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We report here the development, validation, and application of a reliable analytical approach to calibrate gaseous formaldehyde (HCHO) using gas chromatography coupled with flame ionization detector and methanizer (GC-FID-methanizer). Contrary to the classical GC-FID, GC-FID-methanizer is capable of measuring HCHO and has a higher detection sensitivity for other oxygenated products. Therefore, it becomes a common analytical technique used in the combustion community. However, a common challenge encountered while using GC-FID-methanizer is that the conversion efficiency reduces over time of use and consequently the initial response factor of HCHO based on methanizer is no longer applicable. Therefore, we have developed a direct HCHO calibration method that consists of using of an aqueous liquid mixture with known concentration of formaldehyde and acetaldehyde as an internal standard. A detailed protocol of this proposed method was established. The method was tested and evaluated in (1) two GC-FID-methanizers (one with low and one with high conversion efficiency, respectively) and (2) a calibrated GC-Mass Spectrometry system. Finally, the method was successfully applied in a study devoted to the characterization of furanic biofuel flames and the impact of biofuels on pollutants formation, including HCHO.

Keywords: Formaldehyde, combustion, gas chromatography, FID-methanizer, quantitative measurement,

Introduction

Understanding the chemistry involved in a complex reaction medium is closely linked to the availability of appropriate analytical techniques. As an example, most of the experimental studies devoted to great societal challenges, such as environmental ones, frequently require establishing detailed databases to clearly characterize the involved processes. The necessary information mainly concerns qualitative and quantitative data which need to be determined with the best accuracy to be really representative. More especially, the combustion field requires powerful technical approaches to well describe the investigated processes. Because the understanding of the kinetics which governs combustion processes allows a better optimization of the operating parameters, it is important to obtain crucial information about specific key chemical species. Formaldehyde (HCHO) is one of these chemical compounds that must be measured. This oxygenated compound is involved in low and high temperature combustion conditions (Strozzi et al. 2019). HCHO is also present in the emissions from internal combustion engines (Gong et al. 2018). As this molecule is highly toxic and carcinogenic (Whalan et al. 2019), it, together with acetaldehyde, will be regulated in future Euro 7 norm. Consequently, this compound is an interesting indicator to report on classical fuels

oxidation (Chena et al. 2019) but also on new fuels' behavior as biofuels that produce HCHO even in highly abundant quantity (Tran et al. 2017). Moreover, formaldehyde is also a very important chemical species involved in various industrial processes, and a ubiquitous indoor air pollutant. Even if HCHO measurement is a real challenge, the community is able to analyze this very important chemical compound in various reactional media. To reach this goal, different experimental approaches are currently used to quantify formaldehyde: often Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC), according to the chemical environment (Nishikawa et al. 1995; Wei et al. 2019; Yoo et al. 2019; Zhu et al. 2019), or more specific approaches such as colorimetry (Feng et al. 2010), Fourier Transform Infrared Spectroscopy (FTIR) (Geng et al. 2015), Infrared Diode Laser Spectroscopy (Hanoune et al. 2006), or Proton Transfer Reaction − Mass Spectrometry (PTR-MS) (Vlasenko et al. 2010). Unfortunately, in combustion set-up and/or representative laboratory-scale reactors, this light aldehyde remains difficult to quantify accurately. Various analytical approaches have been developed to answer this challenge; the most commonly used are Molecular Beam sampling technique coupled with Mass Spectrometric analysis (MBMS) (Dias et al. 2012; Lamoureux et al. 2017), Fourier Transform Infrared Spectroscopy (FTIR) (Serinyel et al. 2020), in-situ laser diagnostic such as Laser Induced Fluorescence (LIF) (Burkert et al. 2016), and more specifically Gas Chromatography (GC) with FID-methanizer detector (Pelucchi et al. 2019; Gong et al. 2018; Luong et al. 1996; Tran et al. 2015).

Methanizer contains a catalyst (commonly nickel) for hydrogenation and is located before FID. In contrast to classical GC-FID, GC-FID-methanizer is able to measure HCHO, CO, CO_2 and has a higher detection sensitivity for other oxygenated species. Therefore, the latter technique is largely and commonly used in combustion studies. GC-FID-methanizer measurements are doubtless useful for combustion studies, which have been proved to be accurate and reliable with error around 10% (Rodriguez A. 2016; Tran et al. 2015; Tran L. 2013). However, a common challenge encountered while using GC-FID-methanizer is that the conversion efficiency reduces over time of use and consequently the initial response factor of HCHO based on methanizer (i.e. the same as that of CH_4) is no longer applicable. To the best of our knowledge, no specific study devoted to catalyst deactivation in GC methanizer has been carried out to date. Therefore, among different deactivation mechanisms (poisoning, fouling, thermal degradation, …) which are generally considered for heterogeneous catalysts (Argyle et al. 2015), the main one involved is not yet understood. Changing a methanizer is financially demanding and time consuming and it becomes necessary to intervene on the system. In the present study, a direct calibration method is proposed to allow to continue using low efficient conversion GC-FID-methanizer devices with an equivalent precision as an optimal GC-FID-methanizer. This method is not only limited to such FID-methanizer but also useful for controlling the performance of any GC-FID-methanizer and for calibration HCHO in GG-MS.

The paper structure is organized as follows. First, the experimental device that includes a flame burner and a GC system is described. Next, the proposed method for formaldehyde calibration is detailed with regard to principle of the method, solution preparation protocol, response factor measurements, and error estimation. Then, validation and application of the method are presented. Finally, the work and the obtained results are synthesized.

