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Effect of fuel type on equivalence ratio measurements using chemiluminescence in premixed flames

Influence du combustible sur la mesure de richesse par chimiluminescence dans les flammes prémélangées

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ABSTRACT

Local temporally-resolved measurements of chemiluminescent intensity from OH*, CH* and C₂* radicals were obtained in premixed counterflow flames operating with propane and prevaporised fuels (isooctane, ethanol and methanol), for different equivalence ratios and strain rates. The results quantified independently the effects of fuel type, strain rate and equivalence ratio on chemiluminescent emissions from flames. The ability of chemiluminescent intensity from OH*, CH* and C₂* radicals to indicate heat release rate depends strongly on fuel type. The intensity ratio OH*/CH* has a monotonic decrease with equivalence ratio for all fuels and can be used to measure equivalence ratio of the reacting mixture. For propane and isooctane, the OH*/CH* ratio remains independent of flame strain rate, whereas some dependence is observed for ethanol and methanol.

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R É S U M É

Des mesures locales et résolues en temps de l'intensité de chimiluminescence des radicaux OH*, CH* et C₂* ont été réalisées dans des flammes à contre-courant alimentées par du propane ou des combustibles prévaporisés (isooctane, éthanol, méthanol) pour différents taux d'étirement et différentes richesses. Les résultats quantifient indépendamment l'influence du combustible, du taux d'étirement et de la richesse sur les émissions de chimiluminescence des flammes. La capacité de l'intensité de chimiluminescence à décrire le taux de dégagement de chaleur dépend fortement de la nature du combustible. Le rapport d'intensité OH*/CH* décroît de façon monotone avec la richesse pour tous les combustibles et peut être utilisé pour mesurer la richesse du mélange réactif. Pour le propane et l'isooctane, le rapport OH*/CH* est indépendant du taux d'étirement de la flamme, alors qu'une dépendance est observée pour l'éthanol et le méthanol.

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1. Introduction

Over the last two decades, enforced environmental regulations have led gas turbines manufacturers to develop new concepts of combustors in order to reduce pollutant emissions. However, more stringent future regulations will ask for improved operation of combustion systems. Increasing combustors performances requires a better understanding of the thermophysical phenomena occurring within the chamber. In particular, it is well known that pollutant emissions from a flame are related to quantities such as local heat release rate, equivalence ratio and degree of premixedness of the reacting mixture. It is, thus, important to have a method which can measure these quantities. An extensive review in Ref. [1] showed that flame spectral analysis has often been used to provide information on flame front structure, heat release rate and flame stoichiometry in various types of combustors operating with different fuels. However, the influence of all combustion parameters (i.e. equivalence ratio, heat release rate, temperature, pressure, flame strain rate, air preheating and type of fuel) on flame chemiluminescent emissions was not evaluated. In addition, no information was given about which radicals are more appropriate for measurements of equivalence ratio or heat release rate. This suggests a need for a parametric study in a flow where these parameters can be controlled independently from each other. Some attempts in this direction have been presented, although limited to methane or natural gas-fuelled flames [1–3]. Unfortunately, such information for other fuels of practical interest is not available in the literature, and this paper aims at providing some answers. The dependence of chemiluminescent intensity on the parameters mentioned above has led researchers to consider ratios of chemiluminescent intensities from different radicals to remove some of these dependences, in order to measure equivalence ratio, Φ . For example, in premixed and diffusion laminar flames of methane, propane and butane, intensity ratios C_2^*/CH^* or $(C_2^*)^2/(CH^* \times OH^*)$ were found to be proportional to Φ [4]. In a later study, for a burner with a similar geometry operating with methane, the ratio C_2^*/CH^* was correlated to Φ [5]. Interestingly, Φ was also correlated with the ratio C_2^*/CH^* in an Internal Combustion engine fired with propane or indolene [6], and that study claimed that the ratio C_2^*/CH^* was independent of temperature. In a premixed methane/air flame, the ratio CH^*/OH^* was found to increase monotonically with Φ [7]. In a premixed counterflow burner fuelled with natural gas, Hardalupas and Orain [1] have shown that the OH^*/CH^* intensity ratio was independent of strain rate and could be used to measure equivalence ratio in flames, whereas other ratios such as C_2^*/CH^* and C_2^*/OH^* were inappropriate. This is similar to results in a laminar premixed Bunsen burner fuelled with methane, although the potential influence of strain rate could not be eliminated in the Bunsen burner flames [8]. Apart from the study of Hardalupas and Orain [1], all the experiments mentioned above were performed in flows with simultaneous variations of equivalence ratio, strain rate, temperature and sometimes pressure. Therefore, there may be a large scattering of data for a given fuel. The purpose of this study is to systematically examine the influence of fuel type on chemiluminescent emissions under controlled operation of equivalence ratio and strain rate. Most of the chemiluminescent intensity measurements were performed using optical arrangements based on lenses, and line-of-sight integration may have influenced conclusions from these studies. Various attempts for improving the spatial resolution of chemiluminescent intensity measurements have been reported in the literature (see Ref. [1]). For example, a Cassegrain telescope system, called MICRO (Multi-colour Integrated Cassegrain Receiving Optics), was developed by Wakabayashi et al. [9], with nominal spatial resolution of $0.2 \times 1 \text{ mm}^2$, which removed chromatic aberrations associated with the light emitted by different radicals. This optical system was applied to provide information on flame front structure [10–13], or for measurements of flame equivalence ratio [8,14]. Hardalupas and Orain [1] used the MICRO system to measure chemiluminescent intensities of OH^* , CH^* from C_2^* radicals in natural gas-fuelled counterflow flames for different flow conditions and the potential of the OH^*/CH^* intensity ratio for measurement of equivalence ratio of the reacting mixture has been identified. The intensity ratio OH^*/CH^* was successfully applied in a micro gas turbine [15] and in swirl-stabilised flames [16] fuelled with natural gas to measure local equivalence ratio and degree of premixedness.

The present article investigates the effects of equivalence ratio and strain rate on the local chemiluminescent intensities of OH^* , CH^* and C_2^* radicals in a counterflow premixed burner operating with propane or prevaporised fuels (isooctane, ethanol and methanol) using the MICRO system. The purpose is to assess the influence of fuel type on the chemiluminescent intensity and its ability to describe heat release rate and measure flame equivalence ratio in combustors. The remaining paper comprises three sections. The next section describes the experimental flow and apparatus. The following section presents results in the counterflow flames and discusses the findings. Finally, the paper ends with a summary of the main findings.

2. Experimental setup

The counterflow burner used for this work is the same as that described by Hardalupas and Orain [1], except that the gas fuel supplied for the present experiments was propane. It comprises two opposed brass pipes with inner diameter $D = 30 \text{ mm}$, separated by a distance $H = 25 \text{ mm}$. The distance was selected as a compromise between maintaining a constant strain rate across the stagnation plane and having a non-uniform velocity profile at the outlet of each pipe. Propane and air were premixed and subsequently injected in both opposed jets through four pipes, parallel to the burner axis, to ensure a symmetrical flow in the opposed jets. The counterflow burner geometry was chosen, because it offers the possibility to control, independently, the equivalence ratio of the reactants and the strain rate across the flame. Experiments were also performed in counterflow flames operating with different prevaporised liquid fuels, which required modifications of the fuel supply line to the counterflow burner. Only air was supplied to the lower duct of the burner, while the upper

duct was connected to a custom-made air/fuel mixture prevaporiser which was used to produce a homogeneous mixture of fuel vapour and air with controlled flowrates at steady state conditions. Temperature of the air/fuel mixture was 420 K in the upper duct of the burner. This arrangement led to one flat flame being formed at the upper side of the stagnation plane of the flow. The liquid fuels considered in the present experiments were selected because of their use in different practical combustors. For example, iso-octane is widely used in research Spark Ignition Internal Combustion engines as an alternative fuel to commercial gasoline. Several types of gas turbines make use of propane for electricity or heat generation. Finally, ethanol is currently added in commercial automotive fuels in Europe, while some automotive engines are operating with methanol in Brazil. Experiments were performed with equivalence ratio, Φ , from 0.5 to 1.4, and area-averaged gas velocity at the jet exit, V_0 , from 2 to 5 m/s, leading to bulk flow strain rates between 160 and 400 s⁻¹ which was evaluated by the mean flow strain rate as $S = 2V_0/H$. The Reynolds number was between 4000 and 8000, and was evaluated as $Re = DV_0/\nu$. The operating conditions were imposed by flame extinction.

