone (O<sub>3</sub>) emissions: Maximum emission recommended by WHO, OSHA, FDA of 0,05 ppm by volume. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) emissions: OSHA recommended maximum emission of 1 ppm (8 hour time-weighted average) [12] [57] [58].**

%	O <sub>3</sub>	300 m <sup>3</sup>					8 m <sup>3</sup>				
		0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm	0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm
H <sub>2</sub> O <sub>2</sub>											
0,25%		0,049 (O <sub>3</sub> )	0,149 (O <sub>3</sub> )	0,299 (O <sub>3</sub> )	0,699 (O <sub>3</sub> )	0,899 (O <sub>3</sub> )	0,019 (O <sub>3</sub> )	0,119 (O <sub>3</sub> )	0,269 (O <sub>3</sub> )	0,669 (O <sub>3</sub> )	0,869 (O <sub>3</sub> )
0,50%		0,048 (O <sub>3</sub> )	0,148 (O <sub>3</sub> )	0,298 (O <sub>3</sub> )	0,698 (O <sub>3</sub> )	0,898 (O <sub>3</sub> )	0,012 (H <sub>2</sub> O <sub>2</sub> )	0,088 (O <sub>3</sub> )	0,238 (O <sub>3</sub> )	0,638 (O <sub>3</sub> )	0,838 (O <sub>3</sub> )
0,75%		0,048 (O <sub>3</sub> )	0,148 (O <sub>3</sub> )	0,298 (O <sub>3</sub> )	0,698 (O <sub>3</sub> )	0,898 (O <sub>3</sub> )	0,044 (H <sub>2</sub> O <sub>2</sub> )	0,057 (O <sub>3</sub> )	0,207 (O <sub>3</sub> )	0,607 (O <sub>3</sub> )	0,807 (O <sub>3</sub> )
3,00%		0,040 (O <sub>3</sub> )	0,140 (O <sub>3</sub> )	0,290 (O <sub>3</sub> )	0,690 (O <sub>3</sub> )	0,890 (O <sub>3</sub> )	0,327 (H <sub>2</sub> O <sub>2</sub> )	0,225 (H <sub>2</sub> O <sub>2</sub> )	0,072 (H <sub>2</sub> O <sub>2</sub> )	0,329 (O <sub>3</sub> )	0,529 (O <sub>3</sub> )
4,95%		0,034 (O <sub>3</sub> )	0,134 (O <sub>3</sub> )	0,284 (O <sub>3</sub> )	0,684 (O <sub>3</sub> )	0,884 (O <sub>3</sub> )	0,573 (H <sub>2</sub> O <sub>2</sub> )	0,471 (H <sub>2</sub> O <sub>2</sub> )	0,318 (H <sub>2</sub> O <sub>2</sub> )	0,089 (O <sub>3</sub> )	0,289 (O <sub>3</sub> )
17,95%		0,009 (H <sub>2</sub> O <sub>2</sub> )	0,091 (O <sub>3</sub> )	0,241 (O <sub>3</sub> )	0,641 (O <sub>3</sub> )	0,841 (O <sub>3</sub> )	2,211 (H <sub>2</sub> O <sub>2</sub> )	2,109 (H <sub>2</sub> O <sub>2</sub> )	1,956 (H <sub>2</sub> O <sub>2</sub> )	1,548 (H <sub>2</sub> O <sub>2</sub> )	1,344 (H <sub>2</sub> O <sub>2</sub> )

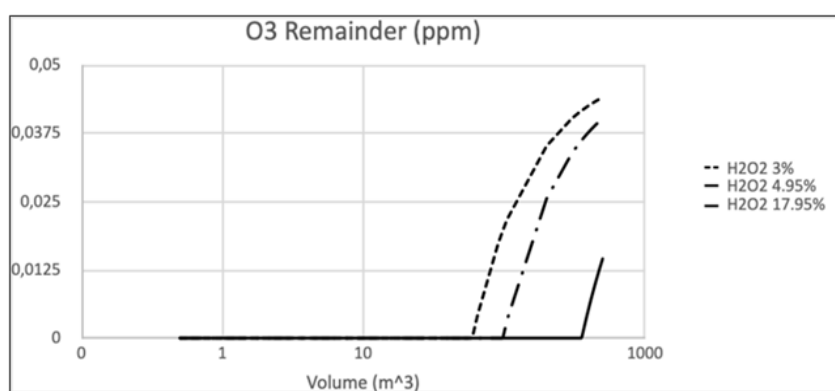


For ozone, the maximum recommended emission for WHO, OSHA, FDA is 0,05 ppm by volume. For hydrogen peroxide, the maximum emission recommended by OSHA is 1 ppm by volume.