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Experimental system

As mentioned above, the scientific background was to better understand the kinetic mechanisms involved during the oxidation of furan and tetrahydrofuran (THF) as lignocellulosic biofuels in flame conditions. Development of a calibration method and quantification of HCHO are an important part of this study and are detailed in the present paper. The global experimental setup (Figure 1) consists of a flame burner, a specific sampling system, and two GC devices. In this section, we briefly present the experimental set-up and more especially the GC devices and protocols used to establish the detailed database.
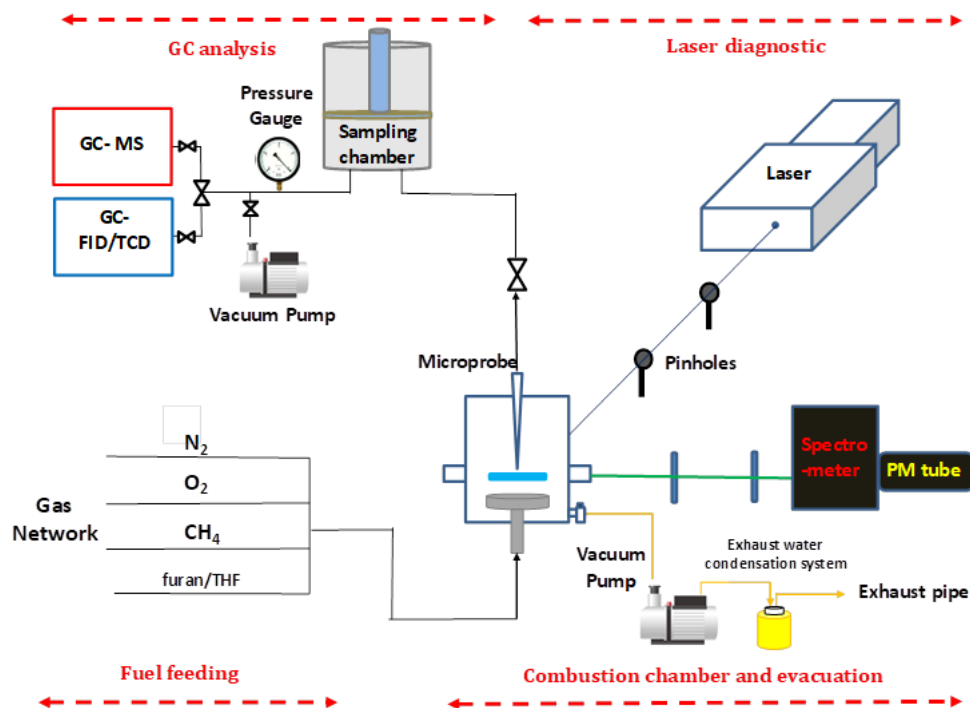

Figure 1. Global schematic view of the experimental set-up used to characterize CH_4/biofuel/O_2/N_2 flames structures. The laser system was used for temperature measurements.

Premixed flames as kinetic reactor

Premixed laminar flames are highly useful as ideal reactor in kinetic studies to obtain experimental data, such as temperature and chemical species concentration evolutions. This kind of kinetic reactor is commonly used for the development, optimization and validation of detailed kinetic mechanisms, notably for fuel oxidation and/or pollutants formation. This reactor can be coupled with different analytical devices such as laser diagnostic systems, FTIR-spectroscopy and GC devices.

To study furan and THF oxidation and their impact on pollutants formation, especially HCHO that is discussed in the present paper, six low-pressure CH_4/biofuel/O_2/N_2 premixed laminar flames were investigated at two equivalence ratios (ϕ) and 68% N_2 dilution. Stoichiometric (ϕ=1) and slightly fuel-rich (ϕ=1.2) flames were stabilized on a McKenna burner housed in a vacuum chamber maintained at 5.3 kPa. For the two equivalence ratios, the fuel conditions considered were pure methane, used as reference flames, a mixture furan (50%) / methane (50%) to study the furan effect, and a mixture THF (50%) / methane (50%) to evaluate the impact of THF. The chemical

structure of these flames was characterized by establishing the mole fraction profiles of stable intermediates and products as a function of the height above the burner (HAB) using gas chromatography techniques.

Gas chromatography setup

To analyze stable chemical products in the studied flames, we collect gaseous samples at different HABs using an appropriate quartz microprobe (250 μm orifice). To access the qualitative and quantitative information of these chemical species present in the reactional mixture, these samples are analyzed by two GC systems.

The first GC system (Agilent Technologies 5975C) is coupled to a mass spectrometer (MS) with electron ionization at 70 eV for the identification of the hydrocarbon and oxygenated species. The collected species are separated using a Rt-QBond capillary column (30m×0.25mm×8μm, 100% divinylbenzene, Restek) with helium as carrier gas. The comparison of the experimental mass spectra to the NIST Database (NIST 2020) allows to identify the species eluted from the gas chromatographic device.

The second GC device (Perkin Elmer Clarus 580) is coupled with two detectors placed in parallel, a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) with methanizer (nickel catalyst hydrogenating reactor). This analysis system allows to establish the relative evolution profiles of the stable chemical species detected in the flames, and, in a second step, to quantify these species. A 10-port-gas-valve with diaphragm (Gas Sampling Valve, GSV) equipped with 2 injection loops enables to simultaneously inject the gaseous samples in two different columns connected respectively to TCD and FID detectors. Helium is used as carried gas for the FID channel and argon for the TCD channel.