Local measurements of the chemiluminescent intensity from OH*, CH* and C₂* radicals were performed by using the Cassegrain optical system of Akamatsu et al. [10] connected to the spectroscopic detection unit detailed in [1]. The Cassegrain optics had a theoretical probe volume with diameter 100 μm and length 2 mm, which can resolve local flame characteristics. The light collected by the Cassegrain optics was focused on a pinhole placed in front of an optical fibre, which was connected to the photodetector unit. The light was split up into three parts using two dichroic mirrors with efficiencies above 90% for three considered wavelengths. Each part was directed on appropriate interference filters specific to the radical considered. The filters were centred at 310.4, 430.5, 515.9 nm with corresponding efficiencies of 22%, 45.3%, 71.7% and bandwidths of 13.5, 1.9, 2.1 nm for the OH*, CH* and C₂* radicals respectively. The collected light intensities were transformed into electrical signals by three photomultipliers. The corresponding intensity signals were first amplified and digitised simultaneously using a 16 bit A/D card and recorded onto a PC. The sampling frequency was 50 kHz for each signal and the duration of each measurement record was 1.64 s per radical, which was long enough to obtain statistics over at least 1000 cycles of flame fluctuation, which had a typical timescale of the order of 0.5 ms. For each flow condition, measurements were repeated four times to verify the reproducibility of the results. The statistical uncertainty for the time-averaged values obtained from these records was less than 5%. It is noted that changing the fuel type did not influence the minimum time duration of the experiments to obtain reliable statistics. The raw intensities were corrected for the efficiency of the dichroic mirrors, filters and the response of the photocathode of the photomultipliers to each wavelength. This provided intensity measurements in relative terms compared to an irradiant source of light rather than absolute measurements. However, the results indicate the relative change as a function of the different conditions appropriate to each flame. Intensity measurements were obtained on the burner axis at the location of the maximum of CH* intensity within the flame front generated by the upper duct of the burner, which was identified by traversing the optical probe along the centreline of the opposed jet configuration, and, therefore, normal to the flame. It is noted that the measurement location (along the burner axis) changed for each flame condition, because the flame stabilised at different axial positions. The measurement location was chosen to correspond to the maximum CH* intensity because this radical gave the largest signal. The time-dependent signals of chemiluminescent intensity from OH*, CH* and C₂* radicals and the intensity ratio OH*/CH* were analysed using Processing 1 as described by Hardalupas and Orain [1]. We shall only briefly recall the data analysis method here. First, a threshold was selected for the raw intensity CH* signal; which allows the detection of signals above the background noise. Second, samples above the threshold for the CH* signal were identified; these were considered to arise from chemical reaction in the optical probe volume. The corresponding points in time in the OH* intensity signal were identified to evaluate the instantaneous OH*/CH* ratio. Within the interval of the signal record being above the threshold, we identified the maximum values of the CH* and OH* signals. If the maxima of the intensities coincided, we calculated the instantaneous value of the OH*/CH* ratio from these two maxima. Third, the mean and rms of the fluctuation of the samples of the OH*/CH* ratio, determined as above, were calculated from the instantaneous OH*/CH* ratio taking into account the different efficiencies of the interference filters, dichroic mirrors and the response of the photocathodes in the detection unit. Changing the fuel type did not influence the measurement uncertainty, which remained the same as for Hardalupas and Orain [1] and was of the order of 5% for the measurements of the intensity ratio and around 2% for the individual intensities.

Some comments are required on the spatial resolution of the Cassegrain optics. The main limitation on the spatial resolution is the potential contribution of light from outside the nominal probe volume. A focussed Cassegrain optical system collects light from regions outside the nominal probe volume, weighted with distance from the probe volume, and the current optical system collects light from the probe volume with a weighting factor more than 2 orders of magnitude larger than that for light from outside the probe volume. This implies that the volume of the flame emitting light from outside the probe volume, which was collected by the Cassegrain telescope, must become more than two orders of magnitude larger than the probe volume in order to have significant contribution to the measured intensity. This limitation has been identified by Kojima et al. [17,18] and it was suggested that this effect could be minimised by placing appropriate masks in front of the optics, to improve the spatial resolution of the optical system and also to enhance the Signal-to-Noise Ratio. This suggestion was adopted in the current experiment (similarly to our work in Ref. [1]), because the flame was flat and hence light emitted from outside the probe volume could be collected only from within the plane of the flat flame. The mask aperture was oriented horizontally so that the centreline of the mask slit was parallel to the flame inclination. This arrangement reduced the possibility of light collection from outside the probe volume. However, some light could still be collected from outside the probe volume, which was responsible for the presence of non-zero background intensity in the detected signals. This effect has been considered experimentally and numerically by Hardalupas et al. [15,19] who have

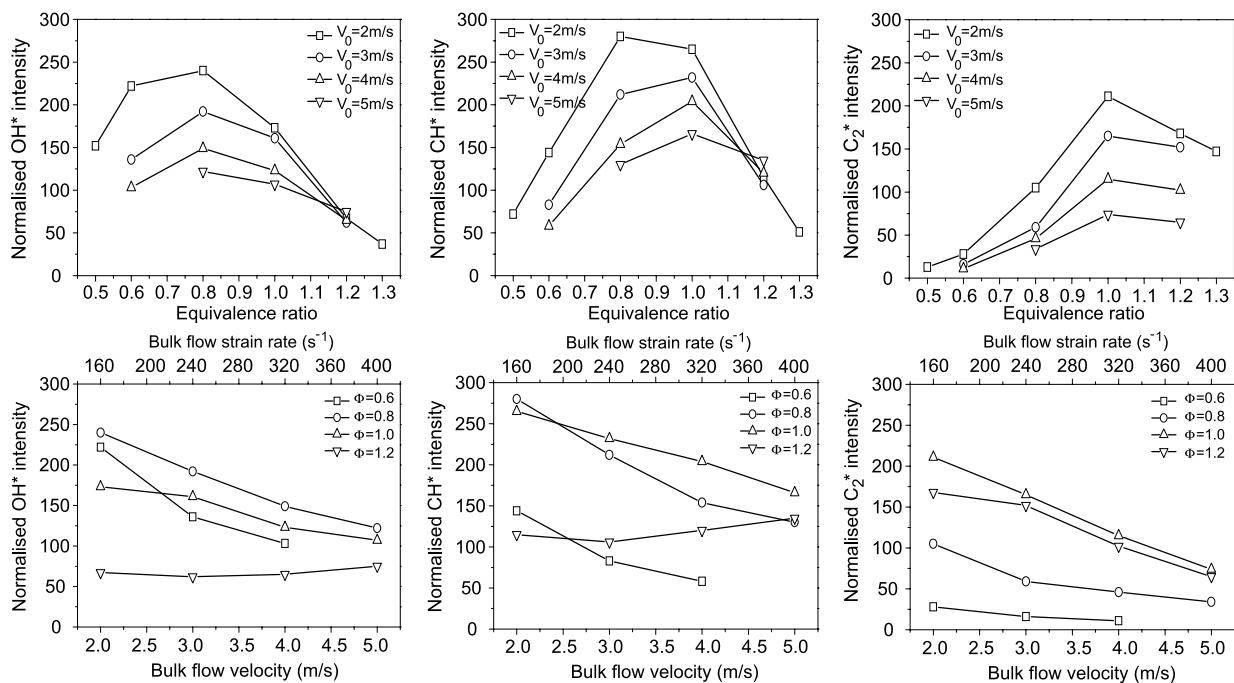


Fig. 1. Mean local chemiluminescence intensity from OH^* , CH^* and C_2^* radicals as a function of equivalence ratio (first row) and strain rate (second row) of the counterflow flames operating with propane.

shown that if the notional axis of the Cassegrain optics is placed tangentially to a cylindrical flame, the spatial resolution of the sensor is appropriate for local measurements in flames with diameter smaller than 70 mm, which is the case of the current flames. Nonetheless, despite improved spatial resolution, in the worst case, it is expected that the Cassegrain optics cannot differentiate a strong chemiluminescent emission linked with chemical reactions taking place out of the probe volume from no event in the probe volume, as shown in a Bunsen burner [19]. Nonetheless, such possibility does not occur in the current flames.

