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Biogas combustion: Chemiluminescence fingerprint

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ABSTRACT

A numerical and experimental study was conducted, with the purpose of inferring the influence of the CO_2 concentration (x_{CO_2}) for different equivalence ratios (ϕ) on CH_4/CO_2/air (biogas) flames chemiluminescence. A thorough analysis on the signals of OH^*, CH^*, C_2^* and CO_2^* was performed. Typical biogas compositions were tested under laminar atmospheric flame conditions, within the unburned equivalence ratio of 0.9 and 1.14 with CO_2 concentrations up to 40% in the blend. Experimental measurements of chemiluminescence were done using spectroscopy in the UV–visible region of the spectra. Simulations were performed with the GRI-Mech 3.0 mechanism without accounting for the nitrogen chemistry, extended with a chemiluminescence kinetics of OH^*, CH^*, C_2^* and CO_2^*, in a burner-stabilized frame in CANTERA. Experimental measurements and numerical simulations are compared and generally are in good agreement. It was verified that CO_2 dilution leads to a regular decrease in the emission intensities of OH^*, CH^*, C_2^* and CO_2^*. Relations between chemiluminescence intensity ratios and x_{CO_2} and ϕ were found. It was shown that OH^*/CO_2^* and C_2^*/CO_2^* have the potential predict x_{CO_2} in CH_4/CO_2/air flames. Moreover, it was verified that OH^*/CH^*, OH^*/C_2^* and CH^*/C_2^* are well suited to infer ϕ for the blends tested. It was verified that x_{CO_2} does not cause relevant changes in the chemiluminescence ratios when inferring ϕ.

1. Introduction

Greenhouse gas emissions and climate change are a major concern today and biogas, a product of anaerobic digestion, is a contributor towards a growing interest on a wider use of biofuels [1]. Biogas is mainly composed by methane (CH_4) and carbon dioxide (CO_2), typically accounting for 40–95% and 5–55% of the blend respectively [2,3]. Additionally, trace amounts of other species such as water vapor (H_2O), nitrogen (N_2), hydrogen (H_2), oxygen (O_2), carbon monoxide (CO), hydrogen sulphide (H_2S) and ammonia (NH_3) can be found in biogas composition [4,5]. The performance of biogas when burned is mostly affected by the CO_2 content of the mixture as well as the equivalence ratio, which may vary its behaviour dramatically. To know and control these parameters in real time is essential so that acoustic instabilities, soot and pollutants formation, among other problems, can be avoided. To tackle these challenges, non-intrusive monitoring techniques come into play. In hydrocarbon flames, there are three radicals with a strong and spontaneous narrow band emission: OH^*, CH^* and C_2^* [6–8] (the asterisk denotes an electronically excited state). This phenomenon permits a characterization of the burning conditions through its chemiluminescence and this has been widely used to infer several properties of the mixtures burned, such as the equivalence ratio [9–11], based on the ratios among these emitters [12–14]. The chemiluminescent emissions in spark ignition engines [15] and gas turbines [10] have been found to be like those observed in laminar premixed flames, and that makes the analysis in canonical burners relevant to understand this behaviour in widely used combustors. The study of OH^*, CH^* and C_2^* intensities on flames requires a consideration of the effect of the broadband emission attributed to CO_2^* emitters. These narrowband radicals emit in the ultraviolet/visible regions of the electromagnetic spectrum, with OH^* presenting its main peak emission centred at 309 nm, CH^* at 430 nm and C_2^* at 515 nm [16].

The chemiluminescence intensity is related with the corresponding reaction rates [10] and therefore a study of the reaction kinetics opens the possibility of modelling flame chemiluminescence. Detailed kinetic mechanisms have a high computational cost [17] and so most combustion kinetics do not include the excited radicals kinetics [18]. However, reduced mechanisms that provide reliable results for parameters such as S_L (laminar flame velocity) and T_{ad} (adiabatic flame temperature) are often used along with the addition of the excited radicals' kinetics to interpret experimental results. Some efforts to understand and model the kinetics of OH^*, CH^* and C_2^* of hydrocarbon flames have already been done, mainly focused on conventional fuels [19–27]. Furthermore, extensive studies have presented results for the

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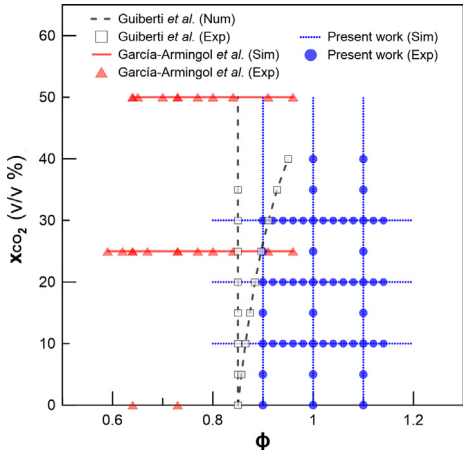

Fig. 1. Overview of similar researches on biogas chemiluminescence studies. Sets of fuel blend and equivalence ratio tested and simulated by other authors are displayed [14,18]. Blend composition is expressed in CO_2 volume content. Lines correspond to numerical simulations range and symbols to experimental conditions.

