Influence of the flame’s secondary reaction zone on a chemiluminescence analysis

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“Non est ad astra mollis e terris via”
- Seneca (4 BC – AD 65)
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Resumo

No âmbito desta tese, é estudada a quimiluminescência das espécies OH*, CH*, C₂*, bem como CO₂*, em chamas de Bunsen laminares de pré-mistura de ar-metano e ar-propano, entre condições pobres e ricas, com razões de equivalência entre 0.8 e 1.1. Para tal, foram feitas medições espectrométricas em diferentes coordenadas axiais e radiais das diferentes chamas, em seguida foram aplicados quatro métodos para extração do sinal quimiluminescente baseados no máximo ou na integração da banda de cada espécie selecionada, e finalmente os sinais foram reconstruídos através de três métodos tomográficos (Abel, ART e Onion Peeling) com a intenção de avaliar qual o impacto da pluma (ou zona secundária de reação da chama) num modelo de quimiluminescência. Os resultados obtidos demonstraram i) como as variações de razão de equivalência e os diferentes combustíveis influenciam o sinal de cada espécie, ii) como a tomografia afeta este tipo de análise, e iii) quais os métodos mais adequados (e para que intervalo de valores de razão de equivalência) para um modelo de quimiluminescência.

Palavras-chave: quimiluminescência de chama; pluma; medicação da razão de equivalência; tomografia de chama; metano; propano.
Abstract

This thesis focuses on the study of the radical species OH*, CH*, C₂*, as well as CO₂* on premixed methane-air and propane-air Bunsen flames from lean to rich conditions, with equivalence ratio values ranging from 0.8 to 1.1. By taking spectroscopic measurements in different axial and radial coordinates of the different flames, applying different methods to extract chemiluminescent signals of the selected excited radicals based on bandhead (type A) or integrated bandwidth (type B) and then reconstructing the signal through three different tomographic methods (Abel, ART and Onion Peeling), with the intention of evaluate how the flame’s secondary zone has an impact on the final model of a chemiluminescence analysis. The results have shown i) how variations in the equivalence ratio and the fuel type influence each specie’s signal, ii) how tomography affects this type of analysis, and iii) which methods are more adequate (and within which range of equivalence ratio) for a chemiluminescence model.

Keywords: flame chemiluminescence; secondary reaction zone; equivalence ratio sensing; flame tomography; methane; propane.
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Nomenclature

Greek symbols

\( \lambda \) Wavelength.
\( \phi \) Equivalence ratio.
\( \rho \) Molar density.

Roman symbols

\( HRR \) Heat release rate.
\( I \) Light intensity.
\( L \) Length of the burner’s nozzle.
\( Q \) Volumetric flow rate.
\( R \) Radius of the burner’s nozzle exit.
\( r \) Radial distance to the center of the flame.
\( z \) Dimensionless axial distance to the burner’s nozzle exit.

Subscripts

\( i, j, k \) Computational indexes.
\( P \) Projected function.
\( x, y, z \) Cartesian components.

Superscripts

\(^*\) Free Radicals.
Chapter 1

Introduction

1.1 Motivation

Since the acknowledgement of its potential use and due to its multiple usages (ranging from usages as complex as aircraft and spacecraft propulsion, ground transportation, industrial processing, and electrical generation to some as domestic as heat generation, and food preparation), the combustion phenomenon has long been the most widely used source of controllable energy on earth, making up to approximately 82% of the global demand for energy by 2011 [1].

However, combustion emissions account for a great fraction of pollutant species such as carbon monoxide (CO), nitrogen oxides (NO$_x$), and unburned hydrocarbons (UHC), as well as over half of the fine particle (PM$_{2.5}$) air pollution and most of the primary particulate organic matter [2]. In fact, the contributions of residential coal combustion to the total air pollutants concentrations of PM$_{10}$, SO$_2$, NO$_x$, and CO represent approximately 11.6%, 27.5%, 2.8% and 7.3%, respectively, during the winter heating season [3]. In particular, global emissions of nitrogen oxides have been increasing steadily over the past 150 years, mostly due to combustion of biomass and fossil fuels, and therefore contributing to photochemical smog, to acid rain formation, to the destruction of the ozone layer and to global warming [4].

Thus, it’s not surprising that increasingly stringent emission legislations have been established in order to ensure that the combustion process won’t surpass certain values which, over the years, are more and more conservative. The rate of generation of species such as CO, NO$_x$ and UHC is known to be a strong function of the equivalence ratio: generally speaking, in hydrocarbon flames, CO and UHC production increase with increasing equivalence ratio in fuel-rich flames, while NO$_x$ production increases with decreasing equivalence ratio in fuel-lean flames [5, 6].

The equivalence ratio of a gas premixture is denoted by the greek letter $\phi$ and defined as the ratio between quantities of fuel and air, at actual and stoichiometric proportions [7] ; hence, $\phi = 1$ evidently stands for a flame in stoichiometric conditions, $\phi < 1$ refers to a flame in fuel-lean conditions and $\phi > 1$ implies a flame in fuel-rich conditions. This particular concept will be further analyzed in the next section of this work.
Therefore, a tight process control over equivalence ratio in hydrocarbon combustion is crucial in order to maintain optimal conditions and thus, not only minimizing pollutant emissions, but also improving the economic value from a conventional (non-renewable) source of energy.

Conventional combustion control systems rely on monitoring the CO$_2$ and/or O$_2$ content of the exhaust gases, consequently having inherent time-lag efficiency limitations [7]. Other control systems explored for flame control include the use of in-flame solid-state sensors [8], but these suffer erosion due to the harsh thermo-chemical flame environment and may require maintenance or a regular response calibration.

Another control system involves the use of optical techniques, in particular flame chemiluminescence, which will be the method used throughout the experimental procedure of this work. Since it is a relatively fast technique with a straightforward implementation, flame chemiluminescence is a good alternative to the methods listed above, and due to its simplicity and since it may operate away from the extreme combustion conditions (because it isn’t an intrusive technique) it has applications not only in active combustion control but also in microgravity experiments [9]. This method will be explained in further detail in chapter 2.

Still, despite the many studies on flame chemiluminescence already referenced above, basic information on how the two different regions of a premixed laminar flame affect this methodology have yet to be discussed thoroughly in the literature. Previous studies have shown that, in a partially premixed system, combustion occurs in two stages: a primary flame, which is first established, consumes all primary fuel and produces most of the heat release, and a secondary reaction zone that appears behind the primary flame, when fuel fragments from the rich zones, oxidizer separates from the lean zones and combustion products mix. There is still controversy on whether this last stage can be seen as a diffusion
flame and described by diffusion flame models or should be described as distributed combustion [10].

This secondary reaction zone becomes particularly important when applied to the concept of “microflame”, which is one of the hot topics in recent combustion studies due to the growing need for portable power generation and the development of microburners [11], microcombustors and micropower devices [12].

Since the scale of microflames ranges over a few hundred micrometers to a few millimeters, the experimental investigation of microflames does not allow using intrinsic measurements such as ion probes, thermocouples, or a hot wire flow velocimetry, and therefore, flame chemiluminescence turns out to be an important alternative methodology [13]. Furthermore, also due to its scale, there is significant contribution from both reaction zones (since the secondary zone’s influence per unit of power it’s greater than in bigger and hence more conventional flames) and in systems in which burners are placed side by side like the ones on K. Kuwana’s work [14], there is an overlap of secondary reaction zones.

1.2 Objectives

As mentioned above, flame chemiluminescence is widely used for monitoring and controlling the equivalence ratio on a combustion system; in particular, chemiluminescence of OH*, CH* and C2 excited species is a especially effective methodology, since the emission from hydrocarbon flames in the 250-600 nm is overpowered by these three species and their emission is generally believed to be primarily chemiluminescent rather than thermal in nature [5, 15].

The present work intends to analyze the local chemiluminescence emissions on the two already stated distinct regions of a laminar premixed flame (a narrow primary zone and a wider secondary zone) and thus evaluate their influence on the chemiluminescent transfer function of the equivalence ratio - this concept will be further discussed on chapter 2.

Thus, the tracing of spectral signals was made through a pinhole that restricted the line of sight of the spectrometer, and later the acquired radiation was subjected to tomographic algorithms in order to access the local radiation emissions. This analysis was conducted for three different axial dimensions, for four different equivalence ratios (lean, stoichiometric and rich mixtures) and for premixed air-methane and air-propane mixtures. In order to understand the influence of the secondary reaction zone on the chemiluminescent transfer function, the tracing of spectral signals was made through a pinhole that restricted the line of sight of the spectrometer, and later, the acquired radiation was subjected to tomographic algorithms in order to access the local radiation emissions. This analysis was conducted for three different axial dimensions, for four different equivalence ratios (lean, stoichiometric and rich mixtures) and for premixed air-methane and air-propane mixtures.

In order to determine the equivalence ratio, it is usually used ratios like OH*/CH* or C2/CH* [7, 5, 16], which also attenuate the geometric effects on the signal, caused by the observation area of the optic sensor. Then, it is possible to compare ratios of signals obtained by the spectrometer (raw data) with ratios of the ones already treated with tomographic methods (local data). Afterward, both signals will also be compared with values from other referenced works. The experimental procedure will be further...
explained on chapter 3 and the numerical model on chapter 4.