The GC/FID/TCD analytical procedure is set out schematically in Figure 2. The gaseous sample is first sent to the GSV valve to fill the two injection loops (Position 1 in Figure 2). For the injection of the gaseous samples into the two columns, the GSV rotates to allow the passage of the carrier gases, which push the samples towards the two detector channels (Position 2 in Figure 2). On the TCD line, the Haysep column allows to protect the molecular sieve (MS5A 1/16" 2m×1mm ID) from hydrocarbon contamination. On the other hand, the FID line is equipped with a Rt-QBond capillary column (30m×0.25mm×8μm, 100% divinylbenzene, Restek; the same column as the one used in the GC/MS device) to analyze hydrocarbons and oxygenated compounds. After the gases are eluted from the Haysep column, the V3 valve turns in back-flush position to eluate hydrocarbons towards vent B (Position 3 in Figure 2). At the end of the analysis procedure, both valves return to "Position 1".

As mentioned above one of the objectives of this study is to develop a direct calibration method for HCHO with GC-FID-methanizer, especially useful when the conversion efficiency of the latter system reduces. Therefore, two FID-methanizers were used alternatively for the second GC device. The first FID-methanizer has low conversion efficiency (to apply the proposed calibration method), for which the response factor of HCHO based on methanizer (i.e. the same as that of CH_4) is no longer applicable. The second one has a high conversion efficiency (>98%) and is used to validate the calibration method. The validation of the method has been also performed using the first GC system, i.e. GC-MS. The calibration method and protocol will be presented in the next sections.
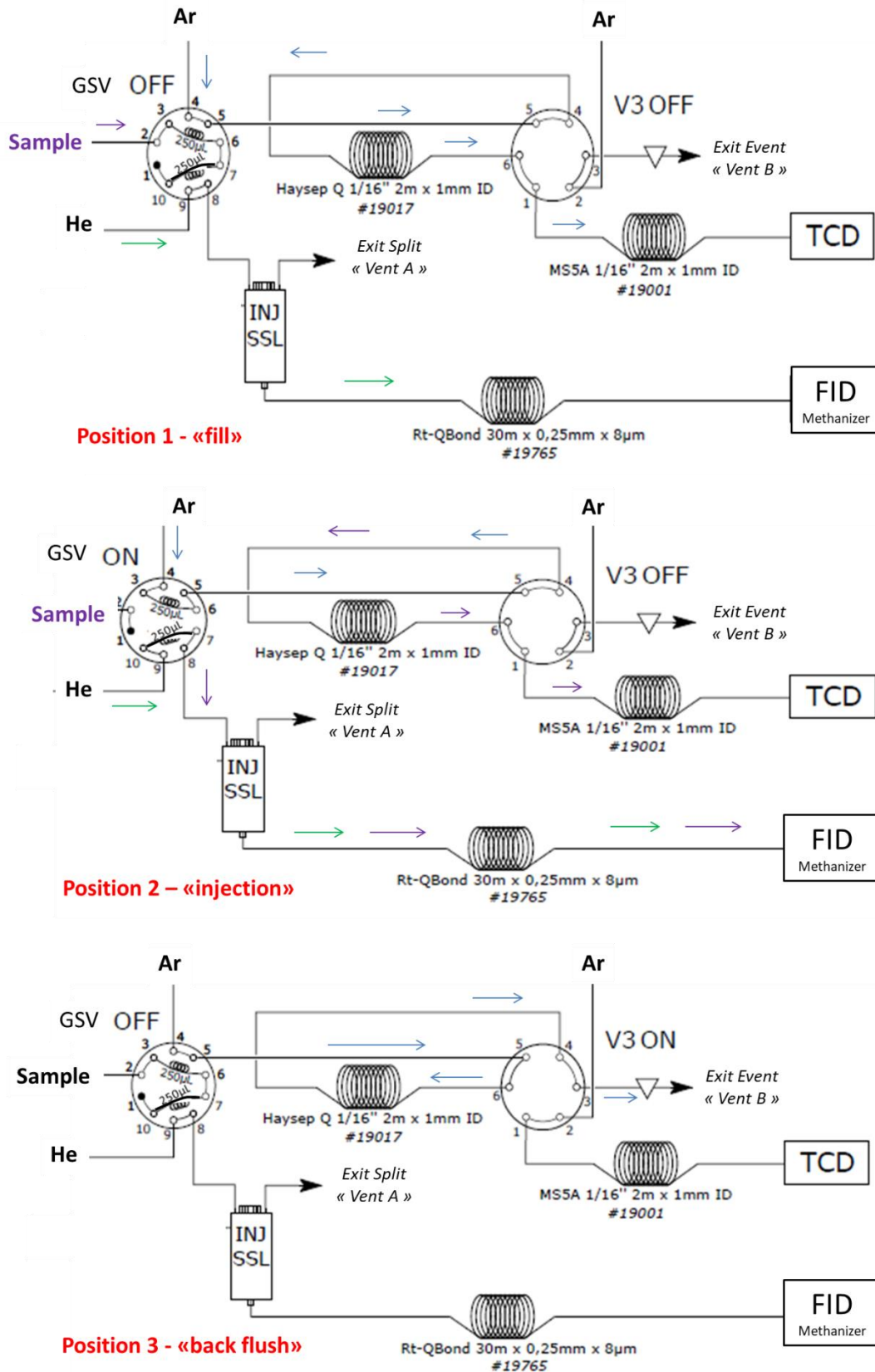
Figure 2. Principle of analysis of gaseous samples from CH_4/biofuel/O_2/N_2 premixed laminar flames by using GC/FID/TCD device.