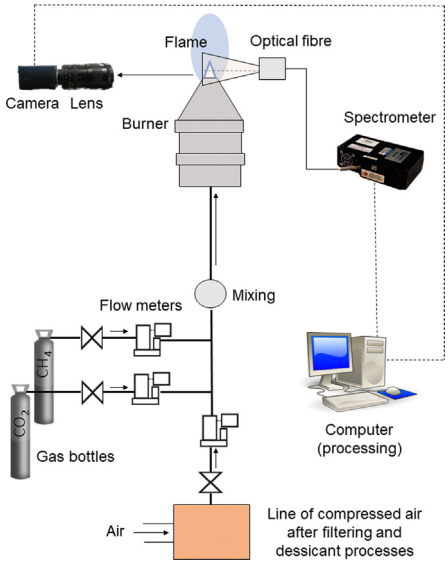

Fig. 2. Scheme of the experimental setup.

kinetic modelling of biogas combustion, mostly validated through traditional characteristics such as the S_L and T_{ad} [28–31]. Even though a large variety of mechanisms have already been applied to biogas combustion, a general conclusion taken from the literature is that GRI-Mech 3.0 [32] works very well overall. However, there very few studies on the chemiluminescence properties of biogas or binary fuel mixtures of CH_4/CO_2.

Fig. 1 exhibits an overview of selected researches on biogas chemiluminescence similar to this work. Hossain et al. [33] have shown that for a 50%CH_4/50%CO_2 the relation of the total chemiluminescence emission with the heat release was no longer linear as for pure CH_4. However, the research focused on counter diffusion flames, and so it is not included in Fig. 1. García-Armingol et al. [14] presented experimental and numerical results for three CH_4/CO_2 blends (0%, 25% and 50% of CO_2), with the equivalence ratio ranging from 0.6 to 0.96. Simulations were performed with an extended version of GRI-Mech 3.0 and reached good results for the OH^*/CH^* ratio, which is expected to be applicable to blends with different CO_2 mole fractions to infer ϕ. They also demonstrated that for the tested blends, the flame spectra (in the UV/Visible range) do not change their shape, *i.e.*, the bands structure maintain their head wavelengths, when CH_4 is diluted with CO_2. Guiberti et al. [18] performed experiments with CH_4/CO_2 blends between $0.85 \leqslant \phi \leq 0.95$, and CO_2 mole fractions up to 40%. The research was both numerical and experimental, and focuses on the behaviour of OH^*, CH^* and the CO_2^* broadband. Simulations were performed with an extended version of the Lindstedt detailed mechanism [34] with the kinetics of OH^* and CH^* proposed by Luque et al. [27]. It was found that the ratio OH^*/CO_2^* should be applicable to assess the CO_2 content in lean CH_4/CO_2/air flames.

Considering previous work exhibited on Fig. 1, the flame chemiluminescence study of binary blends of CH_4 and CO_2 has been limited to OH^*, CH^* and CO_2^* in narrow ranges of ϕ, and always for lean conditions ($\phi < 1.0$) [14,18]. However, from a detailed observation of CH_4/CO_2/air flame spectra from previous research [14], an emission peak surrounding the wavelengths attributed to C_2^* is noticeable, exhibiting considerable contributions to the chemiluminescent emissions in the presence of CO_2 in binary CH_4/CO_2 blends. Thus, it is desired to explore C_2^* in this chemiluminescence analysis because it is expected that the presence of CO_2 in the fuel blend produces an effect on C_2^* chemiluminescence intensity. It is known that when dealing with low quality biogas blends, *i.e.* with high quantities of CO_2, the range of equivalence ratios that provide higher flame stability are in rich conditions [35]. This is usually found, for example, in domestic appliances where biogas replaces natural gas [36]. In addition, a new engineering application is stratified combustion, used to extend flammability limits, which consists of a smooth continuous from lean to rich flames [37,38]. To the authors knowledge, no research on CH_4/CO_2/air flames chemiluminescence that includes C_2^* kinetics and under rich conditions has been published. In the present work, the effects of the variation of the equivalence ratio and the CO_2 content on the flame spectra were extensively studied. Several tests were conducted to collect experimental results of the chemiluminescence through flame spectroscopy. Furthermore, results for S_L were also collected to validate the biogas combustion kinetics with the addition of OH^*, CH^*, C_2^* and CO_2^* kinetics. Numerical and experimental results of chemiluminescence are then compared. The main goal is to provide clues on how CO_2 concentration and equivalence ratio can be measured in CH_4/CO_2/air flames using chemiluminescence, including C_2^* for a wide range of equivalence ratio.

In Section 2 the experimental setup and procedure are exposed, as well data processing details. The description and details of the performed simulations as well as the chemiluminescence kinetics used are described in Section 3. Section 4 compiles the results from this work and detailed analysis on what was obtained. A summary and conclusions of the work are presented in Section 5.

2. Experiment

2.1. Setup

The experimental setup used (scheme in Fig. 2) is composed by a Bunsen burner connected to three flow meters which control the intake of methane (CH_4), carbon dioxide (CO_2) and air in the mixture.

Atmospheric air is drawn from a compressor line after filtering and desiccant processes. Methane and carbon dioxide are stored in research grade bottles, with a purity of at least 99.95%. The flow controllers are from Alicat Scientific, Series 16 (20, 5 and 1 SLPM[1]). A maximum ϕ uncertainty of ± 0.025 computed using error propagation was registered. At the bottom section, the burner has four tangential fuel + air inlets and at the top it ends with a circular open nozzle with a diameter of 20 mm. It is made of stainless steel and has a high area contraction ratio of 25. Every mixture goes through one set of honeycombs before entering the final contraction zone that leads to the nozzle outlet. The wall at the outlet is very thin (~ 0.2 mm) to reduce heat losses to the

[1] Standard litter per minute