3. Results

3.1. Chemiluminescent emissions as an indicator of heat release

Heat release rate depends on parameters such as flame equivalence ratio, fuel mass flowrate, temperature, pressure, local flame strain rate and type of fuel. The definition of heat release rate is the heat released due to reaction per unit of time and unit of volume (i.e. units of $\text{J}/\text{m}^3\text{s}$): the reference volume for the heat release rate is the probe volume of the Cassegrain optics in the present experiments. Heat release rate is expected to increase as equivalence ratio increases towards stoichiometry or slightly rich mixtures, due to higher reaction rate, and then decreases for richer mixtures. Similarly, heat release rate is expected to increase with turbulence intensity or strain rate up to a critical value and then decrease, although this may not be valid close to extinction limits either lean or rich [20,21]. Therefore, any radical used to characterise heat release rate should follow these two trends. Moreover, in different burner geometries operating with premixed flames, for a given equivalence ratio, several authors reported a linear dependence between chemiluminescent intensity and fuel mass flowrate, at least in flows with Reynolds number up to 13 000 [2,3,22,23]. As a consequence, the normalisation of the chemiluminescent intensity by the fuel mass flowrate has been commonly used in the literature. However, flame strain rate and/or high turbulence levels can also influence flame chemistry and introduce non-linear effects between emitted intensity and mass flowrate [22–25]. In the present study, Reynolds number is in the range 4000–8000 and the flow is mildly turbulent. For each flow condition, the mean intensity results for each radical obtained with the data processing described in Section 2 are normalised by the corresponding fuel mass flowrate (Figs. 1 to 4). Therefore, the influence of equivalence ratio, strain rate and type of fuel on chemiluminescent intensity can be evaluated independently of the fuel flowrate effect, and the reported intensities are representative of the heat release rate per unit of fuel mass. As a result, intensities can be compared between the different conditions in relative terms.

3.1.1. Results

Figs. 1 to 4 present mean chemiluminescent intensity from OH^* , CH^* and C_2^* radicals as a function of equivalence ratio and strain rate in the counterflow flames operating with propane, isoctane, ethanol and methanol. Fig. 1 shows that, in

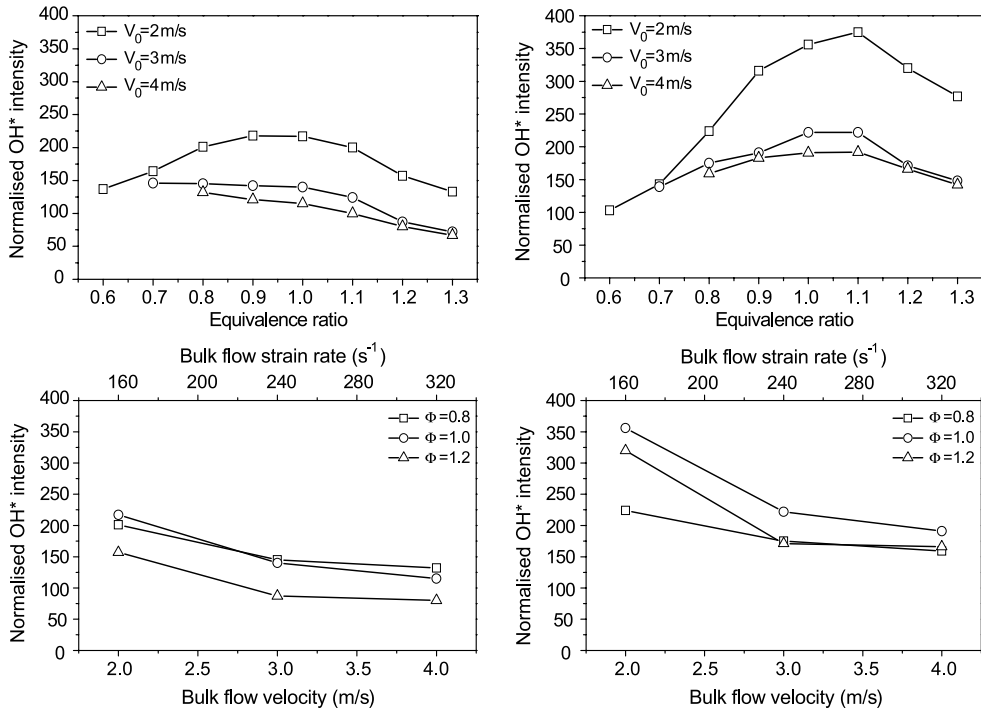


Fig. 2. Mean local chemiluminescence intensity from OH* and CH* radicals as a function of equivalence ratio (first row) and strain rate (second row) of the counterflow flames operating with isooctane.

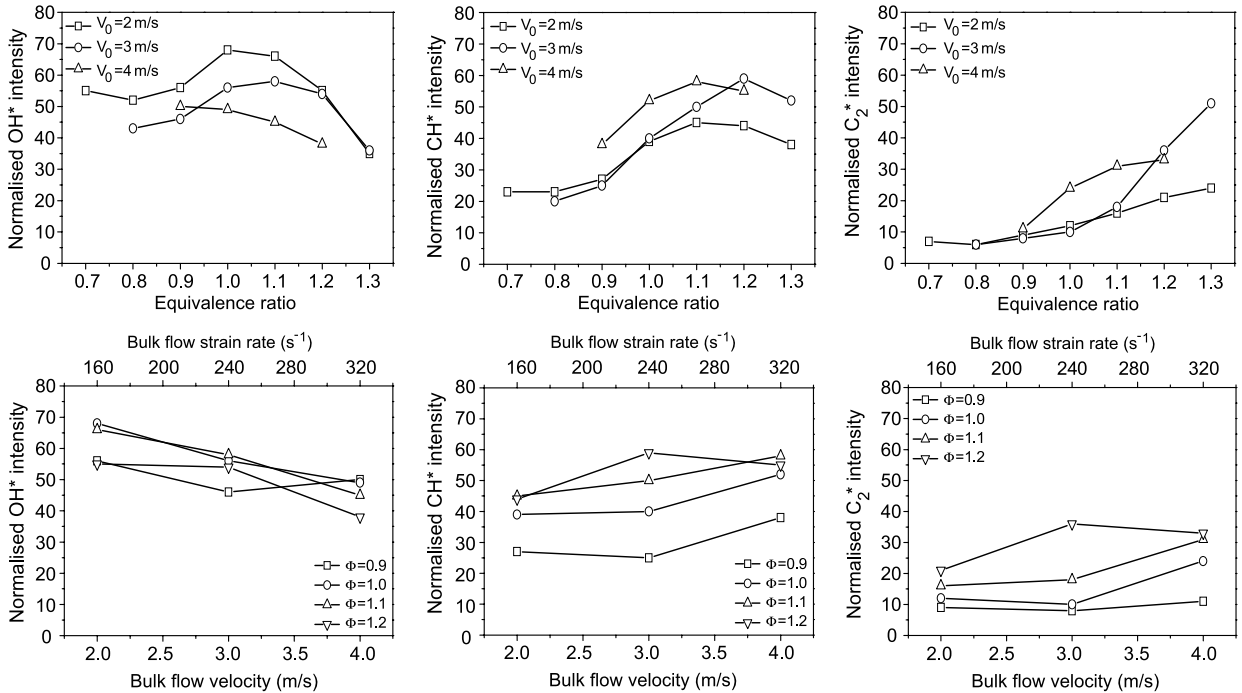


Fig. 3. Mean local chemiluminescence intensity from OH*, CH* and C₂* radicals as a function of equivalence ratio (first row) and strain rate (second row) of the counterflow flames operating with ethanol.