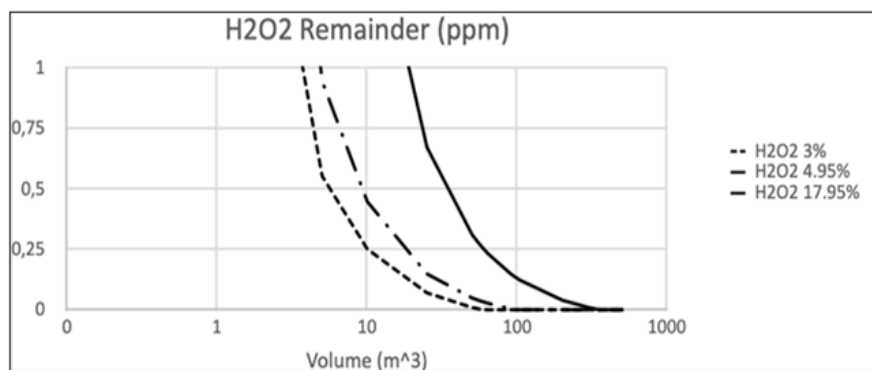
For this reason, and according to the regulations governing the maximum ppm for ozone and hydrogen peroxide, for large volumes (300 m<sup>3</sup>) a hydrogen peroxide of 17,95% purity should be used, whereas for small volumes (8 m<sup>3</sup>), a peroxide of 4,95% purity should be used.

The graphs in **Figure 7 and Figure 8** show the evolution of the residuals of the reaction between ozone and hydrogen peroxide, expressed in ppm per 8h, for an ozone concentration of 0,05 ppm and as a function of the alteration of the two remaining degrees of freedom: the purity of the peroxide and the volume where the reaction takes place. Linking these last two graphs with the previous ones, it can be seen how both residuals are zero at the optimum volumes corresponding to 100% efficiency, increasing as the volume of the room deviates from the optimum situation.

With regard to the reaction residues, starting from an initial ozone concentration equal to its maximum legal limit (0,05 ppm), this will never be exceeded. However, it should be noted that the hydrogen peroxide residues are lower than the legal limit of 1 ppm from a certain volume value for each purity. In other words, choosing a volume for the reaction lower than the minimum required value (corresponding to the 1 ppm residue) for a given purity value would imply non-compliance with the regulation.



**FIGURE 7: Ozone residues as a function of volume and for different purity values according to the results of the theoretical reaction efficiency. Ozone concentration constant at 0,05 ppm (legal maximum for 8 hours).**



**FIGURE 8: Residues of hydrogen peroxide as a function of volume and for different purity values according to the results of the theoretical reaction efficiency. Ozone concentration constant at 0,05 ppm (legal maximum for 8 hours).**