The results will allow concluding what is the impact of the secondary zone on the mentioned chemiluminescent signal ratios as well as on the interpretation of the chemiluminescent signals. They will also permit to analyze if there are signal variations throughout the flame, based on the three axial dimensions considered. Moreover, it will also allow evaluating how the type of fuel influences this methodology, since the experimental procedure was repeated for both air-methane and air-propane premixed flames. All results will be exhibited on chapter 5.

1.3 Thesis Outline

This thesis is organized in 6 chapters:

- Chapter 1 is an introduction to the present work, focused in exploring the motivation and defining the main objectives for this thesis.

- Chapter 2 gives an expanded explanation on the notion of flame chemiluminescence while providing a description of the state-of-the-art of that field of studies. In this chapter, it is also made a detailed analysis of the selected excited chemical species already mentioned on the subsection above (OH*, CH*, C2* and CO2) and some other properties (the equivalence ratio, type of fuel, and the measuring and processing methods in particular) that influence the radiation emitted by the flame.

- Chapter 3 lays out the details of the experimental setup, in particular the methodologies applied on the three major systems that constitute the experimental setup: the burner system, the premixture control system and the chemiluminescence system.

- Chapter 4 discusses the numerical model applied in order to obtain the local radiation signals, from obtaining the individual signal for each specie (using four different methods) to reconstructing the signal using three different types of tomographic techniques: Abel, ART and Onion Peeling.

- Chapter 5 presents all the numerical results obtained from applying the experimental and numerical procedures detailed in the previous chapters. It starts by exhibiting the reconstructed signal for CO2*, OH* and CH* (since this last specie is representative of C2* as well). Then explores the influence of the processing method by comparing the raw signal (directly obtained from the experimental spectra) with the reconstructed signal (after applying a tomographic technique) while comparing methods of obtaining the individual signal of a specie. Finally, it draws a comparison between the two types of fuel used throughout this thesis.

- Chapter 6 summarizes the conclusions based on the results in the previous chapter and the ones present in the literature, and finally discusses possibilities for future work in this field of study.
Chapter 2

Flame Chemiluminescence

Gaydon’s pioneer work on spectroscopic analysis of flame light emission identified two types of features in the ultra-violet and visible regions of the emission spectrum: one associated with background phenomenon of broadband emissions, and other relative to narrow band emissions having band heads located at specific wavelengths [15]. These narrow band emissions exist due to the radiation spontaneously emitted during a combustion phenomenon by chemical species at an electronically excited state. Throughout the reaction, these highly unstable species tend to change towards a lower state of energy, releasing its energy excess through different channels: one of them in particular is the emission of radiation, whose energy (usually denoted by $h\nu$) corresponds to the transition gap from the initial excited state to a lower state (typically its ground state), which is called chemiluminescence and it’s the base of a technique called flame chemiluminescence, used for flame diagnostics.

As shown in several of the cited works, and as it will be further explained in section 2.2, flame spectral analysis has the capacity to determine the location of the reaction zone, as well as provide information on a range of other flame’s parameters (like its reaction rates, equivalence ratio, etc.) in numerous combustors operating with different types of fuel [17]. Still, the individual influence of each of those parameters on the flame chemiluminescent emissions is yet to be thoroughly evaluated – even though some research is being done in this direction [18, 19].

Following the work by Trindade [7], this thesis concerns only premixed air-methane (CH\textsubscript{4}) or air-propane (C\textsubscript{3}H\textsubscript{8}) laminar Bunsen burner flames, while investigating the radiation spontaneously emitted as a consequence of the reactive process and its dependency on the sampling location (i.e. radial distance from the center of the flame and axial distance from the base of the burner) and the equivalence ratio – other parameters will be mentioned later in chapter but will not be further considered in this work.

2.1 Chemiluminescent Emitters

In combustion of carbon base fuels the excited radical emitters that generates the strongest narrow band feature in the ultraviolet-visible regions (in particular, between 250 and 600 nm [5]) are the excited radical forms of hydroxyl (OH\textsuperscript{*}), methylidyne (CH\textsuperscript{*}) and diatomic carbon (C\textsubscript{2}*) , which can be clearly detected
particularly on the spectra of slightly rich flames, and is generally believed to be primarily chemiluminescent rather than thermal in nature. It should be noted that a chemical specie on an electronically excited state is here referred with the superscript *, as usual on combustion literature.

Typical air-methane and air-propane flames and emission spectra (for the same burning conditions) are shown below.

![Flame of Methane](image1)

![Flame of Propane](image2)

Figure 2.1: Laminar air premixed flames (both for $\phi = 1.1, z = .25h, r = 0mm$)

![Spectrum of Methane](image3)

![Spectrum of Propane](image4)

Figure 2.2: Emission spectra of laminar air premixed flames (both for $\phi = 1.1, z = .25h, r = 0mm$)

As evidenced by the figures, there is an obvious resemblance between the spectra from the two flames, even though the radiance of air-methane is always lower than the air-propane flames at similar burning conditions (this aspect will be further explained in the following subsection), and $C_2$ emission is relatively stronger in air-propane flames. It is also visible that OH* emissions are much more prominent in both flames, $C_2$ emissions are generally weak (except in very rich flames, which are out of the scope of this work), and the background phenomenon of broadband emissions is also a larger fraction of the CH* and $C_2$ peak emission signals.
This background phenomenon of broadband emissions shouldn’t be confused with the background emissions that will be mentioned in section 3: the latter is related with the radiation acquired in the experimental procedure in the absence of flame, emitted by the burner and the surroundings themselves, and the first is a superposition of contributions from different radical emissions.

For the two types of fuel mixtures studied in this thesis, carbon dioxide (CO\textsubscript{2}) is the main responsible for the broadband background radiation in the UV and VIS bands [20]; nonetheless, there are other minor radical emitters where formyl (HCO\textsuperscript{+}), formaldehyde (CH\textsubscript{2}O\textsuperscript{+}), methylene (CH\textsubscript{2}\textsuperscript{+}), hydrocarboxyl (CHO\textsubscript{2}) and carbon monoxide (CO\textsuperscript{+}), are only some examples [7]. According to Gaydon’s work [15], in real flames, the intensity of each of those minor chemiluminescence species mentioned above is considerably low when compared to the OH\textsuperscript{+}, CH\textsuperscript{+}, C\textsubscript{2}\textsuperscript{+} and CO\textsubscript{2}\textsuperscript{+} emissions. Therefore, the individual influence of those emitters is neglected in the present thesis.

As shown in figures 2.2, the chemiluminescence spectrum of a hydrocarbon flame in the displayed range has seven major narrow band systems clearly identifiable: the first two are related to OH\textsuperscript{+} emissions (as ultraviolet radiation), the next two are associated to CH\textsuperscript{+} emissions (in the blue region) and the remaining three band systems belong to C\textsubscript{2} emissions (in the green visible range). The already mentioned broadband background radiation in the UV and VIS bands correspondent to CO\textsubscript{2} emissions is also easily identifiable.

The OH\textsuperscript{+} is more likely to be found under lean flame conditions, where there is an excess of oxidizers (namely OH, O and O\textsubscript{2}), being their maximum emission located at a lower equivalence ratio values. A contrary behavior is produced by radical C\textsubscript{2}, showing higher densities at low oxygen environments and thus richer flames, for both methane and propane fuels. Finally, in the CH\textsuperscript{+} formation kinetics are involved a combined contribution of oxidizer and reducer (like C\textsubscript{2}H and C\textsubscript{2}) species, which forces the maximum emission to be at an intermediate location of the spectrum, around \(\phi = 1.2\) in both cases [7].

Unlike the species described above, studies on CO\textsubscript{2} chemiluminescence and its formation are still underdeveloped [21]; however, work by Samaniego et al. [17] was able to establish the relation between CO\textsubscript{2} emission intensity, H-atom concentration, and heat release rate. Furthermore, it has verified that the continuum emission corresponds to more than half of the total UV/VIS radiant flux in methane flames, and higher and almost constant percentages are found on the lean side, which increases towards a maximum around \(\phi = 1.05\) and sharply decreases along richer flame conditions [7, 17]. In fact, according to Guyot et al. [22], the spectral distribution of CO\textsubscript{2} emission intensity can be described by the following expression:

\[
I_{CO_2}(\lambda) = \zeta \times \exp \left[ -\exp \left( -\frac{(\lambda - \lambda_0)}{w} \right) - \frac{(\lambda - \lambda_0)}{w} + 1 \right]
\]  

(2.1)

where \(I_{CO_2}\) is the CO\textsubscript{2} chemiluminescence intensity, \(\zeta\) a scaling factor, \(\lambda\) the radiation wavelength, \(\lambda_0\) the band head wavelength, and \(w\) an extent parameter related to the wide band length.
2.2 Dependency on other properties

Past studies have been able to establish the dependence of chemiluminescence signals on multiple flame properties: fuel type [7, 18, 20, 23], heat release rates and heat release oscillations [19, 24, 25, 26, 27], pressure [28], NO\textsubscript{x} pollutant emission [7, 27, 28], flow rates [23, 26, 29], and air-to-fuel and equivalence ratios of the mixture [7, 18, 19, 23, 26, 27, 28, 30, 31, 32, 33]. Furthermore, the intensity from OH\textsuperscript{+}, CH\textsuperscript{+}, C\textsuperscript{2} and somewhat from CO\textsubscript{2} emitters, as well as the ratios of pairs of emitters’ intensity, have been use to determine the geometric location of the reaction zone and the flame structure, and also to validate turbulent combustion models [17, 29, 30, 34].