propane-fuelled flames, the profiles of OH* and CH* intensity are similar with a maximum for $\Phi = 0.8$ for all strain rates. OH* chemiluminescent intensity has a flatter profile than CH*, similarly to observations in natural gas-fuelled flames [1]. Fig. 1 shows that C₂* intensity has a maximum at $\Phi = 1.0$ for all the strain rates considered, which is different from natural gas where it only increases with Φ [1]. Nonetheless, C₂* intensity is fairly low for lean mixtures ($\Phi < 0.8$), which is expected

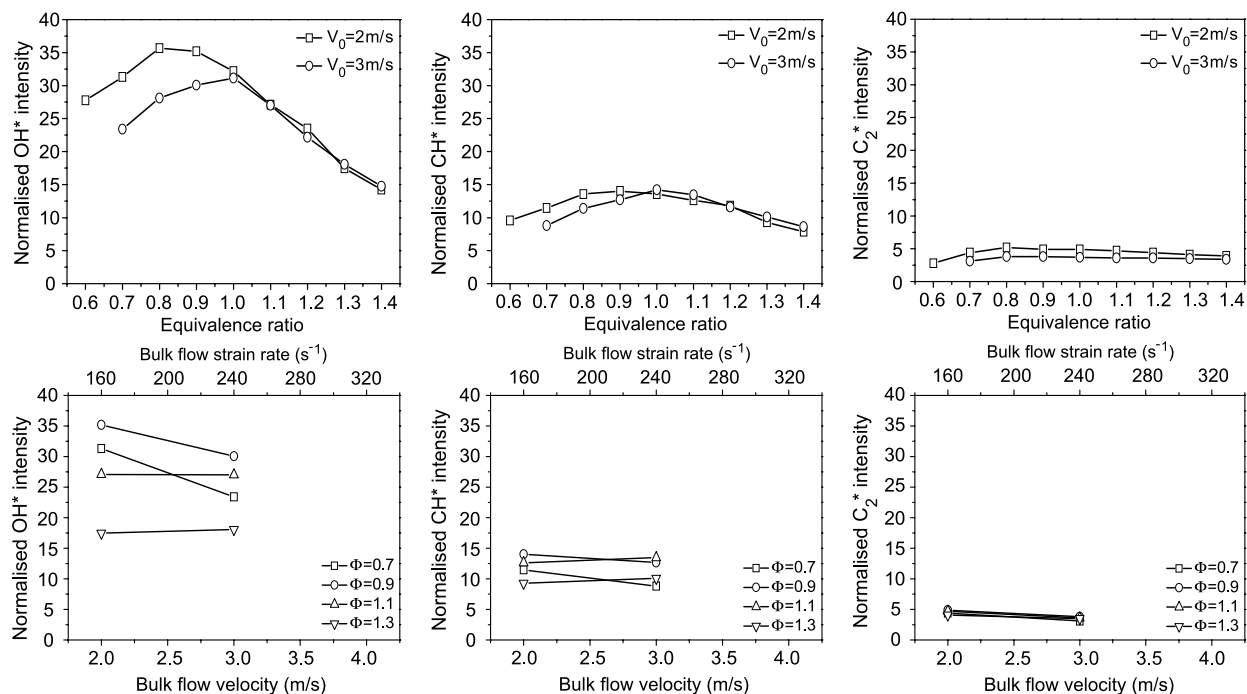


Fig. 4. Mean local chemiluminescence intensity from OH^* , CH^* and C_2^* radicals as a function of equivalence ratio (first row) and strain rate (second row) of the counterflow flames operating with methanol.

as C_2^* radicals are mainly present in rich flames [26]. Therefore, measurements using the chemiluminescent intensity emitted from this radical are associated with large uncertainties in lean flames and should be avoided. For all equivalence ratios, OH^* , CH^* and C_2^* intensities decrease with strain rate, except for $\phi = 1.2$ where OH^* and CH^* intensities remain roughly constant, Fig. 1. For isooctane-fuelled flames, the mean chemiluminescent intensity from CH^* radicals exhibits a maximum at $\phi = 1.1$ for all strain rates considered, Fig. 2. OH^* intensity has a maximum at $\phi = 1.0$ for $V_0 = 2$ m/s, remains constant up to $\phi = 1.0$ for $V_0 = 3$ m/s and decreases as ϕ increases for $V_0 = 4$ m/s. Similarly to findings with natural gas and propane fuels, OH^* intensity has a flatter profile than that of CH^* . Both OH^* and CH^* mean intensity decreases with strain rate for all equivalence ratios considered, which is similar to findings in propane-fuelled flames, Fig. 2. No measurements of C_2^* chemiluminescence intensity are available for isooctane fuel because of technical problems which occurred on the photomultiplier tube recording C_2^* chemiluminescence at the time of experiments with isooctane. Fig. 3 shows that, in ethanol-fuelled flames, profiles of OH^* and CH^* intensity have maxima between $\phi = 1.0$ and $\phi = 1.2$, except for OH^* with $V_0 = 4$ m/s where it only decreases with ϕ . For $V_0 = 4$ m/s, chemiluminescent intensity measurements could not be obtained for $\phi < 0.9$ due to flame unstable operation. C_2^* intensity is very low for lean flames ($\phi < 1.0$) and increases with ϕ for all the strain rates considered, similarly to natural gas-fuelled flames. Similarly to observations with previous fuels, OH^* intensity has a flatter profile than that of CH^* . Fig. 3 shows that CH^* and C_2^* intensity globally increases with strain rate for the four equivalence ratios considered, whereas OH^* intensity decreases. For methanol-fuelled flames, the mean chemiluminescent intensity from OH^* and CH^* radicals exhibits maxima between $\phi = 0.8$ and $\phi = 1.0$, Fig. 4. As opposed to findings with other fuels, CH^* intensity has a flatter profile than OH^* intensity. Comparing Figs. 3 and 4 shows that OH^* and CH^* intensity are about two or three times lower for methanol than for ethanol. Over the whole range of equivalence ratios considered, mean chemiluminescent intensity of C_2^* radical is fairly constant and it is extremely low for all the conditions examined; in particular, it is much lower than in ethanol-fuelled flames (between two and eight times). In fact, C_2^* chemiluminescence was barely detectable for all conditions, which was expected because methyl alcohol-fuelled flames are known to exhibit extremely low C_2^* chemiluminescent emissions [26]. Here, we did not perform measurements for three strain rates as for the other fuels, nonetheless, the general trend seems to indicate that chemiluminescent intensity from OH^* radicals decreases with strain rate, whereas that of CH^* and C_2^* radicals remains fairly constant, Fig. 4.

3.1.2. Comparison with findings from the literature

Comparison of the present chemiluminescence results with those from the literature is somehow difficult as the detection systems usually have different efficiencies, or most simply because of the lack of experimental results with the fuels investigated here, which emphasises the novelty of the current measurements. Nonetheless, a few results could be found in flames operating with propane. For example, in a propane-fuelled premixed jet flame. Itoh et al. [4] have observed that OH^* and CH^* chemiluminescent intensity peaks at equivalence ratio of 1.05 and 1.2 respectively. By contrast, in a propane-fuelled non-premixed jet flame, Yamazaki et al. [27], have found that OH^* and CH^* intensity increases linearly with overall equiva-