## 2.5 Kinetic Study

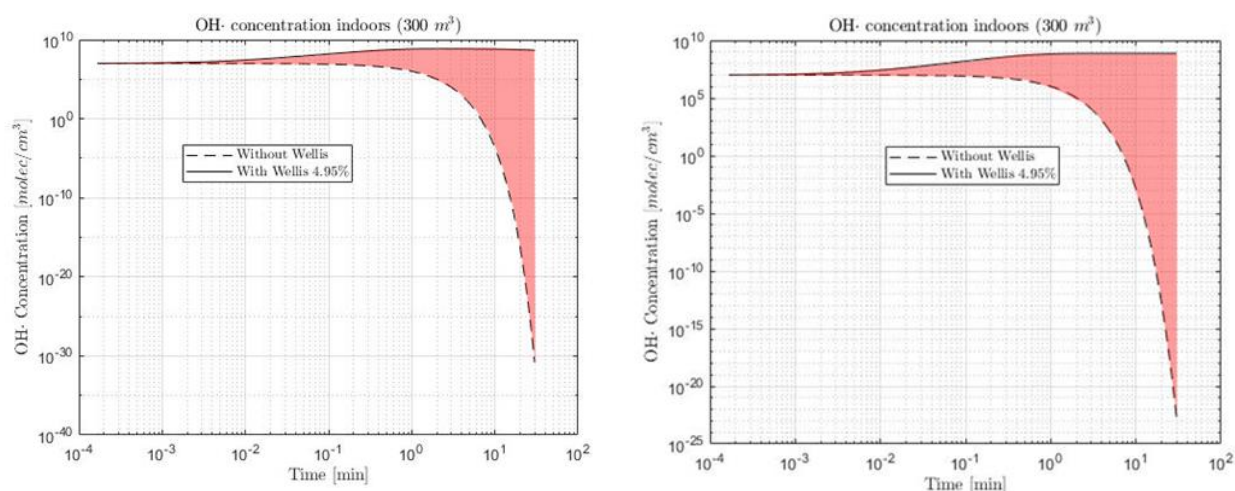
The final results for the kinetic study are presented below. These have been obtained using the expressions R22-R32, presented in the previous section, and evaluated for all time instants. Specifically, the differential equations have been integrated for a time span of 30 minutes, considering the initial conditions of the concentrations of the environmental reagents indicated in R10-R13. First of all, the chemical kinetic constants of the various reagents involved are shown in the following table:

**TABLE 6**  
**RATE CONSTANTS FOR THE REACTION OF OH RADICALS WITH CONSIDERED REAGENTS [52] [53] [54].**

Compound	Rate Constant · 10 <sup>-12</sup> [cm <sup>3</sup> /(molec·s)]
n-Butane	2.16E-12
n-Pentane	3.73E-12
n-Hexane	5.33E-12
n-Heptane	6.94E-12
n-Octane	8.84E-12
n-Nonane	11.8E-12
Benzene	1.08E-12
Toluene	5.69E-12
Carbon dioxide	9.77E-18
Bicarbonate ions	1.41E-14

This study is carried out for a single volume of 300 m<sup>3</sup> (without air renewal), during the 30 minutes of simulation and for two analogous cases with the presence of 1 or 50 people, as could be the case in an entertainment hall, in order to observe the impact of the exhalation of CO<sub>2</sub> from multiple people. For each of these two cases, the increase in radiative emission obtained by using the OAF generator device is compared with the case of natural evolution.

The graphs in **Figure 9** show the evolution of the hydroxyl radical concentration over time for 1 and 50 persons respectively. In addition, each graph compares the case with and without activation of the HFO generator device. The data have been obtained as a function of the initial concentration of the environmental reagents, integrating the system of differential equations and identifying the contribution for the case of OH·, as stated in R26 or R27. However, it should be noted that these expressions are dependent on the instantaneous concentration of the rest of the reagents, which will also be evaluated in each iteration of the time integration.



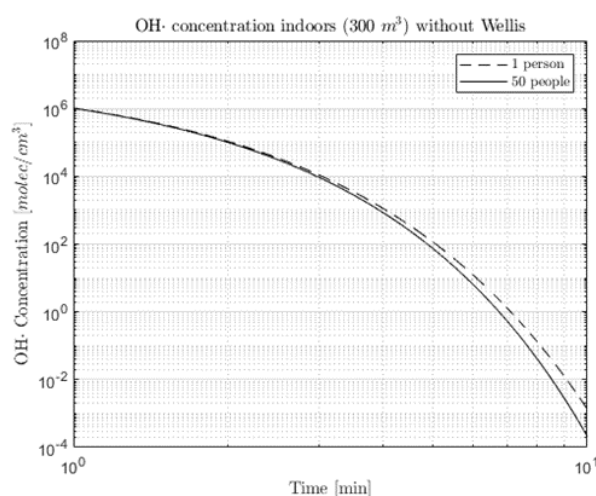
**FIGURE 9: Time evolution of OH· in free air in the absence and presence of a source of radicals ("Wellis"), in the presence of 1 person (A) or 50 persons (B), taking into account an adult physiology in the frequency and value of carbon dioxide emission.**