The present thesis is focused on the analysis of the influence of the equivalence ratio on the chemiluminescent signal, while simultaneously evaluating the effects the secondary reaction zone, the sampling and data processing methods, and the type of fuel have in this kind of analysis.

2.2.1 Fuel type

In order to explore the influence of the fuel type on a chemiluminescent analysis, this thesis will apply this method of flame diagnosis to premixed laminar methane (CH\textsubscript{4}) and propane (C\textsubscript{3}H\textsubscript{8}) Bunsen burner gas combustion, such as those of domestic appliances.

![Figure 2.3: Simplified mechanism of CH\textsubscript{4} oxidation][7, 24, 34]

The primary motivation for this choice is related with their representativity of the hydrocarbon family: as the smallest hydrocarbon molecule, methane is the smallest hydrocarbon molecule and therefore represents the simplest alkane fuel structure to investigate, and propane is lightest weight of the simple hydrocarbons that starts to exhibit general features of chain processes (typical of heavier molecules) like decreasing significantly the ignition delay times and increasing flame burning velocities. Furthermore, they are widely used and the most investigated gas aliphatic hydrocarbons in combustion applications and both have great economic relevance: natural gas is mostly constituted by methane and is the primary fuel for industrial uses, and propane is the main component of liquefied petroleum (or LPG), and both fuels have multiple applications ranging from gas turbines and massive industrial furnaces to less complex domestic boilers [7].
As stated before in section 2.1, even though the two types of fuel mixtures investigated in this thesis have different dynamics, the behavior of OH$^+$ and CH$^+$ (as well as C$_2^+$ to a smaller extent) emission features are quite similar and there is a resemblance in the emission distribution profile from flames of both fuels (see figure 2.2). Nonetheless, the intensity of methane flames is always lower than the propane flames for the same burning conditions, which can be explained by the higher laminar flame burning velocity of propane, which reflects in a higher heat release rate (or HRR, which is also referred to fuel power in the literature since it is measured in units of Watts), compared to that of methane – intensities increase with HRR for laminar and weakly turbulent premixed flames [7, 17, 18].

The burning velocity mentioned above should not be confused with the other two combustion velocities defined during flame propagation: flame speed, and the expansion velocity; the aforementioned laminar flame burning velocity in most literature represents the unstretched, adiabatic, flame front propagates into the unburned gas. As for the flame speed is the velocity of the flame front relative to a fixed position, while the expansion velocity is the difference between the flame speed and the burning velocity. [35, 36].

Furthermore, as stated in the work by Trindade [7], propane flames have much stronger broadband background emissions than methane flames: in fact, it can be stated a surplus of 71%, in average. This discrepancy in the values for background radiation intensity can be justified by the higher carbon content of propane flames in relation to that of methane: premixtures of identical HRR have a 17% molar excess of atomic-C specie in propane than in methane fuels.

2.2.2 Measuring and processing methods

Following the work by Morrell et al. [26] and García-Armingol et al. [32], this thesis will also analyze the influence of the measuring method on chemiluminescence intensities, using different methods to quantify the individual signals from each of the selected species. However, since one of the objectives for this work is to understand the influence of the secondary reaction zone on chemiluminescent intensities, the optical setup will be fixed and therefore its influence on the chemiluminescence analysis is outside the scope of this work: instead of the method used in most of the cited works, in which flame emissions are collected globally, corresponding to a flame intensity spatially integrated along the line of sight [19, 21, 28, 32, 33, 37], this experimental procedure will acquire the signals through spatially resolved measurements made by a fiber optic attached to a spectrometer – as seen in previous works [16, 19, 30] –, and will subsequently apply tomographic techniques [7, 38, 39, 40], which will be discussed in further detail in section 4.2. In fact, due to aerodynamic, thermal or kinetic effects, real flames (as opposed to perfect, theoretical flames) have anisotropic flame fronts, and therefore the use of the sampling method present in this thesis is relevant in order to evaluate the flame’s light emission distribution [7].

An alternative technique to the one described above is based on filtered intensified CCD cameras, as seen in [24, 41, 33]; yet, this type of approach uses optical interference filters to select the radiation wavelength range, thus having the disadvantage to blur the separation between the desired radical emissions and contributions from the broadband emissions [7, 24].
This work will evaluate several methods to quantify the individual signal from each species which can be divided into two types: one regarding the choice of band integration vs. band peak (i.e. zero width) - types A and B -, and the other concerning the subtraction or not of the broadband background radiation - types 1 or 2.

**Table 2.1: Methods applied to quantify the individual signal from each species - types A1 and B1**

<table>
<thead>
<tr>
<th>Type</th>
<th>Images</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td><img src="A1.png" alt="Image" /></td>
<td>[32, 33]</td>
</tr>
<tr>
<td>B1</td>
<td><img src="B1.png" alt="Image" /></td>
<td>[32, 33]</td>
</tr>
</tbody>
</table>
The tables above summarize the methods applied in the scope of this work and which ones were used in previous works. Previous works have found that background corrections usually improve the sensitivity of the chemiluminescence technique, peaks are more influenced by resolution of the optical sensor (higher resolutions yields for narrower but higher peaks) than band areas, and peak-to-background ratio increases with resolution [7, 28, 32, 37].

It was also found that the contribution of CO\textsuperscript{2+} background made up only a relatively small fraction (20\%) of the total OH\textsuperscript{+} signal, but contributed as much as 70 – 90\% of the nominal CH\textsuperscript{+} signal [42]. Similarly, the background corrected \(\text{CH}^+ / \text{OH}^+\) ratio (i.e. obtained from type 2 signals) has a higher sensitivity to the variation of the equivalence ration when compared to measurements without background correction (i.e. type 1 signals). Thus, according to Nori [42], the uncorrected \OH and \CH chemiluminescence signals do not offer any advantage for heat release or equivalence ratio sensing applications.

Furthermore, according to García-Armingol et al. [32], the experimental results for background-corrected measurements indicate that the normalized curves as well as the uncertainty analysis are valid for different sensors and optical setup, and that background-corrected band peaks (i.e. type A2 in
the table 2.2) exhibit the best metrological properties for lean premixed methane-air flames: high sensitivity, monotonic dependencies for a wide range of equivalence ratios and therefore lower uncertainties in estimated values of equivalence ratio.

**Intensity ratios**

As stated in the previous sections, the chemiluminescent intensity from \( \text{OH}^* \), \( \text{CH}^* \), and \( \text{C}_2^* \) (as well as \( \text{CO}_2^* \)) depends on flame parameters which influence the heat release ratio, such as equivalence ratio, fuel mass flow rate, temperate, pressure and local flame strain rate; thus, through the use of emission intensity ratios in the vicinity of an operating condition, it may be possible to remove the dependence from other parameters and remain only a function of the flame’s equivalence ratio, as suggested by Sandrowitz et al. [5] and Orain and Hardalupas [18]. However, even though some attempts were made in this field [5, 33], only Hardalupas et al. [30] have been able to uncouple the equivalence ratio and the strain rate, controlling both parameters independently.

Nonetheless, several works in the literature - such as [7, 18, 19, 22, 30, 42] - reported that some hydrocarbon flames at certain conditions showed the variation of chemiluminescence intensity ratios, such as \( \text{OH}^*/\text{CH}^* \) or \( \text{C}_2^*/\text{OH}^* \), with equivalence ratio to be promising for equivalence ratio sensing. The preferential use of \( \text{OH}^*/\text{CH}^* \) in the present literature can be explained by the fact that, as stated in the previous sections, leaner flames of propane and methane tend to produce residual emissions of \( \text{C}_2^* \) (i.e. of the same order as noise emission), causing a degradation in the chemiluminescence signal and thus deeming ratios involving this specie as not sensible enough for this type of analysis, in contrast with \( \text{OH}^* \) emissions, which tend to decrease for richer flames but are still far removed from to the emission produced by noise and the surroundings of the flame being studied [7].

Among the three intensity ratios (and their respective inverse) that can be calculated for \( \text{OH}^*, \text{CH}^*, \) and \( \text{CO}_2^* \), García-Armingol et al. [32] has found that the ratio \( \text{OH}^*/\text{CH}^* \) yields the best results for premixed methane-air flames, followed by \( \text{CH}^*/\text{CO}_2^* \); according to the same work, the first ratio has “a good sensitivity, a wide range of monotonic variation, the smallest influence of the spectral bandwidth and the lowest uncertainty in terms of equivalence ratio”. These results are also established in the work by Nori [42], which has verified that the chemiluminescence intensity ratio the \( \text{CH}^*/\text{OH}^* \) increased monotonically with equivalence ratio for atmospheric pressure conditions, even though the variation of the same ratio was not the same at elevated pressures. Furthermore, recent works were able to prove that the ratio \( \text{CH}^*/\text{OH}^* \) is independent of the air mass flow for a premixed natural gas flame in a swirl-stabilized burner [22] and that, even though \( \text{CH}^* \) chemiluminescence is more dependent on strain than \( \text{OH}^* \), the ratio \( \text{CH}^*/\text{OH}^* \) is not very sensitive to strain rate for methane (varying by only 10% over a wide range of strain rates) and propane flames [18, 42, 27].

