Proceedings of the 10th World Congress on Momentum, Heat and Mass Transfer (MHMT 2025) Barcelona, Spain - April, 2025 Paper No. CSP 119 DOI: 10.11159/csp25.119

Spatially Resolved Chemiluminescence Measurements for Equivalence Ratio Estimation

Henrique Santos¹, Edgar C. Fernandes²

¹Instituto Superior Técnico Av. Rovisco Pais, n.º 1, Lisboa, Portugal henriquepsantos@tecnico.ulisboa.pt; edgar.fernandes@tecnico.ulisboa.pt ²Instituto Superior Técnico Av. Rovisco Pais, n.º 1, Lisboa, Portugal

Abstract - Chemiluminescence-based measurements of equivalence ratio (φ) in flames typically rely on sampling at specific locations or integrating over the entire flame volume. This work presents a comparative study between the two measurement approaches. Using a water-cooled flat-flame burner, OH* and CH* emissions were measured across various equivalence ratios ($0.70 \le \varphi \le 1.30$) and thermal powers (1.0-2.0 kW). Both measurement methods demonstrated strong exponential relationships between the OH*/CH* ratio and equivalence ratio. A systematic difference in the logarithmic offset between methods (b = 4.2183 vs 3.9433) suggests underlying physical phenomena that warrant further investigation. The results indicate that both approaches are viable for equivalence ratio estimation, with the choice between them potentially depending more on practical implementation considerations than measurement accuracy. Results suggest that measurements based on an integrated method likely underestimate the equivalence ratio at the reaction zone.

Keywords: OH* Chemiluminescence, CH* Chemiluminescence, Equivalence ratio estimation, Flat-flame burner, Spatially resolved spectroscopy, Premixed flame, Combustion diagnostics

1. Introduction

Combustion systems play a critical role across numerous applications, from industrial to domestic. One diagnostic and control parameter that remains vital in these applications is the equivalence ratio (ϕ), since it influences the process efficiency, emission of pollutants and operational stability.

Optical diagnostics have many sought-after advantages, namely their relative simplicity, potential for real-time monitoring and non-intrusive nature. These techniques are based upon the visible and ultra-violet emissions of flames, emerging from the chemical pathways, through a process known as chemiluminescence. In particular, the hydroxyl (OH*) and methylidyne (CH*) radicals show relatively large dependence on φ individually. The ratio OH*/CH* has been used successfully to estimate this parameter, by various means [1-3]. Other potential applications involve cost-effective methods for estimating φ in real-time, although the authors [4] caution that such methods cannot replace the latest LASER methods such as PLIF for accurate species estimation.

Traditionally, obtaining spectroscopic data of radicals presents some challenges. The largest of these being the fact that, for a traditional Bunsen-type burner (and, in fact, most other kinds of burner), most optical arrangements would sample from all sections of the flame, including the flame front and the plume, or combustion products, regions. This, in turn, makes the resulting correlations very dependent on the type of burner used and the relative contributions of the plume and flame front to the overall signal.

This work investigates the differences in measurement method, comparing between acquisition performed at the flame front and an integration of height-resolved spectra. Often measurements are taken at the reaction zone [5], but care must be taken in extrapolating this data to areas that may include the plume. Conclusions can be drawn on the practical difference between an acquisition accounting only for the flame front and one performed in the perpendicular direction.

2. Experimental Setup and Methodology

The experimental setup consists of a water-cooled, stainless-steel flat-flame burner manufactured by Holthius & Associates, a power-calibrated Ocean Optics QE65000 spectrometer and two Alicat mass flow controllers. Additionally, the acquisition of spectra is aided by two DC translation stages with stepper motors, to ensure reliability in the positioning

throughout tests. A collimating lens and slit were placed in front of the fibre optic collector, to ensure that the collection height at the flame front was 1mm.

A simplified version of the acquisition setup, foregoing the two translation stages, is shown in Fig. 1.



Fig. 1: Experimental setup with gas sources, burner and spectrometer.

The burner was controlled by supplying Methane (CH₄) and Air, to obtain flames with predefined φ and power. Nitrogen (N₂) was used as a shielding gas, supplied on the outer ring of the burner, to ensure that no reaction occurred between the reagents and the atmospheric air. Table 1 summarizes the conditions used for these experiments.