lence ratio between 0.7 and 1.4. However, chemiluminescence emissions in premixed and diffusion flames do not necessarily display the same behaviour with equivalence ratio [26]. Indeed, in diffusion flame, the local equivalence ratio of the reaction zone is mainly close to the stoichiometric value, whatever the global equivalence ratio is. Therefore, the increase of OH* and CH* chemiluminescence intensity with equivalence ratio observed by Yamazaki et al. [27] probably comes from the increase of heat release due to increase of fuel mass flowrate. In addition, both studies [4,27] make use of detection systems based on lenses and monochromators, and do not mention the potential influence of strain rate on chemiluminescent emissions that could not be eliminated in the jet flame; this may have influenced the results. Fansler et al. [28] measured chemiluminescence from OH*, CH* and CN* radicals in an Internal Combustion (IC) engine fired with propane. These authors have found that OH* intensity has maximum for $\phi = 1.3$, while CH* intensity linearly decreases with increasing overall equivalence ratio up to a value of 3. However, it is possible that the observed trend for OH* and CH* intensity in the engine is due to simultaneous variations of equivalence ratio, strain rate, temperature and pressure. Such variations do not occur for a given flow condition in the counterflow flame used for the present experiments. Finally, comparison with the work of Ikeda et al. [11], who used a Cassegrain optics to investigate chemiluminescence intensities from OH*, CH* and C₂* radicals in a propane-fuelled turbulent premixed jet flame for equivalence ratio between 0.9 and 1.4, shows good agreement with our results. Indeed, these authors have shown that chemiluminescent intensity from OH* and CH* radicals decreases over the range of equivalence ratio considered (however, they did not determine the equivalence ratio where OH* and CH* intensity peaks), whereas that of C₂* radical increases. Apart from the work of Aleiferis et al. [29], no measurements describing the influence of equivalence ratio or strain rate on chemiluminescence emissions in flames operating with isooctane could be found in the literature. However, these authors present only the evolution of the OH*/CH* intensity ratio with equivalence ratio in an IC engine (this issue will be discussed later in the article), but do not show individual results for OH* and CH* intensities. Sparse chemiluminescence measurements in flames operating with ethanol are reported in the literature [30,31]. Nonetheless, these experiments do not display the effect of equivalence ratio or strain rate on chemiluminescent emissions in those flames. Bertran et al. [30] simply suggested that chemiluminescence emissions are lower in ethanol-fuelled flames compared to that in flames operating with acetylene. In low-pressure ethanol-fuelled flames, Benvenuti et al. [31] have shown that for stoichiometric condition, OH* intensity is larger than that of CH*, which in turn is larger than C₂* intensity; this is similar to the present results (at least for $V_0 = 2$ and 3 m/s). Singh et al. [32] studied chemiluminescence emissions in a methanol-fuelled jet-stirred reactor at very high temperature (1870 K), for equivalence ratio between 0.7 and 1.4. The authors have found that OH* intensity peaks at about $\phi = 1.1$ and CH* emission has maximum for $\phi = 1.2$, while no C₂* chemiluminescence was detected. Difference on the position of the maximum for OH* and CH* emission between these results and our findings may come from the large preheating in Singh's experiments. In addition, Singh et al. [32] mentioned mixing inhomogeneities in the reactor and this may have influenced the results. Iida [33] performed chemiluminescence measurements in methanol-fuelled Bunsen burner flames. Although no graphs describing the influence of equivalence ratio on chemiluminescent emissions was shown, a careful look at the chemiluminescence images presented in the article suggests that OH* and CH* emissions peak at 1.0 and 1.1 respectively, whereas C₂* emissions are very low and almost constant with equivalence ratio. This is similar to the current measurements.

3.1.3. Discussion

It can be noticed that for flames operating with propane or isooctane, chemiluminescent intensities are about two times higher than those measured in the counterflow natural gas-fuelled flames [1]. Such a large difference may be due to the larger laminar burning velocity, which expresses the heat release rate, of propane or isooctane compared to that of methane [34]. In ethanol or methanol-fuelled flames, intensities are significantly lower than those observed in natural gas, propane or isooctane-fuelled flames. The lower chemiluminescence intensities observed with alcohol fuels compared to those measured in flames operating with alkane fuels may come from different combustion chemistry of alcohol-fuelled flames, which leads to different chemical reaction pathways and rates of formation of excited radicals, as will be discussed now, with a special emphasis on OH* radical. Many references describing the chemical reactions leading to the formation of OH*, CH* and C₂* radicals in flames can be found in the literature [26,35–39]. For hydrocarbon/air flames, it is generally considered that OH*, CH* and C₂* are formed via the following routes:



It is noted that Haber and Vandsburger [40] recently revisited OH* chemiluminescence modelling and proposed a global model based on the HCO radical via the reaction:



These authors have shown that their model agrees well with experimental results obtained in a methane-fuelled laminar flat flame, whereas calculations performed with the model of Dandy and Vosen [35] showed poor agreement. Haber and Vandsburger [40] claimed that their model yield better agreement because it removes the typical uncertainty related to the calculation of CH concentration which is inherent to the model using the reaction (R1). However, in alcohol-fuelled flames, other chemical reactions leading to the formation of OH* radicals have to be considered [31,41]. Please note that although both ethanol and methanol have an OH bond in their chemical formula, it does not necessarily imply that the formation of OH* radicals will be favoured compared to fuels without OH bond, despite what might be assumed in a first hypothesis. For example, Marchese et al. [41] studied the combustion of n-heptane and methanol droplets under microgravity conditions and have shown that OH* chemiluminescence intensity is significantly lower with methanol than with n-heptane. This qualitatively confirms our observations showing that OH* emission is reduced in alcohol-fuelled flames compared to flames operating with alkane fuels. Marchese et al. [41] have shown that the reaction (R1) is the route to form OH* radical in n-heptane combustion. By contrast, in methanol-fuelled flames, the authors indicated that OH* radical are not formed via the reaction (R1), but rather by thermal excitation within the flame via the reaction:



where M is a collision partner. Marchese et al. [41] claimed that the reaction (R8) should be favoured over the reaction (R1) for the formation of OH* radicals in methanol-fuelled flames because the oxidation mechanism of methanol results in very little production of CH₃ and C₂H₂ species which are the precursors for the CH radical involved in the formation of the OH* radical. By contrast, in the combustion of alkane fuels, CH₃ and C₂H₂ are produced in larger quantities and, therefore, the reaction (R1) dominates for the formation of OH* radicals. In ethanol-fuelled flames, despite CH₃ radical is the main precursor for the production of most of the excited species, Benvenuti et al. [31] have shown that the reaction (R1) is not the way of formation of OH* radicals. Instead, using sensitivity analysis and comparing modelling results with experimental data in a low-pressure combustion chamber, these authors have found that the reaction (R9) is the main responsible, despite the rate constant of the reaction (R9) being significantly higher than that of the reaction (R1):



Benvenuti et al. [31] indicated that the reaction (R9) is the dominant pathway for the formation of OH* radicals due to the high concentration of H atom in ethanol-fuelled flames. Nonetheless, the concentration of OH* radicals is expected to be lower than in alkane-fuelled flames, and so are OH* chemiluminescence emissions. Please note that the reaction (R9) also occurs in hydrogen and acetylene flames together with the reaction (R10):



Concerning CH* and C₂* radicals, Benvenuti et al. [31] have shown that, in ethanol-fuelled flames, CH* radical is formed via the reaction (R4), while 63% of C₂* radical is formed via the reaction (R5) and the reaction (R6) contributes to the remaining 37%. The lower intensities from CH* and C₂* radicals in ethanol-fuelled flames are linked with the lower concentrations of C₂H₄ and C₂H₂ (which are the precursors for the CH₂ and C₂H radicals involved in the formation of CH* and C₂* radicals) compared to that in flames operating with alkane fuels. In methanol-fuelled flames, using results from gas sampling measurements, Singh et al. [32] suggested that chemiluminescence emissions from CH* radicals are lower than in flames operating with methane due to lower concentrations of CH_x and C₂H_y species in methanol-fuelled flames relative to methane-fuelled flames.

For the four fuels investigated, chemiluminescence from OH* and CH* radicals first increase with ϕ and then decreases, which agrees with the expected dependence of heat release rate upon equivalence ratio. In propane-fuelled flames, chemiluminescence from C₂* radicals also agrees with the expected dependence, whereas it disagrees in flames operating with ethanol and methanol. For propane and isooctane-fuelled flames, chemiluminescence intensity from the different radicals decreases with strain rate, therefore, the current results seem to indicate that chemiluminescent intensity may not be a good indicator of heat release rate in those flames. However, the Markstein number, which characterises the effect of flame stretch on laminar burning velocity, is larger for propane than for methane [42]. Therefore, this suggests that the behaviour of heat release rate with strain rate observed by Hardalupas and Orain [1] for methane (i.e. an initial increase followed by a decrease) for strain rates between 160 and 320 s⁻¹ is expected to be shifted towards lower strain rates for propane. This is coherent with the results of Abdel-Gayed et al. [43] who have found that, in propane/air premixed flames, for a given equivalence ratio, laminar burning velocity decreases with increase of Karlovitz number, which is a dimensionless stretch rate, between 0.2 and 1.2. It is noted that the rate to which the laminar burning velocity decreases with increase of Karlovitz number also depends on equivalence ratio. Karlovitz number between 0.2 and 1.2 corresponds to stretch rates between 80 and 600 s⁻¹, which covers the range investigated in the present experiments. As a result, in the range [80, 600] s⁻¹, the heat release rate of premixed propane reaction is reduced with the increase of strain rate. This behaviour is observed for chemiluminescent intensity from OH*, CH* and C₂* radicals and, therefore, these can be considered as good indicators of heat release rate in propane-fuelled flames for the present range of strain rate. Similarly, Bradley et al. [44] have found that laminar burning velocity, hence the heat release rate, decreases in isooctane-fuelled flames for stretch rate between 100 and 400 s⁻¹. Therefore, in this range of stretch rate, any marker of heat release rate should follow this trend. Such a behaviour is observed for chemiluminescent intensity from OH* and CH* in the present experiments, which suggests that these radicals can be used to indicate heat release rate in isooctane-fuelled flames for