Based on experimental data, it is possible to establish an empirical relation between chemiluminescence ratios and the equivalence ratio, approximating their dependency by a curve fit. In fact, several works in the literature have suggested their own model, ranging from simple exponential relations to more complex equations involving more coefficients; the table below summarizes some of these models for \( \text{OH}^*/\text{CH}^* \), \( \text{C}_2^*/\text{OH}^* \) and \( \text{CH}^*/\text{C}_2^* \) in both air-propane and air-methane flames.
Table 2.3: Chemiluminescent models from previous works (* refers to natural gas, i.e. 94% methane)

<table>
<thead>
<tr>
<th>Propane</th>
<th>$OH^<em>/CH^</em>$</th>
<th>$\exp[-46.6585 - 53.7547 \phi^2 + 37.6942 \exp(\phi)]$</th>
<th>[7]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$0.527 + 1.135 \exp[-(\phi - 0.6)/0.171]$</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.80 \exp(-1.563\phi)$</td>
<td>[43, 44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$13.97 \exp(-1.596\phi)$</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$31.27 \exp(-2.551\phi)$</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$25.25 \exp(-2.877\phi)$</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>$C_2^<em>/OH^</em>$</td>
<td>$\exp[39.6179 + 48.6207 \phi^2 - 32.7889 \exp(\phi)]$</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.0005 \exp(\phi/0.163)$</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>$CH^*/C_2$</td>
<td>$(-2.40116 + 1.61557 \phi)/(1 - 1.69343 \phi)$</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[0.0032 \exp(\phi/0.222)]^{-1}$</td>
<td>[43]</td>
</tr>
<tr>
<td>Methane</td>
<td>$OH^<em>/CH^</em>$</td>
<td>$\exp[-65.1546 - 72.4618 \phi^2 + 513362 \exp(\phi)]$</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.597 + 2.107 \exp[-(\phi - 0.7)/0.260]$</td>
<td>[18, 19, 30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[0.0393/0.0305 \phi^{(5.44-2.68)}]^{-1}$</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[1.134 - (0.692/\phi)]^{-1}$</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[2.812 - (1.581/\phi)]^{-1}$</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>$C_2^<em>/OH^</em>$</td>
<td>$\exp[103.462 + 117.553 \phi^2 - 82.1060 \exp(\phi)]$</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>$CH^*/C_2$</td>
<td>$(-1.38889 + 0.93833 \phi)/(1 - 33391 \phi)$</td>
<td>[7]</td>
</tr>
</tbody>
</table>

However, as it’s possible to conclude from a brief analysis of the table above, current studies only have reported empirical correlations for a specific burner and detection system, and most of them considered flows with simultaneous variations of strain rate, temperature or pressure in addition to equivalence ratio, all of which (as seen in the previous sections) have a strong influence in a chemiluminescent analysis, and thus may not be generally applicable [42]. Therefore in order for this method to be directly implemented as a diagnostic input for process control and prove itself as practical, application to numerous systems involving hydrocarbon combustion (already mentioned in section 1.1) further work must be carried out in order to uncouple the multiple parameters which affect this type of analysis and thus make it possible to establish an unique chemiluminescent model.
Chapter 3

Experimental Procedure

As stated before, this work carries on the work developed by Trindade [7] and, consequently, the experimental procedure described in this section is largely based on his experimental setup. The goal of the experimental section of this work is to obtain a correlation between the combustion phenomena in study and the chemiluminescence signal obtained. Thus, the assembly for this work is constituted by three major systems: i) the burner system, ii) the premixture control system, and iii) the chemiluminescence detection system.

The burner system includes the whole physic system responsible for the gas premixture conditions at the exit of the burner's nozzle (such as temperature, degree of premixness, etc.), igniting and maintaining the flame and its geometry.

The premixture control system is constituted by the gas containers (that will make up the premixture), the flow controllers and the computer with the software used to control them, and the mixing chamber before the burner and, as its name implies, is in charge of controlling the gas premixture conditions (such as its composition and the flow rate of each gas).

The chemiluminescence detection system includes all the equipment used in tracing the signal produced by the flame: the spectrometer and the computer with the appropriate software to receive its signal, and the probe used to restrict the spectrometer’s conical field of view.

![Figure 3.1: Experimental procedure assembly](image)

(a) Laboratory facilities

(b) Burner system and gas containers
3.1 Burner System

The Bunsen burner assembly used on this work was designed by Trindade [7] and was conceived to ensure a steady and fully developed gas flow on laminar regime at the nozzle level. The burner is a circular open nozzle of 20 mm in diameter at the exit, with a high area contraction ratio of \( A_{\text{ratio}} = 25 \) between the entrance and exit section areas. Its aim is to uniformly accelerate the flow, further reducing the flow turbulence and non-uniformities.

The smooth contoured nozzle design shown above was based on low-speed wind tunnels contraction [45] and follows a standard fifth order polynomial equation given by:

\[
y = (-10 \xi^3 + 15 \xi^4 - 6 \xi^5) \cdot (y_i - y_0) + y_i
\]

where \( \xi \) is the dimensionless ratio between \( z \) and \( L \), being \( z \) the axial burner coordinate and \( L \) the length of the nozzle (equal to 100mm, as evidenced by figure 3.2). The corresponding radial coordinate at position \( z \) is denoted by \( y \), and \( y_i = 50mm \) and \( y_0 = 10mm \) are the radii to the contraction wall from the center line at inlet and outlet, respectively.

The burner assembly is entirely made of stainless steel 304 and comprises three sections of identical length, as shown in figure 3.3. Between each section there is a distribution plate made of low porosity sintered glass (ROBU Ø 100mm×5 mm, \( \varepsilon \leq 100 \mu m \)) with the aim of straightening the flow, breaking the gas radial and angular velocity profiles. The bottom section has four tangential gas inlets equally distributed throughout the chamber wall, the interior of which is filled with Raschig rings (Ø 5mm) acting as a jet breaking and spreading evenly the flow. The intermediate section is an open cylindrical chamber used to equalize gas pressure all over the second sintered plate area. The outer section is the contraction zone, which is responsible for the velocity equalization at the burner exit.
3.2 Premixture Control System

The burner setup requires a gas flow control system upstream to ensure the development of stable burning conditions. Air was drawn from the laboratory compressor line after desiccant and filtered operations. The fuels used were bottled research grade methane and propane gases (Alphagaz™ N35, Air Liquide) with a minimum purity of 99.95%. Precision gas flow controllers (Alicat Scientific, Series 16) of 20 and 5 SLPM models were used to separately regulate the air and fuel flow rate selection points. Precision on gas flow adjustment has been set for all fluids by factory calibration certificate as average error equivalent to 0.8% of the flow measured over 0.2% of its full scale. Controllers were operated through FlowVision™ software package that enables individual monitoring of gas flowrate/pressure/temperature during the tests performed.
Flow rate proportions between fuel and air were adjusted according to a widely used parameter on combustion literature known as equivalence ratio, $\phi$. As mentioned on section 1.1, the equivalence ratio of a gas premixture is defined as the ratio between quantities of fuel $n_F$ and air $n_A$, at actual and stoichiometric (denoted here by the subscript $st$) proportions.

$$\phi = \frac{n_F/n_A}{(n_F/n_A)_{st}}$$

On this work, there were four equivalence ratio conditions analyzed: two lean (0.8 and 0.9), one rich (1.1) and one stoichiometric (1.0).

It is also possible to rewrite the equation above in order to determine the measurements of volumetric flow rates of fuel $Q_F$ and air $Q_A$ for each one of the equivalence ratio condition previously stated.

$$\phi = \frac{\varphi Q_F \rho_F}{0.2095 Q_A \rho_A}$$

The $\varphi$ corresponds to the stoichiometric coefficient of molecular oxygen for complete fuel oxidation ($\varphi = 2$ for CH$_4$ and $\varphi = 5$ for C$_3$H$_8$), $\rho_F$ and $\rho_A$ are the actual molar density of fuel and air respectively, and the 0.2095 coefficient represents the average molar fraction of O$_2$ in atmospheric air at sea level [46].

Thus, assuming standard conditions were taken at 298.2K and 101.3 kPa, the selected mass densities are: 0.6569 g/dm$^3$ for methane, 1.8316 g/dm$^3$ for propane, and 1.1845 g/dm$^3$ for air [7]. And finally the flow rate conditions for each value of equivalence ratio are obtained by fixing either $Q_F$ or $Q_A$ (in this case, the first condition was chosen).

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>CH$_4$ [SLPM]</th>
<th>Air [SLPM]</th>
<th>C$_3$H$_8$ [SLPM]</th>
<th>Air [SLPM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.900</td>
<td>10.50</td>
<td>0.350</td>
<td>10.30</td>
</tr>
<tr>
<td>0.9</td>
<td>2.056</td>
<td>21.84</td>
<td>0.813</td>
<td>21.90</td>
</tr>
<tr>
<td>1</td>
<td>2.056</td>
<td>19.65</td>
<td>0.813</td>
<td>19.71</td>
</tr>
<tr>
<td>1.1</td>
<td>2.056</td>
<td>17.87</td>
<td>0.813</td>
<td>17.92</td>
</tr>
</tbody>
</table>

### 3.3 Chemiluminescence System

As mentioned in section 1, a pinhole attached to an optical probe was used in order to restrict the line of the spectrometer. The pinhole’s orifice has a diameter of 0.5mm and this assembly has a total length of 147.5mm.