Power [kW]	φ	Power [kW]	φ
2.0	1.30	2.0	0.95
2.0	1.25	2.0	0.90
2.0	1.20	2.0	0.85
2.0	1.15	1.3	0.80
2.0	1.10	1.3	0.75
2.0	1.05	1.0	0.70
2.0	1.00		

Table 1: Conditions tested on the flat-flame burner.

The resulting radiative power spectra were normalized by the flame power and by the emitting volume, such that the results could be analysed as volumetric emissions. Each condition was evaluated at 19 different heights, in increments of 0.5mm, from the plane of the burner up to a distance of 9mm.

3. Results

Fig. 2 defines the Z-axis used for acquisitions and a methane flame with $\varphi = 1.0$, accompanied by three example spectra acquired at different heights.



Fig. 2: Spectra for a methane flame at $\varphi = 1.0$ taken at z(a) 0.5, (b) 2.5 and (c) 4.5mm.

An example set of spectra, acquired for three conditions tested at the flame front (defined as the height of maximum OH* emission), is shown in fig. 3. The spectra reveal distinct variations in radical emission intensities across different equivalence ratios. Most notably, the C₂* bands show significant enhancement under fuel-rich conditions ($\phi > 1.0$), while the OH* emissions demonstrate an inverse relationship, showing stronger signals under leaner conditions.

Although the C_2^* bands appear to be more sensitive to equivalence ratio, this is only the case for fuel-rich conditions; as φ approaches stoichiometry, its variation with φ is significantly reduced. This limitation is particularly evident in fig. 3, where the C_2^* emissions become nearly indistinguishable from background noise for φ nearing stoichiometric. As such, in the majority of cases [1;5;7], the OH*/CH* ratio is used, given its higher sensitivity across a wider range of φ .

Each spectrum was analysed by background removal, followed by CO_2^* broadband removal using the method proposed by Seipel *et al.* [6]. Due to the inherently low signal in measurements of this kind, a more accurate estimation of the radical emissions for each spectrum was obtained by means of a Kernel Density Estimation.



Fig. 3: Experimental results at the flame front for three conditions ($\phi = 0.8$, 1.0 and 1.2). The main radicals used for estimating equivalence ratio in this work OH* and CH*.

For the designated wavelengths (309nm for OH* and 431nm for CH*), a Gaussian-like probability function is constructed to determine the most probable value for the intensity. This approach helps mitigate the effects of noise and

provides more reliable peak intensity values for subsequent analysis. The resulting emissions for each example condition are shown in fig. 3.



Fig. 4: OH* and CH* emissions computed by the above methods. The ratio of these two emissions will be used to estimate the equivalence ratio.

The ratio OH*/CH* plotted across all conditions tested on a linear-logarithmic scale is shown in fig. 5. The data demonstrates a strong exponential relationship between the OH*/CH* ratio and equivalence ratio, with excellent correlation coefficients for both measurement approaches. The flame front measurements show slightly better correlation ($R^2 = 0.9861$) compared to the vertically integrated measurements ($R^2 = 0.9855$). The difference in correlation coefficients is hardly significant, since it is smaller than 1%. The results in fig. 5 were fitted using the least squares method to an equation of the form:

$$ln(OH^*/CH^*) = m\phi + b \tag{1}$$



Fig. 5: Radical ratio OH^* / CH^* as a function of equivalence ratio, for the flame front and for integration by the trapeze method. Error bars for 3σ .

These results are summarized in table 2, with a comparison to Cheng et al. [8].

Method	m	b	R ²
Reaction Zone	-2.8148	4.2183	0.9861
Vertical Integration	-2.7199	3.9433	0.9855
Cheng et al. [8]	-2.8860	3.3515	0.9930

Table 2: Results for the linear fit and comparison with previous works.

4. Discussion

The results are in agreement with literature and show good correlation across a wide variety of equivalence ratios. However, there is a difference of 7% in the offsets (b) between measurements in the reaction zone and traditional measurements that include the plume, which is quite significant. Several hypotheses may explain this difference: different time-of-life for OH* and CH* radicals; different formation distributions with respect to the Z axis; and temperature dependency.

The first hypothesis does not hold up to scrutiny: [9] and [10] report that the lifetime for OH* is around 686 ± 14 ns; for CH* [11] reports that it is 400 ± 60 ns. In either case, a formed radical would only travel a few µm before decaying. Thus, for the spatial resolution of this system, the difference between formation and decay is too small to affect the results.