the current range of strain rate. In ethanol and methanol-fuelled flames, the behaviour of chemiluminescence intensity with strain rate depends on the radical considered. Current results can be compared with findings of Liao et al. [45,46] who have found that laminar burning velocity decreases for stretch rate between 200 and 500 s⁻¹ in flames operating with ethanol or methanol. This trend is observed for chemiluminescent intensity from OH* radicals in the present experiments, but not for CH* and C₂* radicals. This suggests that OH* radical is a good marker of heat release rate in ethanol and methanol-fuelled flames for the current range of strain rate, whereas CH* and C₂* are not. In particular, chemiluminescent intensity from CH* and C₂* radicals shall not be used in methanol-fuelled flames because of very low signals associated with large uncertainties.

Present experiments show that equivalence ratio, strain rate and type of fuel are important parameters which affect chemiluminescent emissions in flames. Results suggest that, depending on the fuel, chemiluminescent intensity of certain radicals may be considered as a good indicator of heat release rate for a fuel whereas it may not for another one. In particular, the common assumption that chemiluminescent emissions from OH*, CH* and C₂* radicals are good markers of heat release rate is not valid for all the fuels investigated here. As a result, no generalisation should be made. Indeed, although the findings of Hardalupas and Orain [1] and current results show that OH* and CH* chemiluminescent intensity is a good indicator of heat release rate in flames operating with natural gas, propane and isooctane (which are all alkanes), it may be that this is not true for other alkane fuels. Therefore, for a given fuel, it is necessary to evaluate preliminary the dependence of chemiluminescent intensity upon equivalence ratio and strain rate in a simple combustor geometry (such as a counterflow burner) for different flow conditions, in order to carefully select radicals suitable for the characterisation of heat release rate in real combustors.

3.2. Chemiluminescent emissions for equivalence ratio measurements

Chemiluminescent intensity from OH*, CH* and C₂* radicals depends on parameters influencing heat release rate, such as flame equivalence ratio, fuel mass flowrate, temperature, pressure and local flame strain rate. Therefore, the ratio of intensities emitted from these radicals may remove the dependence from other parameters and remain only dependent on equivalence ratio. Some attempts have been presented in the literature [4–8,14], but only the work of Hardalupas and Orain [1] has been performed in a flame where equivalence ratio and strain rate could be controlled independently, although limited to natural gas flames. Results for different fuels are reported in this section.

3.2.1. Results

Fig. 5 represents the evolution of OH*/CH* intensity ratio with equivalence ratio and strain rate, the error bars indicate the rms of the fluctuations of the OH*/CH* ratio. OH*/CH* intensity ratio exhibits similar monotonic relation with flame equivalence ratio for the four fuels considered. However, the dependence of OH*/CH* ratio upon the type of fuel is crucial. Indeed, while OH*/CH* ratio exhibits exponential decrease for propane and isooctane (similarly to natural gas), it decreases linearly for methanol and ethanol (for V₀ = 2 and V₀ = 3 m/s). Interestingly, OH*/CH* ratio exhibits exponential dependence upon equivalence ratio for the three alkanes, suggesting possible similar behaviour of the flame chemistry leading to chemiluminescent emissions for these three fuels. Similarly to natural gas-fuelled flames, OH*/CH* ratio is independent of strain rate for propane and isooctane, Fig. 5. It is noted that comparison between current results with propane and those with natural gas in Ref. [1] is straightforward because measurements were performed with the same experimental configuration, whereas experiments with the prevaporised liquid fuels were carried out at higher inlet temperature (420 K). Nonetheless Muruganandam et al. [47] have shown that air preheating has little effect on the CH*/OH* intensity ratio in natural gas-fuelled flames, therefore, comparison between current results with the prevaporised liquid fuels and those with natural gas [1] is not affected by the difference of inlet temperature between the two experiments. By contrast with the alkane fuels above, OH*/CH* ratio decreases as strain rate increases in ethanol and methanol-fuelled flames. As a result, the strategy for measuring equivalence ratio using OH*/CH* intensity ratio is different between alkane and alcohol fuels. Indeed, the independence of the OH*/CH* ratio upon strain rate in propane and isooctane-fuelled flames indicates that equivalence ratio measurements can be performed straightforward in those flames using respectively Eqs. (1) and (2) given below. By contrast, the dependence of the OH*/CH* ratio upon strain rate in ethanol and methanol-fuelled flames suggests that equivalence ratio measurements in flames operating with those fuels require some estimate of the flow strain rate and the appropriate calibration curve must be used (Eqs. (3) and (4) below). It is noted that if the appropriate calibration is not used, equivalence ratio measurements in ethanol and methanol-fuelled flames yield values of Φ with large errors. For the four fuels investigated in the present study, the dependence of OH*/CH* ratio upon equivalence ratio (Φ) can be approximated by:

$$\frac{\text{OH}^*}{\text{CH}^*} = 0.527 + 1.135 \exp(-(\Phi - 0.6)/0.171) \quad \text{for propane} \quad (1)$$

$$\frac{\text{OH}^*}{\text{CH}^*} = 0.344 + 0.999 \exp(-(\Phi - 0.6)/0.314) \quad \text{for isooctane} \quad (2)$$