Since the aperture of the spectrometer is 0.4mm, it is possible to determine the distance of the assembly to the center of the flame using trigonometry, and choosing a value for the acquired area of flame. In this work, the assembly is at a distance of 115mm and has a projected area on the center of the flame of 1.13mm$^2$, which means a diameter of 1.2mm.
Therefore, for each series, the measurements taken are separated by 1mm, starting from the radial center of the flame to 20mm apart. In order to calibrate the position of the pinhole in relation to the flame, a millimetric paper was placed in the burner (as shown in figure 3.6), aligned with its center; then, a laser was attached to the pinhole and projected to the paper, and the pinhole was fixed in the desired position (i.e. in the symmetry axis of the flame and basis of the burner).

Then, assuming the basis of the burner as \( z = 0 \), and as stated in chapter 1, the measurements were taken at three different axial dimensions as shown in the figure bellow. It should be noted that these axial dimensions weren’t taken at the same absolute height, as the were dependent of each flame’s height.

The signal collection system consists in an optical fiber connected to the spectrometer (QE65000) controlled by SpectraVision™ software running on a personal computer. After the burning system stabilization period, each signal acquisition corresponds to record 10 consecutive spectra with integration time of 30s (see figure 3.7 a). Then, each signal is post-processed by a Matlab™ code which removes the background signal (figure 3.7 b) and calculates the mean spectrum for each point, as evidenced by figure 3.8. Results are acquired in the range of wavelength from 198.89 to 1000.14 nm, but only further analyzed in the range 226.24 to 574.61 nm. They are also transformed from the SpectraVision’s default units \( \mu W \, nm^{-1} \, cm^{-2} \) to one that relates with the number of emitted photons \( \# \text{photons} \, s^{-1} \, nm^{-1} \, cm^{-2} \).
Figure 3.7: Typical raw spectra collected

(a) Flame’s raw spectrum
(b) Background’s spectrum

Figure 3.8: Mean spectrum of a typical propane flame and respective degree of uncertainty (shaded)

A schematic for the whole experimental procedure assembly can be found below.

Figure 3.9: Experimental Setup
Chapter 4

Numerical model

As explained in section 1.2, the main goal of the present work is to understand the influence of the secondary reaction zone on the chemiluminescent transfer function; consequently, the spectra obtained from the experimental procedure described in the previous section have to be treated in order to be further analyzed.

4.1 Obtaining the signal for each specie

Namely, the first step in this numerical study is to isolate a selected radical signal by filtering contamination, which can be obtained through spectral processing methods mentioned in 2.2.2 which are based on bandhead (peak) [28, 30] or integrated bandwidth (area) [47, 37]; the first method correspond to the maximum intensity signal of a narrow band and the second one is based on the total intensity emitted in a given band (in this work it was considered that the emission bands for OH, CH and C range between 275 and 329nm, 379 and 447nm, and 454 and 569nm, respectively).

In this work, there’s also a distinction between signals with or without the contribution of the carbon dioxide’s continuum: as stated above, in a flame emission spectrum, it is possible to identify several narrow band systems, in which each one is mainly a result of light emissions from characteristic quantum transitions of a specific chemiluminescence radical. Yet, these band systems (assigned to those emitters) are superimposed to a broadband continuum, roughly extending from 250 to around 650nm, with no apparent band structure [7].

This continuum radiation is associated with the chemiluminescence from CO emitters, as a consequence of radiative recombination of CO molecules with atomic oxygen. Therefore, a raw spectral intensity is roughly a sum of three contributions: the chemiluminescence intensity due to the excited radical emissions (I_{chem} in the figure, the one relevant to our analysis), a continuum radiation intensity attributed mainly to the carbon dioxide emitters (I_{CO2}), and finally the intensity attributed to other emitters (I_{others}), as evidenced in figure 4.1.
Several works in the literature [49, 17] have studied CO$_2^*$ and tried to create polynomial fits for the broadband continuum. However its broad emission spectrum presents itself as difficulty, making it a challenge to isolate it from other emitters’ signal.

Therefore, in this work, it was used a numerical method that would search in a neighborhood of predefined values of wavelength for both the inferior and superior limits of the band for each specie, and then would draw a straight line between the two acquired points, thus setting the area that represents the total intensity emitted by the specie’s band (as evidenced by the shadowed region in figure 4.1).

Finally, after applying one of the four possible methods (i.e. after calculating the integrated bandwidth or the bandhead for each specie, and after subtracting or keeping the signal associated with CO$_2^*$ and other emitters) to the spectrum of every geometric point, it is possible to have four different characteristic signals for each specie with a $(\phi, z, r)$ defined condition. Thus, it is also possible to obtain a geometrical distribution (i.e. $r$ and $z$ dependent, but independent of the wavelength) for each species, for each flame.

Typical geometrical distributions for both OH$^*$ and CH$^*$ (which is also representative of the C$_2^*$ distribution) can be found in the next page. The signals identified in the series of graphs are normalized by the maximum signal for each flame: i.e., each signal was divided by the value in the flame front for each axial coordinate. It is important to notice that even though the absolute values for the intensity of OH$^*$ are very different for each given method, the profiles are approximately equal and therefore the absolute values diverge only by a constant. However, one can also observe that for CH$^*$ (and for C$_2^*$) the result above is not entirely accurate, since there is a much larger dispersion - this result is in concordance with the work of Nori [42], which has stated that CO$_2^*$ background had a much larger contribution to the nominal CH$^*$ signal than for the OH$^*$ one.
Figure 4.2: Normalized signal for both OH$^*$ and CH$^*$ ($\phi = 1.1, z = 0.25h$)

Figure 4.3: Normalized signal for both OH$^*$ and CH$^*$ ($\phi = 1.1, z = 0.50h$)

Figure 4.4: Normalized signal for both OH$^*$ and CH$^*$ ($\phi = 1.1, z = 0.75h$)
4.2 Reconstructing the signal using tomography

To determine each species’ signal at each point, projections of obtained spectroscopic line-of-sight measurements were deconvoluted using tomographic inversion. Three tomographic techniques were investigated: Abel (subsection 4.2.1), ART and Onion Peeling (subsection 4.2.2).

Tomography was first described in a 1953 medical journal’s article by Pollak [38], which used the technique of planography (another word for tomography) of the chest in cases of pulmonary tuberculosis. The method is still mostly used in medical sciences, but has other applications like atmospheric science, archaeology, astrophysics, geophysics, and other sciences.

In this work, tomography is used to reconstruct the “real” signal of the flame: since the flame in study throughout this thesis is hollow, the signal recorded by the spectrometer is relative to a small vicinity of points that encompasses the flame front. However, the spectrometer line of sight is approximately a cylinder that will intersect all zones of the flame cone (on both sides) in sight and therefore the radiation intensity calculated for each radial coordinate in subsection 4.1 is actually a superimposition of signals.

Thus, to determine each species’ signal at each point, projections of obtained spectroscopic line-of-sight measurements were deconvoluted using tomographic inversion.

Essentially, a tomographic reconstruction or deconvolution is an inverse problem that intends to obtain a discrete estimate of a spatial distribution $I(x, y)$ based on the given projection $I_p$, which, for a basic 2D object problem like the one explored in this work, can be described by the following generic equation:

$$I_p = \int I(x, y) \, dA \tag{4.1}$$

4.2.1 Abel

The Abel inversion is a widely adopted tomographic reconstruction method developed by Abel [50], suitable for axially symmetric distributions like the case of the flames here in study and used in some of the cited works [39, 40, 51]. However, according to Deutsch and Beniaminy [51], this tomographic method is usually maligned since it requires the derivative of the projection data to be calculated and also because the integrand diverges at a single point.

Given that an axially symmetric property (in this case radiation intensity), $I(x, y)$ can be approximated to $I(r)$, that $I_p(x)$ is the first derivative of the projection function $I_p(x)$ for a ray passing through the domain of interest, and finally that the radius $r$ can be expressed in terms of $x$ and $y$ (according to the Pythagorean theorem), the well-known analytic inverse of 4.1 can be written as [39, 40, 52]

$$I(r) = -\frac{1}{\pi} \int_r^\infty \frac{I_p(x)}{(r^2 - x^2)^{1/2}} \, dx \tag{4.2}$$

Since the Abel inversion is an exact solution to 4.1, it implies that, in principle, it can be calculated as precisely as desired, and thus its results’ accuracy will only depend on the limitations imposed by numeric integration and noise in the raw projection data when the equation above is applied to experimental
data. However, the usual solution for the equation above is to divide the function \( I_P(x) \) into segments and then to fit each of these segments to a polynomial for which an analytic solution to can be obtained (e.g. Two-Point and Three-Point Abel Deconvolution used by Dasch [53]) which always carries some kind of uncertainty to the process - in general, the greater the number of projections, the smaller the error associated with the approximation and thus the better the reconstruction (although oversampling may increase error) [52, 53].

In this work, it was used a Mathematica program developed by Professor Edgar Fernandes and typical results for this type of tomographic reconstruction can be found below.

![Typical reconstructed signals for OH\(^{+}\) using the Abel method (\( \phi = 1.1 \))](image)

**Figure 4.5:** Typical reconstructed signals for OH\(^{+}\) using the Abel method (\( \phi = 1.1 \))

### 4.2.2 ART vs. Onion Peeling

The Algebraic Reconstruction Technique (or ART) is a family of methods for direct reconstruction of three-dimensional objects used in computed tomography that uses iterative algorithms, developed by Kaczmarz to solve linear equations systems, and first introduced in 1970 by Gordon et al. [54]. Since these methods are iterative, they are more robust in the presence of noise and can successfully incorporate prior information to improve their deconvolutions, and therefore are commonly chosen in most non-medical applications [55].