Presentation of the proposed method for formaldehyde calibration
Principle of the method
The method consists in using an aqueous liquid mixture with known concentration of formaldehyde and of another species used as internal standard. The GC analysis of this liquid sample then allows to determine the ratio of the response factors between formaldehyde and the internal standard. By considering that the value of this ratio does not depend on the initial physical state of the sample, it is then possible to obtain the response factor of formaldehyde for gaseous samples (i.e. in flame condition) from the response of the internal standard.

In our case, and because of its presence in the studied reactional medium (CH_4/biofuel/O_2/N_2 premixed laminar flames), acetaldehyde (CH_3CHO) is the best candidate as an internal standard for formaldehyde aqueous solutions. CH_3CHO is a liquid aldehyde at room temperature conditions, with a chemical structure close to the formaldehyde one. CH_3CHO is produced in abundant quantities in the combustion of several fuels and biofuels (Giarracca, L. 2018; Tran et al. 2017). It is miscible in all proportions with water (Riddick et al. 1986) and can be easily calibrated in the gas phase with GC device by preparing gas mixtures using the partial pressure method.

For liquid samples, the response factor for the (i) species is defined as the ratio of the relevant peak area (A_i) to its mole fraction (χ_i). So, the response factors (α_{liq}^{HCHO}) and ($\alpha_{liq}^{CH_3CHO}$) respectively for formaldehyde and acetaldehyde, are the following:

$$\alpha_{liq}^{HCHO} = \frac{A_{HCHO}}{\chi_{HCHO}} \quad (1)$$

$$\alpha_{liq}^{CH_3CHO} = \frac{A_{CH_3CHO}}{\chi_{CH_3CHO}} \quad (2)$$

We can then formulate the ratio RF between the two response factors in liquid phase:

$$RF = \frac{\alpha_{liq}^{HCHO}}{\alpha_{liq}^{CH_3CHO}} \quad (3)$$

Based on their vapor pressure curves (NIST Chemistry WebBook), HCHO and CH_3CHO are completely in gas phase at conditions in the GC injector (1.7 bar and 250 °C). Therefore, it can reasonably assume that RF is not affected by the physical state of the sample (liquid or gaseous), it becomes possible to determine the response factor of formaldehyde in the gas phase knowing the response factor of acetaldehyde in the gas phase ($\alpha_{gas}^{CH_3CHO}$):

$$\alpha_{gas}^{HCHO} = RF \times \alpha_{gas}^{CH_3CHO} \quad (4)$$

Therefore, the experimental approach consists in three different steps:
-   Preparation of appropriate aqueous samples with known concentration of HCHO and CH_3CHO;
-   GC analysis of these samples to determine the RF ratio;
-   Calculation of the formaldehyde aqueous response factor (α_{liq}^{HCHO}) from RF and the acetaldehyde gaseous response factor ($\alpha_{gas}^{CH_3CHO}$).

For a better accuracy, the value of RF has to be averaged on several injections of HCHO/CH_3CHO/H_2O solutions presenting different concentrations for each compound.

The chromatographic analysis conditions are the same for each kind of samples (gaseous, liquid or flame samples). It is defined and optimized to obtain the best

chromatographic separation in flame conditions and for all the species we analyzed. The main conditions for the chromatographic analyses are reported in Table 1.

Chromatograph	Perkin Elmer Clarus 580
Injection Loop (GSV)	2 loops V = 250 µL T_{GSV} = 150 °C
Injector FID	Split 25:1 ; (Split mode) Split 1:1 (Splitless mode) T = 250 °C P = 1.7 bar
Time events V3	0 min.: OFF: trapping column and molecular sieve are in series 5 min.: ON: trapping column is isolated from molecular sieve 28.3 min.: OFF: trapping column and molecular sieve are in series

Columns	Rt-QBond (capillary column)
	    30 m × 0.25 mm × 8µm,
	    Vector gas: He
	Haysep Q (column for trapping)
	    1/16" 2m × 1 mm
	    Vector gas: Ar
	MS5A (molecular sieve)
	    1/16" 2m × 1 mm
	    Vector gas: Ar

Flow	1 ml/min FID channel 8.5 mL/min TCD channel
Oven temperature programming	40 °C for 5.3 min 10 °C/min--->240°C 240 °C for 3min
Methanizer	T = 350°C
FID detector	T = 400°C H_2 = 40 mL/min Air = 400 mL/min
TCD detector	T=120 °C He (reference) = 5 mL/min

Table 1. Main GC analysis conditions.

Solution preparation protocol

Formaldehyde aqueous solution

Commercial aqueous solutions of formaldehyde are available but mainly in high concentration condition (such as "formalin" which is a saturated aqueous solution with about 40% by volume of HCHO). For concentrations less than 5 mol%, HCHO is usually in aqueous solution in its hydrated form (methylene glycol). As the HCHO concentration increases, the methylene glycol risks leading to the formation of oligomers (Lebrun et al. 2003). To prevent the polymerization process, methanol may be added (10-12% by volume) as stabilizer. However, methanol reacts with formaldehyde in liquid phase to form hemi-formal which affects the volatility of the formaldehyde in solution (Brandani et al. 1985). Therefore, these solutions were not chosen in the present work.

As described elsewhere (Oancea 2010; Delcroix 2013), it is possible to prepare stable HCHO aqueous solutions up to HCHO mole fraction of 10% without methanol. By following the authors' recommendations, we prepared aqueous solutions containing 1% (mole) of formaldehyde by depolymerization of paraformaldehyde in deionized water (Walker 1964). Deionized water was produced with an Aquadem EFP2010 which supplies water with a peak resistivity of 18 MΩ.cm. The appropriate amounts of

paraformaldehyde (Sigma-Aldrich, powder, 95%) and deionized water to prepare about 100 ml of solution are heated around 373 K until complete dissolution of the paraformaldehyde. To favor paraformaldehyde depolymerization, a very small amount (a few drops with Pasteur pipette) of sodium hydroxide solution (0.1 M) is added to the mixture.