It can be observed that the concentration of radicals tends to zero in the absence of the device in both cases, 1 and 50 people, which is justifiable due to the lack of air renewal (the environmental reactions would end up consuming all the radicals). The incorporation of the OAF generating device helps to maintain (and even increase) the OH· concentration in this isolated

enclosure without air renewal. In order to give magnitude to the difference between the 1 and 50 person case, and due to the similarity between the two graphs, the emission gain by the OAF generator device will be quantitatively estimated with respect to the no device case, for both the 1 and 50 person cases. Specifically, the post-processing expressions R31 and R32 above will be applied, using the previously calculated results, giving rise to the following values that indicate the average increase in emission obtained by activating the device:

$$\Delta[OH \cdot]_{N_p=1} = 7.372 \cdot 10^8 \frac{\text{molec}}{\text{cm}^3} \quad \Delta[OH \cdot]_{N_p=50} = 5.911 \cdot 10^8 \frac{\text{molec}}{\text{cm}^3}$$

Note how the increase in emission for the 50 person case is lower than the emission corresponding to 1 person, thus indicating that a higher CO<sub>2</sub> exhalation implies a higher consumption of OH· radicals, as stated in the theoretical model. Finally, this effect can also be seen in **Figure 10**, where only the natural fall of OH· is compared between the cases of 1 and 50 persons, using the results already represented in the previous figure.



**FIGURE 10: Time evolution of OH· for 1 and 50 people, in the absence of a radicals source.**

Again, in the 1 person case the concentration of OH· radicals are always higher than in the analogous 50 person case, as the exhalation of carbon dioxide is lower and consequently the fall of radicals is later. Quantitatively, the magnitude of difference between the 1 and 50 person cases is shown in the following table for the 1 and 10 minute times. Although initially the OH· decay is almost identical, at 10 minutes it is estimated that the radical emission with less CO<sub>2</sub> would be 6,3 times higher than the case with 50 people contributing to the exhalation.

**TABLE 7**  
**COMPARISON OF OH· EMISSION FOR 1 AND 50 PERSONS AT T=1MIN, T=10MIN.**

	1 person	50 people	$r = 1p/50p$
$t = 1min$	$1,034 \cdot 10^6$ [molec/cm <sup>3</sup> ]	$1,017 \cdot 10^6$ [molec/cm <sup>3</sup> ]	1,017
$t = 10min$	$1,35 \cdot 10^{-3}$ [molec/cm <sup>3</sup> ]	$2,14 \cdot 10^{-4}$ [molec/cm <sup>3</sup> ]	6,308

### III. DISCUSSION

Throughout this article, on the one hand, we have tried to answer the question posed at the beginning: What are the main atmospheric reactions involved in the formation of hydroxyl radicals from advanced oxidation processes and how do they evolve over time? With the results obtained, it has been possible to mathematically estimate that the outdoors concentration of OH·, which corresponds to its stationary or equilibrium concentration determined by the natural capacity of this species to transform into other species, is of the order of 10<sup>6</sup> molecules/cm<sup>3</sup> [15], [59]. The involvement of solar irradiation in the generation of OH· is noteworthy, as is the role of water in atmospheric chemistry, as clouds occupy 15% of the troposphere. The reaction rate in the aqueous phase is higher than in the gas phase (they occur earlier and faster), so each droplet acts as a small reactor where photochemically excited species are produced and generate radical species through energy transfer

reactions, such as  $\text{OH}\cdot$  [31]. For this reason, the atmospheric concentration of  $\text{OH}\cdot$  varies between  $10^5$  and  $10^{10}$  molecules/cm<sup>3</sup> [56] and peaks of higher concentration are observed on very sunny days and on rainy days.