The second hypothesis, that there are different formation distributions on the Z-axis, implies that the species have significantly different reaction rates at different heights. While this may be the case, the decline in emissions as Z increases does not seem to be significant enough to justify this hypothesis.

Temperature variations can have a significant influence in the formation and decay of excited radicals. More data is required to assert with confidence that these differences in measurement method can be attributed, at least in part, to temperature differences.

5. Conclusion

This work compared two approaches for measuring equivalence ratio via chemiluminescence: flame front sampling and vertical integration. Both methods demonstrated robust exponential correlations between OH^*/CH^* ratios and equivalence ratio. The flame front method consistently produced higher OH^*/CH^* ratios (7% higher offset) compared to vertical integration, suggesting it may overestimate equivalence ratio when compared to conventional methods that include the flame plume.

The observed difference in offset values cannot be attributed to radical lifetime effects. Temperature variations along the flame's vertical axis emerge as the most probable explanation for the systematic difference between measurement methods, though further investigation with temperature mapping would be needed to confirm this hypothesis.

Acknowledgements

This work was supported by Project EcoCerâmica e Cristal de Portugal, ECP-00076-IST, financed through PRR (Plano de Recuperação e Resiliência) - IAPMEI

References

- N. Docquier, F. Lacas, and S. Candel, "Closed-loop equivalence ratio control of premixed combustors using spectrally resolved chemiluminescence measurements," Proceedings of the Combustion Institute, vol. 29, no. 1, pp. 139–145, Jan. 2002
- [2] Y. Hardalupas and M. Orain, "Local measurements of the time dependent heat release rate and equivalence ratio using chemiluminescent emission from a flame," Combustion and Flame, vol. 139, no. 3, pp. 188–207, Nov. 2004
- [3] S. Shin, M. Kwon, S. Kim, and H. So, "Prediction of Equivalence Ratio in Combustion Flame Using Chemiluminescence Emission and Deep Neural Network," International Journal of Energy Research, vol. 2023, pp. 1–10, Sep. 2023
- [4] J. Kojima, Y. Ikeda, and T. Nakajima, "Basic aspects of OH(A), CH(A), and C2(d) chemiluminescence in the reaction zone of laminar methane– air premixed flames," Combustion and Flame, vol. 140, no. 1, pp. 34–45, Jan. 2005

- [5] J. Kojima, Y. Ikeda, and T. Nakajima, "Spatially resolved measurement of OH*, CH*, and C2* chemiluminescence in the reaction zone of laminar methane/air premixed flames," *Proceedings of the Combustion Institute*, vol. 28, no. 2, pp. 1757–1764, Jan. 2000
- [6] A. Seipel, A. Brockhinke, and K. Kohse-Hoinghaus, "Tp3: Spectroscopic characterization and simulation of chemiluminescence," in 2nd international workshop on chemiluminescence and heat release, München, 2009.
- [7] Y. K. Jeong, C. H. Jeon, and Y. J. Chang, "Evaluation of the equivalence ratio of the reacting mixture using intensity ratio of chemiluminescence in laminar partially premixed CH4-air flames," Experimental Thermal and Fluid Science, vol. 30, no. 7, pp. 663–673, Jul. 2006
- [8] T. S. Cheng, C.-Y. Wu, Y.-H. Li, and Y.-C. Chao, "Chemiluminescence Measurements of Local Equivalence Ratio in a Partially Premixed Flame," Combustion Science and Technology, vol. 178, no. 10–11, pp. 1821–1841, Dec. 2006
- [9] T. Trindade, "Chemiluminescence spectral identity of premixed methane and propane flames," PhD thesis, Lisbon University, 2015.
- [10] W. L. Dimpfl and J. L. Kinsey, "Radiative lifetimes of OH(A2Σ) and Einstein coefficients for the A-X system of OH and OD," Journal of Quantitative Spectroscopy and Radiative Transfer, vol. 21, no. 3, pp. 233–241, Mar. 1979
- [11] E. H. Fink and K. H. Welge, "Lifetime Measurements on CH(A 2Δ), CH(B 2Σ-), and C2(A 3Πg) by the Phase-Shift Method," The Journal of Chemical Physics, vol. 46, no. 11, pp. 4315–4318, Jun. 1967