After cooling at ambient temperature, the formaldehyde solutions are weighed again, and the necessary amount of deionized water is added to compensate the loss of water by evaporation. Acetaldehyde is added in the same range of concentration of HCHO by using two different procedures (see below). The HCHO/CH$_3$CHO/H$_2$O solution is then weighed again, and the final mole fraction for each compound is then calculated. Because of the low acetaldehyde boiling point (20.2 °C), precautions must be taken. Therefore, to avoid any change of the liquid composition and to reduce its volatility, the final solution is cooled down to around 5-10 °C in an ice /water vessel.

Standard solution preparation

To find the best protocol to have stable and reproducible analysis results, we tested two different procedures to obtain the diluted standard solutions for the HCHO calibration step. The first method (called M1) consists in the dilution of the stock solution of formaldehyde (1% mol) with deionized water to obtain two solutions respectively 0.5 % mol and 0.1 % mol. After that, the corresponding quantity of acetaldehyde is added by weighing in each formaldehyde solution to obtain equimolar HCHO/CH$_3$CHO solutions. The second procedure (called M2) consists instead in adding acetaldehyde directly into the stock solution to obtain a final solution characterized by a concentration of 1% mol for each compound. This solution is then diluted to obtain two standard acetaldehyde-formaldehyde solutions at 0.5 % and 0.1 % respectively.

The cold solutions are injected several times using a 1µl syringe into the GC-FID device running with the same method as the one used for gaseous samples analysis (see Table 1). To illustrate the GC method developed in this work, the Figure 3 shows the zone of interest of the chromatogram resulting from the analysis of a standard acetaldehyde-formaldehyde liquid solution. As can be noted that the form of HCHO peak is specific with a long tail that could raise a question about its influence on the peak integration of HCHO and CH$_3$CHO. Two integration strategies were applied: one is based on a common baseline for two species (blue dotted line on Figure 3) and one based on two separate baselines for two species, respectively (red lines). The difference in formaldehyde peak between two strategies is very low (0.3-0.7%), however.
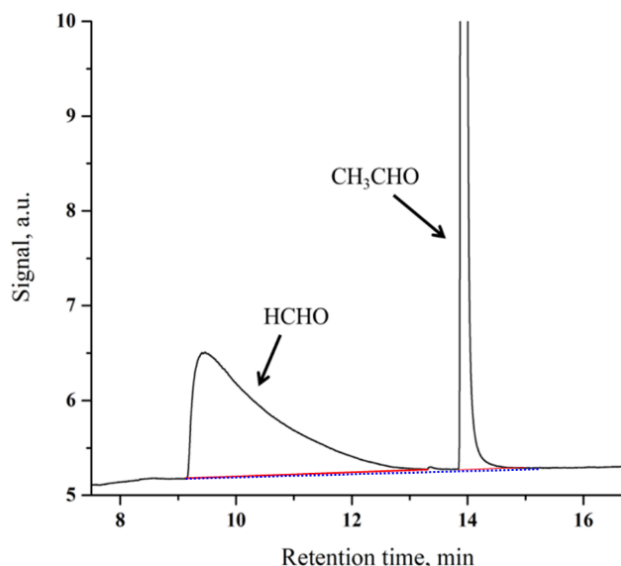
Figure 3. GC analysis of acetaldehyde-formaldehyde aqueous solutions. See GC conditions in Table 1. *Blue dotted line:* common base line of both peaks; *red lines: separated based lines.*

Response factor measurements

After injection of the standard solutions with the low conversion efficiency GC-FID-methanizer, the analysis of the chromatograms allows us to determine the ratio RF as described before. Results are summarized in Figure 4 by presenting the RF values obtained using M1 and M2 methods, as a function of the formaldehyde concentration (molar fraction). The reproducibility is not as satisfying as expected, especially for the lower concentrations. These solutions are the more affected by the high volatility of each aldehyde, inducing significant variation in their relative concentration despite all the precautions taken. Nevertheless, we can consider as reasonable the choice to retain the mean value of RF (RF=0.451 ± 0.085) to calibrate HCHO even if the reproducibility is estimated to be ± 18.87%.
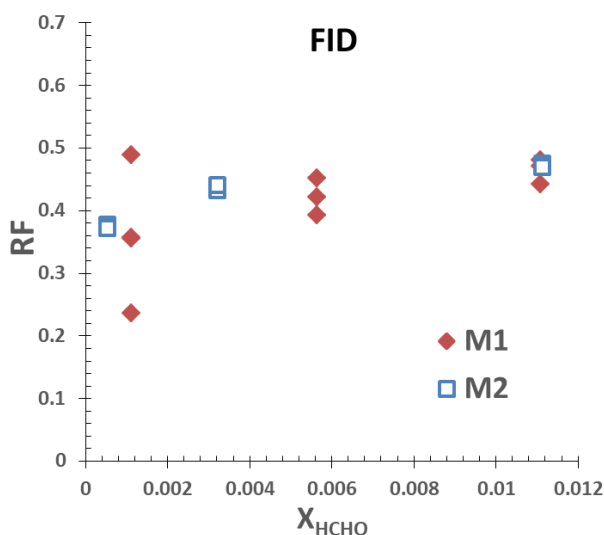

Figure 4. Reproducibility of RF factor for FID detector with M1 and M2 procedures and depending on formaldehyde molar fraction in liquid solutions.