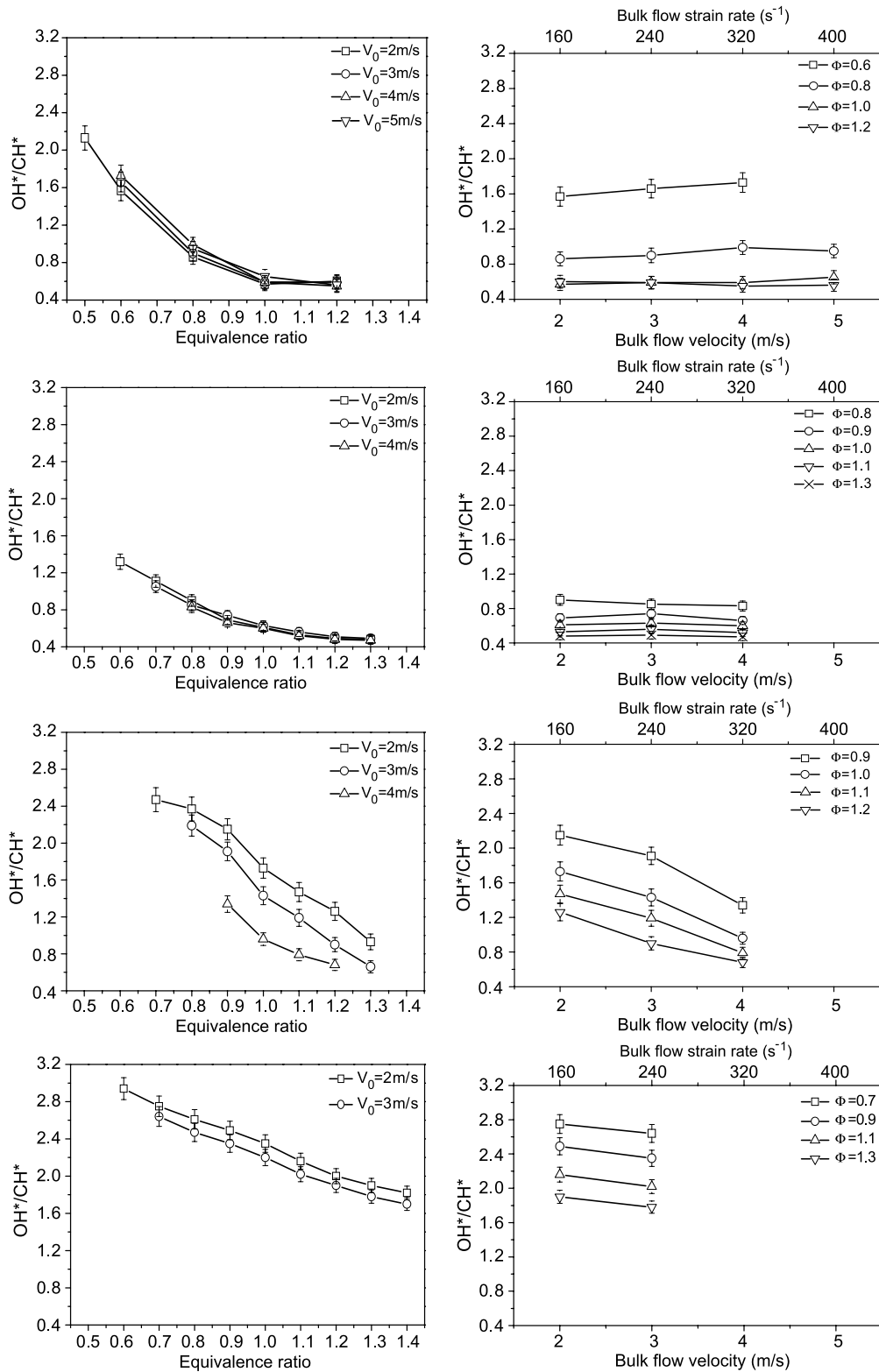


Fig. 5. Mean local chemiluminescence intensity ratio OH^*/CH^* as a function of equivalence ratio (first column) and strain rate (second column) of the counterflow flames operating with propane (first row), isooctane (second row), ethanol (third row) and methanol (fourth row).

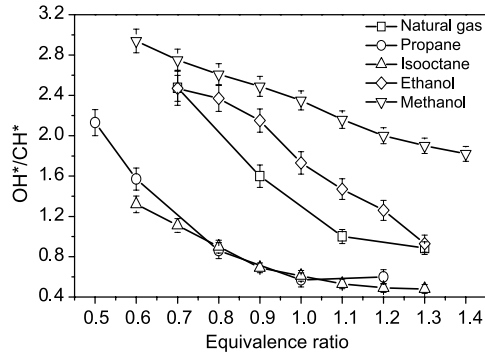


Fig. 6. Mean local chemiluminescence intensity ratio OH^*/CH^* as a function of equivalence ratio of the counterflow flames operating with natural gas (94% methane), propane, isooctane, ethanol and methanol for $V_0 = 2$ m/s.

$$\begin{aligned} \frac{\text{OH}^*}{\text{CH}^*} &= 4.454 - 2.686\Phi \\ \frac{\text{OH}^*}{\text{CH}^*} &= 4.656 - 3.12\Phi && \text{for ethanol } (V_0 = 2, 3 \text{ and } 4 \text{ m/s}) \\ \frac{\text{OH}^*}{\text{CH}^*} &= 0.590 + 0.749 \exp(-(\Phi - 0.9)/0.146) \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{\text{OH}^*}{\text{CH}^*} &= 3.766 - 1.43\Phi \\ \frac{\text{OH}^*}{\text{CH}^*} &= 3.577 - 1.376\Phi && \text{for methanol } (V_0 = 2 \text{ and } 3 \text{ m/s}) \end{aligned} \quad (4)$$

For natural gas (94% of methane), Hardalupas and Orain [1] found:

$$\frac{\text{OH}^*}{\text{CH}^*} = 0.597 + 2.107 \exp(-(\Phi - 0.7)/0.260) \quad (5)$$

For all flow conditions and for a given value of Φ , the OH^*/CH^* intensity ratio lies respectively within 10%, 8%, 8% and 5% of the value given by Eqs. (1)–(4), with respect to each fuel. For natural gas, the OH^*/CH^* ratio lies within 5% of Eq. (5) [1].

The influence of fuel type on the behaviour of OH^*/CH^* intensity ratio with equivalence ratio is summarised in Fig. 6 for $V_0 = 2$ m/s. As can be seen, for lean mixtures, natural gas and propane calibration curves have similar gradients, although not exactly in the same range of Φ . The gradient is about two times lower with isooctane and methanol, which indicates that OH^*/CH^* ratio is less sensitive to equivalence ratio. For ethanol, the gradient lies between that of natural gas and that of isooctane. Therefore, the technique should preferably be used in lean propane or isooctane-fuelled flames, whereas it is valid over a wider range of equivalence ratios in low-strained ethanol or methanol-fuelled flames. Investigation of the influence of pressure and air preheating on chemiluminescent emissions in flames is also needed for applications to practical combustors. Ikeda et al. [12] used a Cassegrain optics to perform spectroscopic measurements in methane-fuelled laminar premixed flames at pressure up to 1.5 MPa and equivalence ratio between 0.9 and 1.3. These authors have shown that OH^* and CH^* chemiluminescent intensity strongly depends on pressure, although the effect of strain rate on chemiluminescent emissions at elevated pressure was not evaluated. In addition, OH^*/CH^* intensity ratio was found to be almost insensitive to pressure effects. Together with the results of Hardalupas and Orain [1], this suggests that OH^*/CH^* ratio may also be used for equivalence ratio measurements in high-pressure combustors fuelled with methane. Dependence of chemiluminescent intensity from OH^* , CH^* and C_2^* radicals and OH^*/CH^* intensity ratio upon pressure and air preheating, for different fuels, in a counterflow flame, remains for future work.

Influence of equivalence ratio and strain rate on C_2^*/CH^* intensity ratio was also investigated for propane, ethanol and methanol, but results are not presented here due to space limitations. The findings show that C_2^*/CH^* ratio increases with equivalence ratio for propane and ethanol (similarly to natural gas results [1]) and shows little variation for methanol. Most important, C_2^*/CH^* ratio exhibits non-monotonic dependence upon strain rate. Therefore, it is not suitable for equivalence ratio measurements in premixed flames operating with propane, ethanol and methanol.

3.2.2. Comparison with findings from the literature

While many publications deal with equivalence ratio measurements using the intensity ratio OH^*/CH^* in methane or natural gas-fuelled flames [1,7,8,15,47], very little publications show the potential of OH^*/CH^* ratio for measuring equivalence ratio in flames operating with propane, isooctane, ethanol and methanol. Current results with isooctane can be compared with those of Aleiferis et al. [29] obtained in a isooctane-fuelled Spark Ignition Internal Combustion engine. For $\Phi \leq 1.0$,

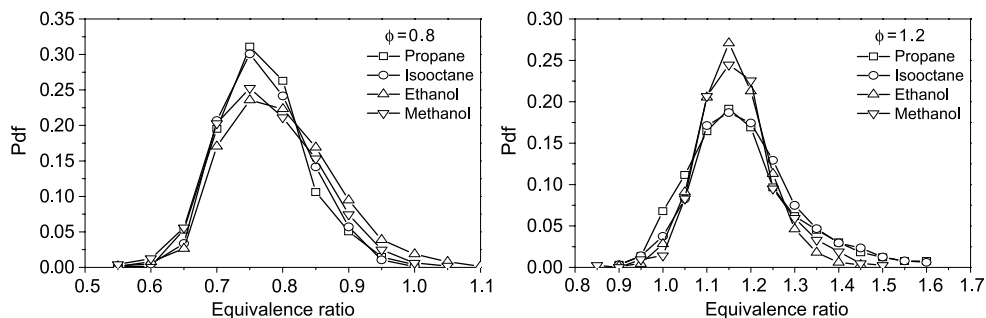


Fig. 7. Probability density function of measured equivalence ratio obtained from time-dependent chemiluminescence measurements in the counterflow flames operating with propane, isooctane, ethanol and methanol for $V_0 = 2$ m/s and metered equivalence ratio 0.8 and 1.2. For each fuel, the calibration curve used is that for $V_0 = 2$ m/s (Eqs. (1)–(4)).