![Visual Representation of the ART family of methods](image)

**Figure 4.6:** Visual Representation of the ART family of methods

25
In contrast to methods like the Abel Inversion, ART uses methods entirely based on numerical approximation and on the re-expression of the problem as a system of linear equations, by discretising the projection operator of the equation 4.1; this is achieved by dividing the object volume’s domain into a grid of pixels [55]. In this work it is assumed that the studied object is axisymmetric and as a result the projected intensity $I_P$ is only dependent of $r$, even though the object’s intensity is dependent of $x$ and $y$ - see figure 4.6.

$$\int I_n(x, y) \, dA_{n,n} = I_{Pn} - \sum_{i=1}^{n-1} \int I_i(x, y) \, dA_{n,i}$$ (4.3)

For this reason, the adapted ART method used in this work starts by taking the value obtained for the furthest point from the center of the flame (20 mm, $I_{P1}$ in the figure 4.6), and assign it as a baseline, i.e. the algorithm assumes that $I_{P1}$ is not a superimposition of signals but the direct projection of $I_1$ (the intensity radiated by the vicinity $A_{1,1}$), and uses geometric formulas to estimate its value. After that, the algorithm takes the next point (19 mm), the projection $I_{P2}$, and assumes that this value is a direct projection of both $I_1$ and $I_2$, thus is able to estimate $I_2$ by subtracting the value related with $I_1$ (encountered in the previous step) and applying similar geometric expressions. The method repeats itself until it reaches the center of the flame.

Similarly to the Abel method, a Mathematica program developed by Professor Edgar Fernandes was used and typical results for this type of tomographic reconstruction can be found below.

Figure 4.7: Typical reconstructed signals for OH$^*$ using the ART method ($\phi = 1.1$)

The Onion Peeling method is also completely based on a numerical approximation and uses an iterative algorithm to solve equation 4.3 [40, 53, 56].

The picture below is a visual representation of this method and it makes clear its similarities with the ART method: it also divides the object volume’s domain into rings (like on an onion, hence the method’s designation) and starts by taking the value obtained from the furthest point from the center of the flame, applying the method until it reaches the center of the flame.

However, the difference lies in how the approximation for $A_{n,i}$ is done; using the ART method, the area is approximated by curvilinear lines (represented by the dashed grey line in figure 4.8) described by trigonometrical expressions. On the other hand, the Onion Peeling code used within the scope of this thesis approximates the area with much simpler functions (full blue straight lines in figure 4.8), which
makes the processing time much faster but also deems the method less accurate when compared with the two previous algorithms.

![Figure 4.8: Visual representation of the ART and Onion Peeling methods](image)

Unlike the previous methods, a Matlab program developed by Professor Teodoro Trindade was used and typical results for this type of tomographic reconstruction can be found below.

![Figure 4.9: Typical reconstructed signals for OH* using the Onion Peeling method (ϕ = 1.1)](image)

4.2.3 Comparison between tomographic methods

It is easily understandable after a quick analysis on the graphics from the figures 4.5, 4.7 and 4.9 that each methods obtains relatively similar profiles (for the same axial coordinate) but different in absolute value, having very different orders of magnitude. Thus, in order to draw any comparison between the three models, is important to normalize them; the figure shown in the following page are normalized using the maximum for each method (i.e. each signal was divided by the signal obtain in flame front's radial coordinate which, in the case of 4.10 corresponds to \( r = 7 \text{mm} \)).

From the same figure it is possible to better understand the differences between each method; using ART as baseline (since the results obtained for this method are in line with the empirical and theoretical data found in the literature), one can find dissimilarities between the profiles obtained for each method which were not obvious in the graphics from the previous sections. In the first sub-figure, even though
the profile obtained by the Abel inversion is very similar to the one obtained ART after the flame front's coordinate \((r > 7\, \text{mm})\), for the profile which corresponds to the inside of the flame \((r < 7\, \text{mm})\) is not the same; as stated before, the analyzed flame is hollow and therefore the obtained signal should only be assigned to the flame front and to a small vicinity of points in the secondary reaction zone, which means that the Abel inversion does not model properly the inside of the flame. In the second sub-figure there’s even more dissimilarities: not only the profile obtained by the Onion Peeling does not model properly the inside of the flame, but it also fails to model the propagation of \(\text{OH}^*\) into the secondary reaction zone (since it goes to approximately zero after the flame front’s coordinate).

![Figure 4.10: Typical normalized reconstructed signals for \(\text{OH}^*\) using each method \((\phi = 1.1, z = 0.25h)\)](image)

However, it is possible to simulate a more precise experimental procedure by approximating the specie’s profile (without reconstruction) by a curve fit: in this work, the constructed line contained points separated by \(0.125\, \text{mm}\) and used the points obtained experimentally as anchors. Applying the Abel and the Onion Peeling methods to these profiles and comparing to the ART baseline (obtained from the experimental points only), the graphics are obtained and its possible to infer that while both profiles are able to better replicate the specie’s behavior inside the flame, the Onion Peeling still fails to model the propagation of \(\text{OH}^*\) into the secondary reaction zone.

![Figure 4.11: Typical normalized reconstructed signals for \(\text{OH}^*\) applying each method to a curve fit \((\phi = 1.1, z = 0.25h)\)](image)
Chapter 5

Results

After applying the numerical model detailed in the previous chapter (chapter 4) on the spectra obtained using the experimental procedure described in chapter 3, the present chapter intends to display the obtained results which hopefully will permit to draw the conclusions described in the following chapter (chapter 6) on the influence of the secondary zone on the chemiluminescent transfer function.

This chapter is divided in three main sections: one regarding the reconstructed species profiles and how each species propagates to the secondary reaction zone, another regarding the measuring and processing methods (which will be subdivided in an analysis for each method to quantify the individual signals for each specie and in a comparison between raw signals and reconstructed signals using ART) and finally, a section regarding the influence of the type of fuel on the chemiluminescent results.

5.1 Reconstructed species profiles

As proved in sub-section 4.2.3, the Abel and the Onion Peeling methods aren’t able to properly model the species’ behavior (at least using only the data obtained using the experimental procedure described in the chapter 3 of this thesis) and thus only ART will be used hereinafter, for simplicity.

The figures in the following pages are relative to the reconstructed profiles for the integrated bandwidth signal for CO\(^2\) and the integrated bandwidth signals without the CO\(^2\) contribution for OH\(^\ast\) and CH\(^\ast\) (the profiles for this last one are also representative of C\(^2\)\(^\ast\) since they differ in value but have approximately the same level of penetration in the secondary reaction zone).

Figures in the same row correspond to the same propane flame (same value of equivalence ratio) and figures in the same column were taken at the same relative axial coordinate. The profiles represent the “real” variation (i.e. the reconstructed signal) of a certain radical along the radial coordinate, starting from the center of the flame \((r = 0 \text{ mm})\), then reaching the flame front (which has a different value of \(r\), depending on the flame) and the secondary reaction zone, until it reaches the furthest point measured \((r = 20 \text{ mm})\) - see figure 5.1.
From the obtained figures it is possible to observe that the CO\(_2^\ast\) radicals has a bigger degree of penetration into the secondary reaction's zone (represented in figure 5.1 with a lighter shade of blue), not only in terms of absolute value but also reaching radial coordinates further to the center of the flame, the OH\(^\ast\) radicals penetrates somewhat into the secondary reaction's zone but its signal goes to approximately zero after the vicinity of the flame front, and finally the CH\(^\ast\) (and C\(_2^\ast\)) radicals have almost no penetration in the secondary reaction's zone, having only signal near the flame front's coordinate.

It is also possible to observe that, apart from the leanest flame, there is an increase in all species' signals along with the equivalence ratio. The different behaviour for \(\phi = 0.8\) can be justified by the fact that this flame had a lower volumetric flow rate of propane than the others, and thus a lower value of HRR - for the same value of volumetric flow rate as the others flames, this one could not be stabilized, and would eventually extinguish (blow off phenomenon), hence the decision to use a different value.

Furthermore, it is also noticeable that the profile for the CO\(_2^\ast\) radical propagates further into the secondary reaction zone as the flame becomes richer; this effect is justified by the fact that the production of this type of radical become slower towards higher values of equivalence ratio. Since the reaction velocity is proportional to the concentration of reactants raised to a power referred to as order of reaction (as well as a constant value which depends on the reaction itself and temperature), as the flame becomes richer, the oxidizer's concentration decreases and thus the velocity of reaction also decreases.
5.2 Comparison between different processing methods

As stated in section 4.1, four different methods were used in the scope of this thesis in order to isolate the signal for each specie; in sub-section 2.2.2 they were divided into two types: one regarding the choice of band integration vs. band peak (i.e. zero width) - types A and B, respectively - , and the other concerning the subtraction or not of the broadband background radiation - types 1 or 2, respectively.

The following results are divided by sub-sections (each one corresponding to a different method), and will disclose the influence that the sampling location and the processing methods have in a chemiluminescent analysis.
First, by plotting the reconstructed ratio (i.e. after applying a tomographic technique) between two species taken at three different axial coordinates (represented by the different colors in the figures on the left) at the respective flame front location versus the flame’s equivalence ratio, it is possible to draw conclusions in respect to the relation between the intensity and the equivalence ratios, but also to evaluate the influence that the axial sampling location has on this type of analysis and whether there is a difference between the processing methods.