Error estimation

For the calibration method, and to limit uncertainties, several injections have been done

to test the reproducibility of the response factors ratio RF. In spite of all precautions, several parameters can however contribute substantially to dispersed or biased measurements. First, the preparation procedure of the standard aqueous solutions is a real source of errors; this includes the sampling by weighing (balance readability ±0.1 mg), the homogeneity of the liquid solutions, the possible loss of matter during successive dilutions (volumetric flask readability ±0.1 ml), or even the aldehydes volatility during all the preparation steps. Second, the analysis procedure strictly speaking also contributes to increase uncertainties and affect reproducibility. As an example, the accuracy of the measurements remains dependent on the quantity of solution injected which is affected by the manual precision of the operator; this is even more so for response factor measurements. Other errors could be directly linked to the analytical apparatus and the data processing; we can mention here a possible loss during sampling and injection steps, some potential cold spots along the analytical line, the stability of the FID detector, the interpretation of the results (integration of peaks ± 1%), the GC signal temporal resolution, etc. Finally, taking into account all these parameters, we estimate that the global uncertainties on the experimental measurements by GC are ± 25% for the calibration of HCHO signal to absolute concentration (mole fraction). This uncertainty range is very acceptable for the "tricky" species like HCHO.

Acetaldehyde response factor measurements using various gaseous standard mixture are easier compared to formaldehyde; in the same way the uncertainties are lower and evaluated to be ±10%.

Test and validation of the proposed formaldehyde calibration method
Comparison with a new optimized GC-FID-methanizer device
The calibrated GC-FID-methanizer above was then used to measure peak mole fractions of HCHO in the six studied flames to test and validate the proposed HCHO calibration and to ensure that this approach is an accurate way to quantify this key species. For this purpose, we have replaced this FID-methanizer by a new optimized FID-methanizer that has high conversion efficiency (>97%) and then compared the results of HCHO peak mole fractions obtained by the two FID-methanizers. This comparison is presented in Figure 5. Note that because of its high conversion efficiency, in the new optimized FID-methanizer HCHO response factor is taken as that of CH_4. The CH_4 response factor is easy to determine by analyzing standard CH_4/N_2 gaseous mixture regulated by mass-flow controller. As demonstrated in Figure 5, the comparison exhibits a very satisfying agreement (difference less than 6%) between the two FID-methanizers, the proposed HCHO aqueous solution method can thus be considered as efficient and reliable.
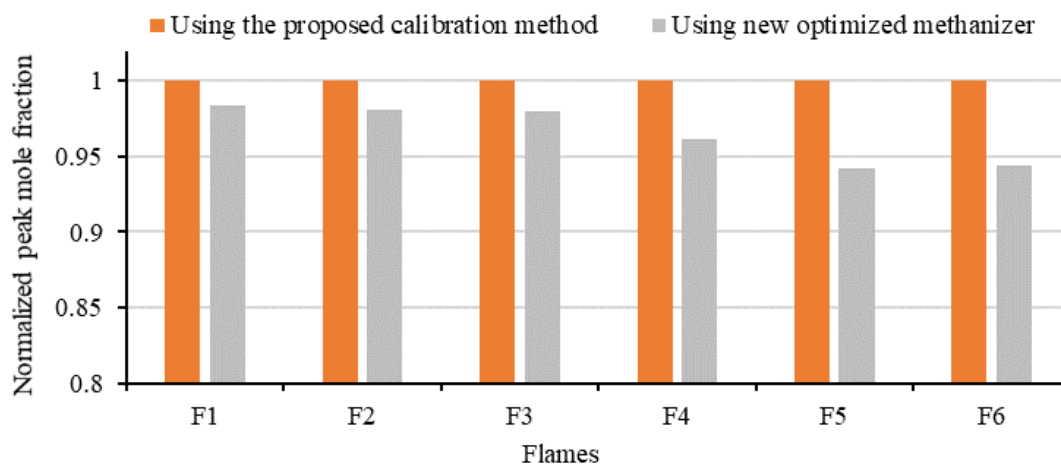
Figure 5. Comparison of peak mole fractions of formaldehyde calibrated with the proposed calibration method and with the new optimized FID-methanizer for the six studied flames (F1 and F2: stoechiometric and fuel-rich $CH_4/O_2/N_2$ flames, respectively; F3 and F4: stoechiometric and fuel-rich $CH_4/furan/O_2/N_2$ flames, respectively; F5 and F6: stoechiometric and fuel-rich $CH_4/THF/O_2/N_2$ flames, respectively). For clarity, normalization by the highest value is performed.

Comparison with a calibrated GC-MS

To further check the reliability of the proposed calibration method, it is also tested with the GC-MS system. The same procedure as the one described previously has been used to determine the FR factor for the formaldehyde/acetaldehyde mixtures. The results are presented in Figure 6 *(left panel)* and lead to a mean value of RF of 0.412 ± 0.042.

By using this RF value, we have calibrated the HCHO relative profile as a function of HAB obtained via GC-MS analysis in a selected flame (stoichiometric $CH_4/furan/O_2/N_2$ flame) and compare to the HCHO profile measured by the GC-FID-methanizer calibrated using the proposed calibration method described above. Figure 6 *(right panel)* presents this comparison.