With the current information, it has been determined that the main source of  $\text{OH}\cdot$  outdoors, accounting for 70% of its generation, is ozone photolysis at wavelengths below 320 nm [40]. On the other hand, its indoors concentration is somewhat lower than outdoors, in the order of  $10^5$  molecules/cm<sup>3</sup>, and its major source is the ozonolysis of alkenes, although the photolysis of nitrous acid (HONO) and formaldehyde (HCHO) is also relevant [20] [48]. Oxidation reactions between ozone and organic compounds (mainly terpenes present in perfumes and cleaning products), produce secondary non-volatile organic compounds in aerosols (SOA) even more dangerous than primary ones, such as formaldehyde [2] [8] [9] [31]. The accumulation of SOA and VOCs indoors is of strong concern due to their effect on human health, an accumulation that does not reach high concentrations in spaces where POA devices are safely used due to the constant promotion of oxidation [12] [20].

On the other hand, for the development of this article, different tests have been carried out, where different concentrations of hydrogen peroxide from 0,25% to 17,95% have been used, and it has been studied how it influences the reaction with 0,05ppm of ozone (**Maximum recommended emission by WHO, OSHA, FDA**), both in a volume of 300 m<sup>3</sup> and in a volume of 8 m<sup>3</sup>. Therefore, the complex reality of the chemical composition of our ambient air has been modelled as involving only two reactants: hydrogen peroxide and ozone, using a subsequent mathematical and analytical method for the final measurement of  $\text{OH}\cdot$ . If you look at figure 6, you can see that for large volumes you would have to use 17,95% hydrogen peroxide as it does not exceed the maximum limit recommended by OSHA of 1 ppm hydrogen peroxide. On the other hand, for small volumes, it can be seen that 4,95% hydrogen peroxide would have to be used, as 17,95% would exceed the maximum permitted limit. In addition, it can also be seen in figure 5, the drop in the emission of hydroxyl radicals where, as the purity of the hydrogen peroxide increases, this drop is delayed.

Finally, with regard to the kinetic study, the general presence of hydrocarbons, carbon dioxide and  $\text{HCO}_3^-$  ions have also been taken into consideration as factors to be taken into account in the rate of evolution of  $\text{OH}\cdot$  concentration over time. Although a more realistic model has been chosen, it is still far from reality. In this case, the differential equations governing the kinetics of chemical reactions in the environment have been solved by numerical methods as an instantaneous measure of the  $\text{OH}\cdot$  concentration. In general, the efficiency of the OAF generator device can be observed, since when this device is used, the hydroxyl radicals are maintained throughout the entire test.

Numerical techniques have been used as a method to measure  $\text{OH}\cdot$ , given the defined model. Therefore, it is necessary to finish corroborating that the present model - preliminarily utopian - gives results consistent with other more realistic models and more experimental measurement methods.

In relation to the models of other studies, it is found that in general all authors conclude that the atmospheric sanitization is dominated by the participation of ozone and the subsequent production of  $\text{OH}\cdot$  e.g. by hydrogen peroxide. However, some  $\text{OH}\cdot$  degradation products do appear in some cases. For example, in one study the participation of other pesticides, such as chlordecone and beta-hex-achlorocyclohexane, is considered, and although they seem to show a much lower reactivity than ozone in the Fenton process, the component hydrochlordecone is obtained as a possible additional degradation product to be considered [60]. On the other hand, a promising UV/O<sub>3</sub> reactor was designed in another study for the degradation of Reactive Blue K-GL (RB), a dye used in the textile industry, and singlet oxygen concentrations are found as the primary species during mineralization, where  $\text{OH}\cdot$  played an indispensable role [61]. However, in general the role of oxygen as a migratory agent in VOC mineralization processes at low temperature is fully confirmed [62]. Therefore, as a first iteration it is fully consistent to model the environment as the key involvement of ozone and hydrogen peroxide, having a suitable environment for the Fenton effect to occur. Also, in other studies it can be seen how with the help of a catalyst and VUV (vacuum ultraviolet) irradiation, it is possible to transform ozone into reactive oxygen species and  $\text{OH}\cdot$ , improving the effectiveness in the mineralization of some VOCs [63]. Finally, a study shows how the kinetics of atmospheric oxidation of aniline (AN) initiated by  $\text{OH}\cdot$  indicates that the dominant chain under atmospheric conditions is the inclusion of OH in one of the rings of AN [64].