Then, it is possible to plot the intensity ratio before and after the application of the ART technique against each other, i.e. the raw signal taken at the the radial center of the flame (which is comparable to integrate the signal of the whole flame, and is represented by the sub-figure on the left from figure 5.7), and the reconstructed signal taken at the flame front’s radial coordinate (which is equivalent to take a local measurement in the flame front, and is represented by the sub-figure on the right from figure 5.7), and thus understand the influence of applying tomography to the data: whether there is a correlation between the groups of results, how does the equivalence ratio influences them, whether there is more or less dispersion of data, and what is the difference from one method to another.

Finally, by testing both results with two different types of ratios, $\text{OH}^*/\text{CH}^*$ and $\text{CH}^*/\text{C}_2^*$, it is possible to draw conclusions on the influence that the choice of ratio has on this type of analysis.

### 5.2.1 Method A1

The first important result shown in the sub-figure a) from the figure 5.8 is that for the evaluated range of values for equivalence ratio in this thesis, the axial sampling location has no influence in the ratio
OH*/CH* with signals obtained from the application of method A1, showing little to none dispersion of data for the same flame (i.e. same value of equivalence ratio).

(a) OH*/CH* for different $z$ and $\phi$

(b) OH*/CH* with and without ART for different $\phi$

Figure 5.8: OH*/CH* ratios using the A1 processing method - propane

However, the same result does not apply to the ratio CH*/C$_2^*$, in which the data dispersion increases towards leaner flames; nonetheless, this outcome doesn't necessarily mean that this method isn't applicable for this specific ratio: for stoichiometric and richer flames, there's little to none influence of the axial sampling location for the same value of equivalence ratio. Furthermore, the dispersion of data for leaner flames can potentially be caused by a numerical error: since the signal from C$_2^*$ radicals decreases with the equivalence ratio and this parameter is the denominator of the ratio, it may be originating the dispersion of data.

(a) CH*/C$_2^*$ for different $z$ and $\phi$

(b) CH*/C$_2^*$ with and without ART for different $\phi$

Figure 5.9: CH*/C$_2^*$ ratios using the A1 processing method - propane
From the sub-figures on the right, one can observe that, as the equivalence ratio decreases, the ratios obtained from reconstructed signals (i.e. after application of the ART method) drift further away from the ratios that use raw signals (i.e. without the application of any tomographic method) and there’s an increase in the amplitude of the variation of data for the same flame (represented by points with the same color). Thus, the results suggest that the application of tomographic methods after using the method A1 for richer flames, can be considered non-essential.

5.2.2 Method A2

The results present in this subsections are very similar to the previous method: both showing approximately the same linear relations between the equivalence ratio and the OH*/CH* ratio for the entire range of flames studied and the CH*/C{subscript 2}* ratio for stoichiometric and richer flames, having little to none dependence on the axial sampling location.

Still, in comparison with the results from method A1, this method shows a better agreement between the data obtained from reconstructed signals at the flame front and the ones that use raw signals acquired at the center of the flame. One can argue that by subtracting CO{subscript 2}* continuum, the results for the two ratios analyzed in this thesis are already similar to the ones obtained by applying ART to the experimental data, and thus the effects of applying tomography may be considered negligible.

Figure 5.10: OH*/CH* ratios using the A2 processing method - propane
5.2.3 Method B1

Unlike the previous methods, the method B1 does not have a strictly linear relation between the equivalence ratio and the \( \text{OH}^*/\text{CH}^* \) reconstructed intensity ratio throughout the studied range for equivalence ratio, showing a maximum for \( \phi \) equal to 0.9 instead of 0.8. This can be justified by the fact that, as stated before, the flame with an equivalence ratio equal to 0.8 had a different volumetric flow rate of propane than the others. Nevertheless, the previous methods showed no signs of being influenced by this circumstance, which could possibly suggest that the method B1 is more fragile to volumetric flow rate variations.

However, it is also notable that the present method has a better agreement between the raw and reconstructed ratios when compared to A1.

Furthermore, it’s also possible to observe that the axial sampling location has a less negligible influ-
ence for this method (when compared with the type A ones), showing more dispersion of data for the \( \text{OH}^*/\text{CH}^* \) ratio. The same occurs for the \( \text{CH}^*/\text{C}_2^* \) ratio even though it's not obvious because of the figure's scale: even though the data are clearly less scattered than the results from the previous methods, the variation amplitude for the same value of equivalence ratio is still relevant, making up to approximately 48% of the dispersion for the four studied flames. One can hypothesize that the decrease of data dispersion in the \( \text{CH}^*/\text{C}_2^* \) ratio is related with the contribution of the \( \text{CO}_2^* \) broadband, which has a bigger importance in the B1 method than the A1 (since it is an integration instead of a band peak with zero width), thus overpowering the variations of \( \text{CH}^* \) and \( \text{C}_2^* \) due to changes in equivalence ratio along the flames.

![Figure 5.13: CH*/C2* ratios using the B1 processing method - propane](image)

**5.2.4 Method B2**

When compared with its analogous type A method, this one shows more dispersion of data for the \( \text{OH}^*/\text{CH}^* \) ratio when plotted against the equivalence ratio; thus, just like the other method from type B, it is possible to discern that the axial sampling location as bigger influence than on the type A ones.

However, the same does not apply for the ratio \( \text{CH}^*/\text{C}_2^* \), in which there is little to no divergence for every flame except the one with equivalence ratio equal to 0.8. This behavior can also be justified by the numerical error caused by decrease of \( \text{C}_2^* \) signal with the equivalence ratio: though the band integration creates an increase of the absolute value of the \( \text{C}_2^* \) signal, and thus attenuating the numerical error for 0.9, the error it's still noticeable for 0.8.

It is also possible to observe that for this ratio there is an approximate agreement between the raw and reconstructed signal (see sub-figure b) from figure 5.14), and apart from the leanest flame, all results are aggregated around the bisector line.
5.3 Comparison between different fuel types

The results found in the previous sections were replicated for methane in order to understand the influence of the fuel type in a chemiluminescent analysis.

In the next page, in figure 5.16, are represented the dimensionless reconstructed species profiles for both propane and methane, which can be considered the analogous results for methane of section 5.1: since the species’ signal diverge so much in absolute value between the two fuels, in order to draw any conclusions, it is necessary to nondimensionalize the signals by dividing them for its maximum.

It is possible to observe from the figure 5.16 that all species have the same dimensionless profile, having only shifted horizontally because they have different locations for the flame front (since the flames are geometrically different and even though the measurements were taken at relatively equal axial coordinates, they are different in absolute values). The degree of propagation to the secondary reaction zone is approximately equal, showing little divergence in the furthest points from the center of the flame; how-
ever, this phenomenon can be justified since the methane flame’s signal is less intense, and therefore is relatively more affected by noise.

![Graph](image)

Figure 5.16: Reconstructed species profiles for both propane and methane (for $\phi = 1.1$ and $z/h = 0.50$)

The analogous results of section 5.2 can be found in the next sub-sections, each one corresponding to a different method.

### 5.3.1 Method A1

In contrast to the findings for propane, the results from sub-figure a) from figure 5.17 suggest a quadratic relation between the OH*/CH* ratio and the equivalence ratio.

Furthermore, as seen for propane, these results also shows that the axial sampling location has little to none influence in this ratio, for the evaluated range of values for equivalence ratio, even though it shows bigger dispersion for leaner flames. As explained in previous sections, this dispersion can potentially be caused by a numerical error and doesn’t necessarily mean that this method isn’t applicable.

![Graph](image)

Figure 5.17: OH*/CH* ratios using the A1 processing method - methane

38
Finally, there is a very clear correlation between the signals with and without application of tomo-
graphic techniques (as seen in figure b) from figure 5.17, where the points are almost overlapping the
bisector line, showing a better agreement than for propane (see figure 5.8).

For the CH*/C\textsubscript{2}* the results are slightly different. Firstly, by looking at the sub-figure on the left it is
possible to observe that, just like for OH*/CH* the axial sampling location also has no influence in this
ratio, but the relation between this ratio and the equivalence ratio is linear instead of quadratic.

Secondly, in the sub-figure on the right it’s possible to observe that the data concentrate along a
vertical line; this means that, without tomography, the results are centered around a certain value and
suggests that the method loses sensibility. This phenomenon is probably caused by a bigger influence
of the secondary reaction zone when compared to propane since methane has a less intense signal,
and thus the secondary reaction zone’s signal overpowers the variations of flame signal due to changes
in equivalence ratio. By applying tomography, the effect of the secondary reaction zone is eliminated
and thus the sensibility of the method increases.

5.3.2 Method A2

As seen in the last method, the figure below (on the left) suggests a a quadratic relation between the
OH*/CH* ratio and the equivalence ratio, with even less influence of the axial sampling location than the
previous method.

Furthermore, it also shows a good correlation between the raw and reconstructed signals (see figure
on the right), specially for richer flames. This means that, for this ratio (and for the studied burning con-
ditions and evaluated range of equivalence ratio), the application of tomographic techniques to signals
obtained using the type A methods is non-essential.
For the CH/C\textsubscript{2} ratio the results are different when compared with A1: first of all, they suggest a quadratic relation rather than a linear one, and the results are more affected by the numerical error associated with leaner flames and already described in previous sections. Since this method subtracts the CO\textsubscript{2} continuum, the value of C\textsubscript{2} decreases even more in absolute value, even tending to zero for \( \phi \) equal to 0.8 and thus having no value for the ratio.