the dependence of OH^*/CH^* intensity ratio upon equivalence ratio exhibits similar trend in the counterflow flames and in the engine, which confirms the applicability of our results to a different type of combustor. However, in the counterflow flames, the values for OH^*/CH^* ratio are about 0.7 times lower than that in the engine. For flames with $\Phi > 1.0$, the slopes of the two calibration curves are slightly different. In particular, Aleiferis et al. [29] have found a linear dependence of OH^*/CH^* ratio for equivalence ratio between 0.75 and 1.25 whereas the current results suggest an exponential dependence. This difference may be due to pressure or temperature effects in the engine, which affect flame reaction rate and chemistry, hence leading to different behaviour of chemiluminescent intensity with equivalence ratio. In addition, it may be that the quenching of chemiluminescence emissions by combustion products (H_2O , CO_2 , etc.) in the IC engine is different from that in the counterflow burner, due to temperature and pressure effects. Therefore, equivalence ratio measurements in a combustor operating at high pressure require preliminary calibration in a pressurised counterflow burner. In methanol-fuelled premixed flames, Iida et al. [48] performed spectroscopic measurements of chemiluminescence from OH^* , CH^* and C_2^* radicals. The authors have shown that the spectrum intensity ratio OH^*/CH^* ratio varies linearly with equivalence ratio, which is in agreement with our findings. As a result, Iida et al. [48] suggested that equivalence ratio can be obtained from chemiluminescence measurements of OH^*/CH^* ratio in methanol-fuelled flames. However, the authors did not investigate the influence of strain rate on OH^*/CH^* ratio. Finally, no measurements of equivalence ratio using OH^*/CH^* intensity ratio in flames operating with propane or ethanol could be found in the literature and, therefore, no comparison with the present results can be made.

4. Uncertainties of the technique

Fig. 5 shows that in natural gas, propane and isooctane-fuelled flames, OH^*/CH^* ratio is sensitive to flame equivalence ratio mainly for $\Phi \leq 1.0$ where the gradient is maximum and exhibits limited sensitivity for $\Phi > 1.0$. This leads to an uncertainty of approximately ± 0.05 on the determination of flame equivalence ratio for $\Phi \leq 1.0$. For $\Phi > 1.0$, the technique cannot measure accurately flame equivalence ratio and larger uncertainties of the order of ± 0.15 are expected. This suggests that OH^*/CH^* intensity ratio can be used for measuring flame equivalence ratio, independently of strain rate, in real burners operating with natural gas, propane and isooctane at atmospheric pressure, with the technique operating with smaller uncertainty for lean flames. In alcohol-fuelled flames, due to the dependence of OH^*/CH^* ratio upon strain rate, equivalence ratio measurements require some estimate of the strain rate. For ethanol, with $V_0 = 2$ m/s, the uncertainty on the determination of equivalence ratio is about ± 0.05 for $\Phi > 0.8$ and about ± 0.1 for $\Phi \leq 0.8$. For $V_0 = 3$ m/s, uncertainty is about ± 0.05 for all Φ . For $V_0 = 4$ m/s, uncertainty is also about ± 0.05 for $\Phi \leq 1.1$, whereas for richer flames, the sensitivity of OH^*/CH^* ratio upon Φ is reduced and the technique has larger uncertainties (in excess of ± 0.1). For methanol, the uncertainty on equivalence ratio measurements is about ± 0.07 for $\Phi \leq 1.0$ and of the order of ± 0.1 for $\Phi > 1.0$. However, as already mentioned, if the appropriate calibration curve for the corresponding strain rate is not used, equivalence ratio measurements in flames operating with ethanol and methanol lead to large errors on the estimation of Φ . Typically, in such a case, the precision on equivalence ratio will be between 0.1 and 0.3 for $\Phi \geq 0.9$ with ethanol and about 0.15 for all Φ with methanol.

Applicability of the technique for measuring time-dependent local equivalence ratio is now discussed. This was done by analysing the time-dependent measurements of OH^* and CH^* chemiluminescent intensities in the counterflow flames operating with propane, isooctane, ethanol and methanol using Processing 1 (described in Section 2) and applying the calibration curves (Eqs. (1)–(4)) in order to measure equivalence ratio. For the four fuels investigated, Fig. 7 shows the probability density functions (Pdf) of the measured equivalence ratio for two values of metered equivalence ratio Φ (0.8 and 1.2) and bulk flow velocity $V_0 = 2$ m/s. Each Pdf is built from about 3000 samples of equivalence ratio measurements. For both metered equivalence ratio (0.8 and 1.2), it is noted that the peak of the Pdf is slightly shifted by 0.05 from the theoretical value. This may be due to the bin of the Pdf which is 0.05 units of equivalence ratio; a better discretisation (of the order of 0.02) would probably lead to a peak closer from the theoretical value. In addition, the Pdf is broadened around

its mean value and some influence of the fuel type on the broadening can be noted. For $\Phi = 0.8$, propane and isooctane have similar profiles, while ethanol and methanol have slightly broader profiles. For $\Phi = 1.2$, propane and isooctane have similar profiles, while that of ethanol and methanol is slightly narrower. Nonetheless, the broadening is different between $\Phi = 0.8$ and $\Phi = 1.2$. Indeed, with $\Phi = 0.8$, the profiles are fairly symmetric with a Gaussian shape (at least for propane and isooctane). By contrast, with $\Phi = 1.2$, for propane and isooctane, the profiles are broader and skewed towards large equivalence ratio. This feature can be explained by the dependence of OH^*/CH^* intensity ratio upon equivalence ratio displayed in Fig. 5. In lean flames, broad Pdfs of OH^*/CH^* ratio occur and this corresponds to fairly narrow Pdfs of measured equivalence ratio. For rich flames, the gradient of the calibration curve is very shallow, which means that a little change of OH^*/CH^* ratio can result to a large change of local equivalence ratio. As a result, the narrow Pdfs of OH^*/CH^* ratio which occur in rich flames ($\Phi > 1.0$) correspond to wide Pdfs of measured equivalence ratio. For ethanol and methanol, the profile of the Pdfs is fairly symmetric because the gradient of the calibration curve is almost linear with equivalence ratio.

5. Conclusion

The dependence of chemiluminescent emissions on fuel type, flame equivalence ratio and strain rate was measured in premixed counterflow flames operating with gaseous propane or different pre-vaporised liquid fuels (isooctane, ethanol and methanol). Chemiluminescent intensity from OH^* , CH^* and C_2^* radicals was measured for equivalence ratio between 0.5 and 1.4 and strain rate in the range $[160, 400] \text{ s}^{-1}$. The findings can be summarised as follows:

- OH^* radicals can be used as an indicator of heat release rate in flames operating with propane, isooctane, ethanol and methanol-fuelled flames.
- CH^* radicals can be considered as a good marker of heat release rate in propane and isooctane-fuelled flames, but are not suitable in flames operating with ethanol and methanol.
- C_2^* radicals are an appropriate indicator of heat release rate in propane-fuelled flames, but cannot be used in flames operating with ethanol and methanol.
- OH^*/CH^* intensity ratio exhibits a monotonic relation with equivalence ratio for all fuels considered.
- OH^*/CH^* intensity ratio is independent of strain rate for propane and isooctane, while showing some dependence for ethanol and methanol.

OH^*/CH^* intensity ratio has the potential for measuring local, time-dependent flame equivalence ratio in premixed flames operating at atmospheric pressure with propane, isooctane, ethanol and methanol. For propane and isooctane, the technique should preferably be used with lean mixtures because it exhibits good sensitivity on equivalence ratio less than stoichiometry; and equivalence ratio measurements can be performed independently of flow strain rate. The uncertainty on measurements is found to be of the order of ± 0.05 units of equivalence ratio for $\Phi \leq 1.0$. Measurements in rich flames have larger uncertainties, of the order of ± 0.15 . For ethanol and methanol, the technique can be used over a larger range of equivalence ratio, and the uncertainty on flame equivalence ratio measurements is between ± 0.05 and ± 0.1 . However, equivalence ratio measurements in flames operating with ethanol and methanol require some estimate of the flow strain rate.

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