In relation to the measurement techniques of other studies we can mainly find a widely used experimental method. The FAGE (Fluorescence Assay with Gas Expansion) technique is used in atmospheric studies, as it provides high sensitivity and selectivity for the species of the present study. In addition, the technique is relatively fast and non-destructive, which makes it suitable for real-time measurements in field situations. The technique is based on the property of certain chemical species to fluoresce when excited with ultraviolet (UV) light. The basic principle involves expanding an air sample through a region of ultraviolet laser light. The laser light is adjusted to a specific wavelength that matches the excitation of the molecules of the target species. When passing through the laser region, the molecules present in the sample are excited and emit fluorescence

[65]. In that study using FAGE, a concentration of  $\text{OH}^\cdot$  in the absence of people of  $5,9 \times 10^5$  molecules/cm<sup>3</sup> was obtained after 8 hours. Finally, another study uses rainfall collection for further analysis of the effect of microorganisms on the  $\text{OH}^\cdot$  concentration of atmospheric water. Subsequently, the detection of  $\text{OH}^\cdot$  is based on the reaction of ambient water with terephthalic acid (TA) and the product of TAOHs is quantified, given its strong fluorescence. Then, by means of chemical kinetics and stoichiometry, the  $\text{OH}^\cdot$  concentration is calculated mathematically. We are therefore faced with another method, with a hybrid characterization between an experimental and a numerical part [66]. The results of the final  $\text{OH}^\cdot$  concentration range from  $2 \times 10^4$  molecules/cm<sup>3</sup> to  $1,20 \times 10^6$  molecules/cm<sup>3</sup>, from the characterization of the sample as rain water to cloud water, respectively. Therefore, cloud water has a higher oxidative capacity and is more consistent with the present study, possibly due to the higher concentration of photochemical sources of  $\text{OH}^\cdot$ . In addition, hydrogen peroxide was found to be the major source of  $\text{OH}^\cdot$  in the TA reaction. In conclusion, this method states that the model used in their study - and therefore in the present article - underestimates the source of the radicals, expecting an even higher  $\text{OH}^\cdot$  emission in reality. Consequently, any advance in a more realistic model would enhance the results obtained, establishing our model and our measurement technique as a conservative and, even so, effective result given the characterization given to the OAF-generating device during the kinetic study.

#### IV. CONCLUSIONS

As it has been observed throughout this article, atmospheric air contains different volatile organic compounds, and it has also been shown that there are different reactants, radicals, anions and secondary compounds generated that intervene in the natural oxidation processes, but for this study only  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  have been selected to analyze the reaction capacity to generate hydroxyl radicals ( $\text{OH}^\cdot$ ) and with an algebraic method a way to balance the stoichiometric redox type equations to measure the quantitative proportions or mass ratios of the chemical elements that are involved. These stoichiometric coefficients will indicate the proportion in which moles of reactants and products are involved in a chemical reaction.

In the stoichiometric study, a series of mathematical formulae were used to calculate both the efficiency of the reactions in % and the concentration of  $\text{OH}^\cdot$  from the purity of the hydrogen peroxide and the initial concentration of ozone, always in a safe way and without exceeding the emission limits established by the International Institutions. From this study and as has been mentioned in the discussions, it has been concluded that, for enclosures areas with large volumes, a peroxide of 17,95% will have to be used to achieve optimum efficiency of the  $\text{OH}^\cdot$  and a higher consumption of the two reactants. On the other hand, for enclosures areas with small volumes, a peroxide of 4,95% will have to be used.

On the other hand, in the kinetic study it has been possible to conclude that, simulating the main reagents present in the air, in a 30 minute simulation without the OAF generator device, after 1 minute, the natural hydroxyl radicals are practically non-existent. In contrast, when the OAF generator device is used, the hydroxyl radicals remain around  $10^8$  molec/cm<sup>3</sup>, a level that can be found directly in nature. Furthermore, by increasing the number of people in a room, the value of hydroxyl radicals will be lower due to the fact that the higher the concentration of  $\text{CO}_2$  and other VOCs, the higher the consumption of these hydroxyl radicals due to a higher radical chain reaction.

To conclude, it has been demonstrated that in an artificial way and with the right combination, it is possible to reach the same value of hydroxyl radicals as in nature using the two reactant elements such as hydrogen peroxide and the almost negligible quantities of ozone, without exceeding **Maximum recommended emission by WHO, OSHA, FDA**.

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