The very satisfying agreement found in Figure 6 *(right panel)* allows us to conclude that the use of the new calibration method is validated and it is also useful for gaseous formaldehyde quantitative measurements with GC-MS devices. A deviation for the measurements located 3.2 mm above the burner may result from the difference in sensitivity between FID and MS detectors or from the uncertainty of the burner position (±0.25mm), and not from the proposed calibration method. Note that in flame species characterization, the most important parts are the flame front and peak mole fraction (HAB≤2 mm), for which an overall good agreement is observed between two systems.
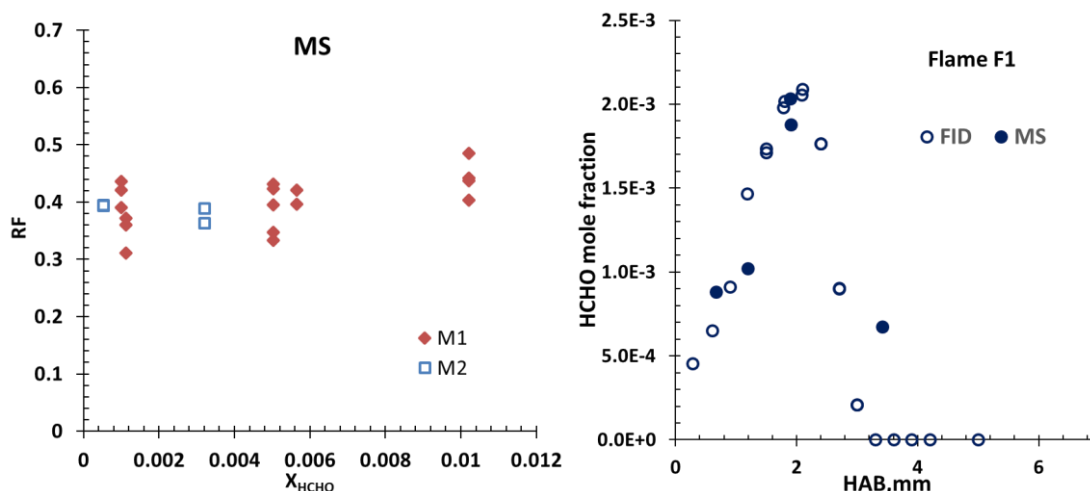
Figure 6. *Left panel*: Reproducibility of RF factor for MS detector with M1 and M2 methods, as a function of the formaldehyde molar fraction in liquid solutions. *Right panel:* Comparison of the formaldehyde experimental mole fraction profiles obtained with GC-MS and GC-FID devices calibrated using the aqueous solution calibration method for a selected flame (F1: stoichiometric CH_4/furan/O_2/N_2 flame).

Application of the obtained calibration factors to a flame chemistry study
Mole fractions profiles of formaldehyde in flames doped with furanic biofuels
Knowing the RF factor and the response factor of acetaldehyde in gas phase, it becomes possible to calibrate the HCHO relative evolution profiles measured in the six studied CH_4/biofuel/O_2/N_2 flames in absolute concentration. To illustrate the final results obtained by applying the new formaldehyde calibration procedure presented in this paper, Figure 7 shows the HCHO calibrated profiles respectively in stoichiometric and fuel-rich conditions.

The comparison of the formaldehyde profiles for each equivalence ratio (stoichiometric or fuel-rich conditions) clearly points out the fuel influence on the HCHO formation. The addition of furan and THF in flame increases the formation of formaldehyde and even more significantly in the THF doped flames. Such information is remarkable for kinetic analysis of the oxidation processes of each fuel (methane, furan and tetrahydrofuran), and for a better understanding of the role of this specific aldehyde. These experimental results also illustrate the flexibility of the procedure which allows to cover a large range of HCHO concentration in flame (from 0.002% to 0.264% in our operating conditions); note that this flexibility is consistent with the analytical needs in combustion field.
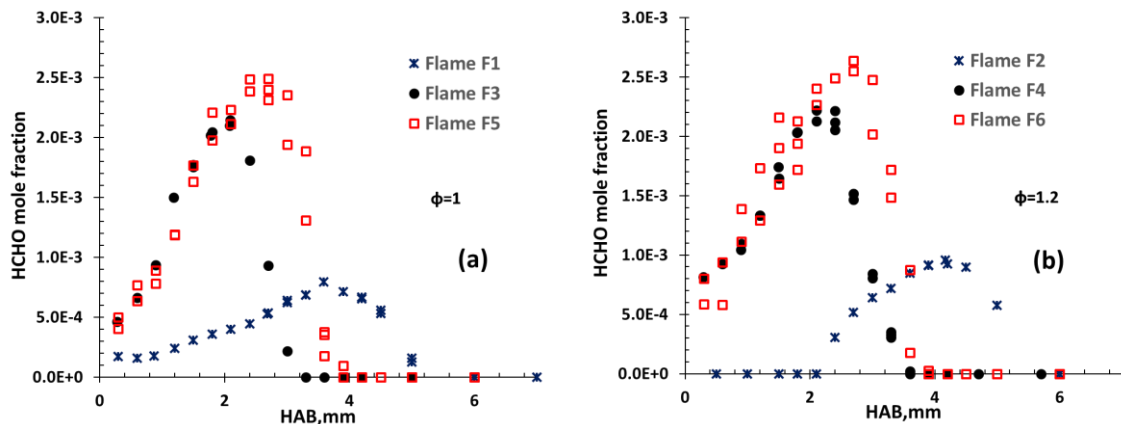
Figure 7. Experimental formaldehyde mole fraction profiles as a function of the height above the burner (HAB) in stoichiometric(a) and fuel-rich (b) flames, seeded or not with furan and THF. F1 and F2: stoechiometric and fuel-rich $CH_4/O_2/N_2$ flames, respectively; F3 and F4: stoechiometric and fuel-rich $CH_4/furan/O_2/N_2$ flames, respectively; F5 and F6: stoechiometric and fuel-rich $CH_4/THF/O_2/N_2$ flames, respectively.