However, this method shows a better agreement between raw and reconstructed signals for richer flames when compared with method A1 and even though there is a bigger dispersion of data for leaner flames (and therefore are not represented in the figure on the right, as it would be necessary an even bigger scale), this method is preferential to A1 when using signals without tomography since it shows bigger sensibility, and it is less influenced by the secondary reaction zone’s signal.
5.3.3 Method B1

This method has a worse behavior for both ratios when compared when compared with type A methods. Firstly, for OH*/CH* also suggests a quadratic relation but shows much more dispersion of data, which means that the axial sampling location has much more influence on this method than on the type A one. Furthermore, as seen for the ratio CH/C\(^2\)\(^*\) from type A1, there is a concentration of data along a vertical line, which deems the use of this method without the application of ART as inadequate for a chemiluminescent analysis.

![Figure 5.21: OH*/CH* ratios using the B1 processing method - methane](image)

For the CH*/C\(^2\)\(^*\), this method is completely inadequate, as it shows no sensibility with or without application of tomographic techniques.

![Figure 5.22: CH*/C\(^2\)\(^*\) ratios using the B1 processing method - methane](image)

These results are in line with what would be expected, since this method is much more affected by the secondary reaction zone's signal (as explained in section 5.3.1), as it uses the bandwidth integrated value and therefore includes a larger contribution of \(CO_2\).
5.3.4 Method B2

Finally, the method B2 shows better results than its analogous integrated method, B1.

Sub-figure a) from figure 5.23 also suggests a quadratic relation between the OH*/CH* ratio and equivalence ratio, while showing little to none influence from the axial sampling location. Moreover, it shows a good correlation between raw and reconstructed signals, specially for richer flames.

Yet, for the CH*/C_2* ratio, the results are not so conclusive; since there is a larger dispersion for leaner flames, where the numerical error increases (and for φ equal to 0.8 there is even no results, since it would be a division by zero), it’s not possible to evaluate if the relation is quadratic or linear. While it’s possible to deem this method as inadequate for leaner flames, the results for richer flames are inconclusive and a wider range of equivalence ratio values would need to be evaluated in order to draw conclusions.
Chapter 6

Conclusions

The present thesis intended to analyze the impact of the flame’s secondary reaction zone on a chemiluminescence model for premixed air-methane and air-propane laminar Bunsen burner flames.

In order to achieve this goal, an experimental procedure was performed, focusing on acquiring light intensity data emitted by 8 different flames - 4 values of equivalence ratio (0.8, 0.9, 1, and 1.1) for each fuel type - at 3 different axial coordinates, and 20 different radial coordinates. The experimental setup followed the work developed by Trindade [7], using the same burner assembly, premixture control system and an adapted chemiluminescence system: in order to restrict the signal acquired by the spectrometer, a pinhole was attached to an optical probe. Then, the flame emissions were acquired in a wavelength vector in the near-ultraviolet/visible regions from 198.89 to 1000.14 nm (but only further analyzed in the range from 226.24 to 574.61 nm), and went through a preliminary process which consisted in removing the background signal (emitted by the surroundings of the flame) and calculating the mean spectrum for each geometrical point.

After the experimental procedure, a numerical model must be applied in order to draw conclusions. Spectral data was processed using 4 different methods to extract chemiluminescent signals of the selected excited radicals (OH*, CH* and C₂*) based on bandhead/peak (type A) or integrated band-width/area (type B) and on whether the signals suffer a subtraction of the CO₂ signal (type 2) or not (type 1). After the application of these methods, it is possible to conclude that the profiles for OH* are approximately equal between themselves but for CH* and C₂* there is a much larger dispersion, since these last two species’ signals have a much more substantial relative contribution of CO₂ when compared to OH*.

However, the species’ signals found using these methods are not the “real” signal of the flame: the Bunsen flame studied in the scope of this thesis is hollow, and therefore the signal recorded by the spectrometer is actually relative to only a small vicinity of points that encompasses the flame front. Thus, to determine each species’ signal at each geometrical point, a tomographic reconstruction must ensue. While 3 methods were explored (Abel, ART and Onion Peeling), only ART modeled appropriately the flame in its entirety. However, the results obtained by a curve fit suggest that, if a more precise experimental procedure (i.e. if the measurements were taken at geometrical points separated by, at
least 0.125mm) was executed, then Abel could also be an suitable model.

The results have shown that there is an increase in all species’ absolute signals (OH*, CH*, \( C_2^* \) and CO\(_2^* \)) along with the equivalence ratio (apart from the leanest flames, for \( \phi \) equal to 0.8, which both had a different HRR). They have also shown that the signal for the CO\(_2^* \) radical propagates further into the secondary zone, as the flame becomes richer. Furthermore, it was also possible to extend these results to both methane and propane, since all studied radicals have the same dimensionless profile (even though they diverge immensely in absolute value), having only shifted horizontally because of their different geometrical locations for the flame front.

The table below summarizes the results obtained from the four different methods and the two studied ratios applied to both fuel types.

### Table 6.1: Summary of the results for propane

<table>
<thead>
<tr>
<th></th>
<th>( \text{OH}^<em>/\text{CH}^</em> )</th>
<th>( \text{CH}^<em>/\text{C}_2^</em> )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Linear</td>
<td>Linear (probably)</td>
</tr>
<tr>
<td></td>
<td>Applicable even without ART</td>
<td>Applicable to flames with ( \phi &gt; 0.8 ), even without ART</td>
</tr>
<tr>
<td>A2</td>
<td>Linear</td>
<td>Linear</td>
</tr>
<tr>
<td></td>
<td>Applicable even without ART</td>
<td>Applicable even without ART</td>
</tr>
<tr>
<td>B1</td>
<td>Linear</td>
<td>Inadequate, even with ART</td>
</tr>
<tr>
<td></td>
<td>Applicable even without ART, but more fragile to axial sampling location and probably volumetric flow rate variations</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>Linear</td>
<td>Linear (probably)</td>
</tr>
<tr>
<td></td>
<td>Applicable even without ART</td>
<td>Applicable to flames with ( \phi &gt; 0.8 ), even without ART</td>
</tr>
</tbody>
</table>

### Table 6.2: Summary of the results for methane

<table>
<thead>
<tr>
<th></th>
<th>( \text{OH}^<em>/\text{CH}^</em> )</th>
<th>( \text{CH}^<em>/\text{C}_2^</em> )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Quadratic</td>
<td>Linear</td>
</tr>
<tr>
<td></td>
<td>Applicable even without ART</td>
<td>Applicable only after applying ART</td>
</tr>
<tr>
<td>A2</td>
<td>Quadratic</td>
<td>Quadratic (probably)</td>
</tr>
<tr>
<td></td>
<td>Applicable to flames with ( \phi &gt; 0.9 ), even without ART</td>
<td>Applicable only after ART</td>
</tr>
<tr>
<td>B1</td>
<td>Quadratic (probably)</td>
<td>Inadequate, even with ART</td>
</tr>
<tr>
<td></td>
<td>Applicable only after applying ART, and more fragile to axial sampling location</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>Quadratic</td>
<td>Inconclusive</td>
</tr>
<tr>
<td></td>
<td>Applicable even without ART</td>
<td>Maybe applicable to flames with ( \phi &gt; 0.9 ), even without ART</td>
</tr>
</tbody>
</table>

As seen from both tables, the most robust methods are from type A. For propane, A1 and A2 show a clear linear correlation for both ratios and are applicable even without ART (even though A1 is limited to \( \phi > 0.8 \)), which means that the flame’s secondary reaction zone has little to no influence in this type of analysis. However, the application of the same method for methane does not have equal results: for \( \text{OH}^*/\text{CH}^* \), there’s still no influence from the secondary reaction zone, but the same doesn’t apply for \( \text{CH}^*/\text{C}_2^* \), where it is necessary to use tomographic reconstruction.

For the type B methods, the results aren’t quite so robust, specially for B1, which is deemed inadequate for \( \text{CH}^*/\text{C}_2^* \) in all conditions and apparently is more fragile to axial location and other parameters variations on either flame. B2 holds better correlations than its analogous integral method, having less
sensibility to the variations described above in the case of the OH*/CH* ratio, while being applicable for 
CH*/C₂ at least for propane flames with φ greater than 0.8.

6.1 Future Work

Like the chemiluminescent models from previous works presented in chapter 2, the empirical correlations obtained within the scope of this thesis are specific for a particular set of conditions (burner, detection system, type of fuels, etc.) and thus, in order for this method to be implemented as a combustion control system for equivalence ratio sensing, further work must be carried out in order to uncouple the parameters that affect this type of analysis.

Therefore, possible evident future works are studies that carry out similar experimental and numerical methods but for different flames: for example different fuels, different range for equivalence ratio (explore the possibility of application of the method B2 for richer flames), etc. Future works can also draw a comparison between the reconstructed signal obtained by application of a tomographic method and the signal obtained with a Cassegrain optical system.

Another potential extension to this work is a study that combines the results from the previous section with the ones from other works like García-Armingol et al. [57] and is able to conclude which is the best procedure for a chemiluminescence analysis, i.e., which method is less influenced by external factors will still maintaining the strong function between a flame’s emitted radiation and its equivalence ratio.

Having a unique chemiluminescence procedure will open possibilities of application in different areas, namely in many industrial sectors that use combustion in their production lines (namely petroleum refining, steel and glass manufacturing, and electricity generation), having the potential to generate an end product capable of diminishing production and maintenance costs as well of decreasing pollutants emissions, while maintaining enough versatility to be used in different industrial sectors.