Comparison of measured formaldehyde profiles with kinetic models

To demonstrate how the HCHO mole fraction profiles calibrated using the proposed calibration method could be useful in the kinetic model optimization, we compare these profiles with the model predictions. To model the studied flames, we have used the BurnerFlame module of Cantera software (Goodwin et al. 2017; Cantera 2020) package as numerical solver and two detailed mechanisms available in the literature and validated in experimental conditions close to ours: the one from Tran et al. (2017) (Model 1), and the one from Fenard et al. (2018) (Model 2). For each flame, the experimental temperature profiles measured using a non-intrusive technique (Laser Induced Fluorescence - LIF) were used as modelling input. The comparison between experimental and simulated mole faction profiles of formaldehyde in the six studied flame are presented in Figure 8 (a-f).

The comparison between the experimental and modelled HCHO profiles exhibits a very satisfying agreement for the $CH_4/furan/O_2/N_2$ flames (Figure 8c,d). The shift in the position (along HAB axis) between the modelled profiles and the experimental ones observed in Figure 8 is simply due to the thermal effect of the sampling microprobe. However, significant discrepancies in peak mole fraction between the models and experiments are observed for the $CH_4/O_2/N_2$ flames (Figure 8a,b). Here, the models overpredict the formation of HCHO. Moreover, the two models predicts very differently HCHO peak mole fractions in the $CH_4/THF/O_2/N_2$ flames (Figure 8e,f). Model 1 is not able to reproduce the difference between furan and THF in their effect on HCHO mole fraction (compare Figure 8c,d with Figure 8e,f). Refinement of the models for HCHO may be useful especially in light of the calibrated flame data reported here.
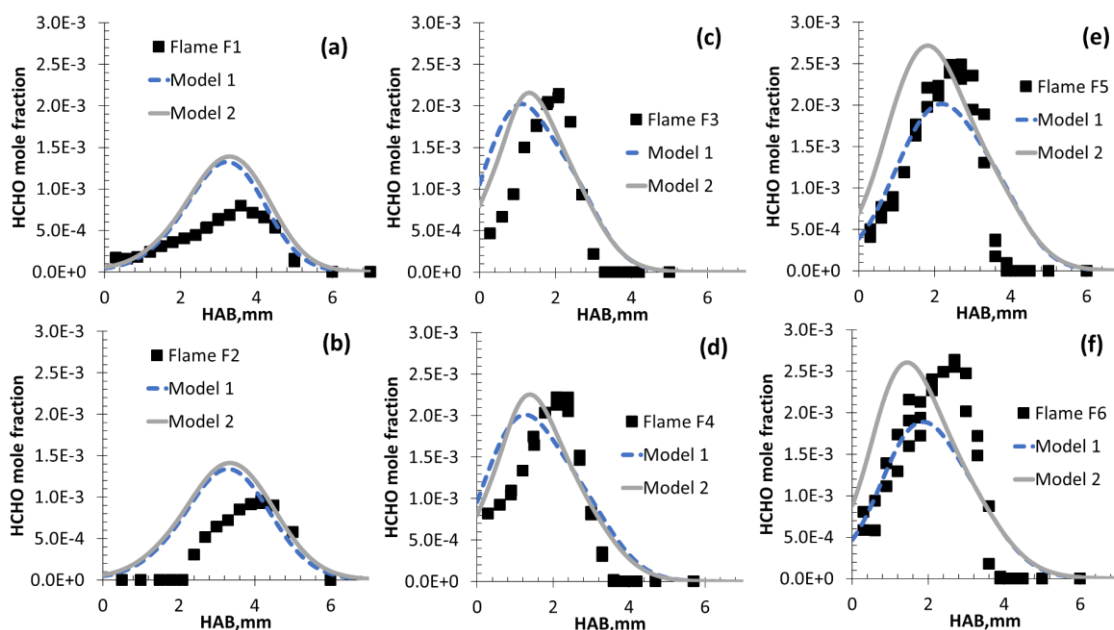
Figure 8. Comparison between the experimental mole fraction profiles of formaldehyde (symbols), determined with the new calibration method, and the modeled profiles (Model 1 and Model 2) (lines) in the six studied CH_4/biofuel/O_2/N_2 flames. F1 and F2: stoechiometric and fuel-rich CH_4/O_2/N_2 flames, respectively; F3 and F4: stoechiometric and fuel-rich CH_4/furan/O_2/N_2 flames, respectively; F5 and F6: stoechiometric and fuel-rich CH_4/THF/O_2/N_2 flames, respectively.

Conclusion

This work focuses on the development of a reliable approach to calibrate gaseous formaldehyde when using a GC-FID-methanizer analytical device. This validated calibration method can be used to directly obtain HCHO quantitative measurements using any GC-FID-methanizer whether or not the catalytic conversion efficiency is optimum. Note that even if the methanizer is characterized by high conversion efficiency, a direct calibration of HCHO is always useful to control its performance. This method is not only limited at FID-methanizers but also useful for calibrating HCHO in GC-MS. The calibration procedure has been found to present global uncertainties less than 25% while constituting an interesting alternative way to calibrate gaseous aldehydes in the 0.002% – 0.500% concentration range. The preparation protocol for aqueous solutions has been described and successfully tested in GC systems with two FID-methanizers and a MS, and then applied to the HCHO calibration in six CH_4/biofuel/O_2/N_2 laminar flames. The calibrated HCHO profiles have showed the influence of furanic biofuels on the formation of this toxic product and demonstrated that more works are needed for optimizing the kinetic models, especially in light of the HCHO data reported here.

Acknowledgements

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