An experimental study of the structure of laminar premixed flames of ethanol/methane/oxygen/argon

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ABSTRACT
The structure of three laminar premixed stoichiometric flames at low pressure (6.7 kPa): a pure methane flame, a pure ethanol flame and a methane flame doped by 30% of ethanol, has been investigated and compared. The results consist of concentration profiles of CH₄, CH₃CH₂OH, O₂, Ar, CO₂, H₂O, H₂, CO, C₂H₆, C₂H₄, C₂H₂, C₃H₈, C₃H₆, pC₃H₄, aC₃H₄, CH₂O, CH₃CHO, measured as a function of the height above the burner by probe sampling followed by on-line gas chromatography analyses. Flame temperature profiles have been also obtained using a PtRh (6%)-PtRh (30%) type B thermocouple. The similarities and differences between the three flames were analyzed. The results show that, in these three flames, the concentration of the C₂ species is much higher than that of the C₃ species. In general, mole fraction of all species in the pure ethanol flame is the highest, followed by the doped flame, and finally the pure methane flame.

Keywords: Premixed laminar flame; Methane; Ethanol.

1. INTRODUCTION
In recent years, announced decrease of petroleum reserves and tightened regulations for emissions of environmental concern from internal combustion engines have stimulated research to find alternative fuels.

Ethanol is regarded as an attractive renewable alternative fuel with a high octane number [1]. This oxygenated fuel can be obtained through the fermentation of sugars or starches which can be produced from very common crops, such as sugar cane or corn [2]. Recently, ways to produce ethanol from cellulose [3] or algae [4] have also been proposed. Therefore, the use of ethanol allows a reduction of the dependence on fossil fuels. Moreover burning this renewable fuel should not lead to an increase of the total amount of greenhouse gases in the atmosphere. In addition, this oxygenated fuel can decrease the formation of soot, CO and unburned fuel or partly oxidized hydrocarbons in practical applications, but tendencies to form aldehydes have been observed depending on fuel structure and combustion conditions [2, 5]. Ethanol is now one of the most common and abundant bio-fuels [6], [7], [8]. Figure 1 shows the worldwide fuel-ethanol production in years 2007, 2008 and 2009 [6]. A noticeable increase of this production can be observed.

FIGURE 1
Several previous studies have already been conducted for better understanding each step of ethanol combustion and for developing an accurate oxidation mechanism. Ethanol combustion has been studied in diffusion flames [9], laminar premixed flame [10], [11], static reactors [12], shock tubes [13], [14]. Some kinetic mechanisms proposed, e.g. by Natarajan and Bhaskaran (in 1981) [15] and by Dunphy et al. (in 1991) [16] were based on experimental data obtained in shock tubes. Norton and Dryer (in 1992) [17] published an oxidation mechanism which has been validated using experimental data obtained in a flow reactor. Later, Marinov et al. (in 1999) [18], Saxena and Williams (in 2007) [19], Li et al. (in 2007) [20], Cancino et al, (in 2010) [21], Lepl et al. (in 2011)
[10] have published the detailed kinetic models for the combustion of ethanol; these mechanisms have been validated by experiments in several devices, including laminar premixed flame ([10]).

Continuous developments and improvements of kinetic mechanisms require new experimental data. In order to further improve the understanding of ethanol combustion, the objective of this study is to experimentally investigate the structure of a laminar premixed stoichiometric methane flame containing 30% of ethanol at low pressure. A comparison of this flame with a flame of pure ethanol and a flame of pure methane is also presented. The use of a methane flame allows us to have a reactive mixture rich in methyl radicals and is more representative of combustion mixtures containing larger hydrocarbons than hydrogen or C2 flames.

2. EXPERIMENTAL METHODOLOGY

The experimental setup used to determine the structure of one-dimensional laminar premixed flames has been described previously [22], [23] and it is illustrated schematically in Figure 2. This apparatus has been developed in our laboratory to study temperature and stable species profiles in a laminar premixed flat flame at low pressure and has been used recently in the case of rich methane flames doped by light unsaturated soot precursors [24], [25], [26].

FIGURE 2

All flames were stabilized on the Mac Kenna burner (diameter 60 mm, water-cooled) housed in a vacuum chamber which is maintained at 6.7 kPa and equipped with a quartz probe with a hole of about 100 µm diameter at the tip for sampling. The cooling water has a constant temperature of 60°C.

Methane (99.95 % pure) was supplied by Alphagaz - Air Liquide. Oxygen (99.5% pure) and argon (99.995% pure) were provided by Messer. Liquid ethanol was supplied by Sigma-Aldrich (purity > 99.5%). Liquid ethanol was contained in a metallic vessel pressurized with argon. After each load of the vessel, argon bubbling and vacuum pumping were performed in order to remove oxygen traces dissolved in the ethanol. The ethanol flow rate was controlled by using a liquid mass flow controller, mixed with the argon and then evaporated by passing it through a CEM (Controlled Evaporator and Mixer). The temperature of this CEM was set at 100°C.

Analysis was made by gas chromatography (GC) with a heated on-line connection from the probe and using three types of columns (carbosphere, HP-Plot U and HP-Molsieve) and two types of detectors (flame ionization (FID) coupled with methanisor and thermal conductivity (TCD)). Stable species were also identified by mass spectroscopy (GC/MS).

Flame temperature profiles were obtained using a PtRh (6%)-PtRh (30%) type B thermocouple (diameter 100 µm). The thermocouple wire was supported by an arm and crossed the flame horizontally to avoid conduction heat losses. The junction was located at the center of the burner. The thermocouple was coated with an inert layer of BeO–Y2O3 to prevent catalytic effects when it is placed in flame [27]. The ceramic layer was obtained by dipping the thermocouple in a hot solution of Y2(CO3)3 (93% mass) and BeO (7% mass) followed by drying in a Meker burner flame. This process was repeated about 10 times until the whole metal was covered. Radiative heat losses are corrected using the electrical compensation method [28].

Initial operating conditions of the three flames used in the current study are presented in Table 1. The cold gas velocity (at 20°C) is 57 cm/s for all flames.

| TABLE 1 |
The flame temperature profiles and mole fraction profiles of reactants, major and intermediate species are presented.

### 3.1. Flame temperature profiles

The experimental temperature profiles constitute an essential parameter for the interpretation of laminar flame data. Figure 3 represents the temperature profiles measured for the three flames without (Figure 3a) and with (Figure 3b) the probe. These figures show that the presence of the probe induces a thermal perturbation causing a lower measured temperature. The maximum temperature of the three flames is almost similar in post flame region.

**FIGURE 3**

### 3.2. Mole fraction profiles of reactants, major and intermediate species

Figures 4-8 present mole fraction profiles of several stable species versus the height above the burner for the three flames. It can be stated that concentrations of most measured intermediate products in the three flames have their maxima at the distance of about 1-3 mm from the burner surface. A displacement of the position of the maximum concentrations is observed for CO, H2, C2H4, C2H2 compounds. The major final products are, to a large extent, CO2 and H2O.

Figure 4 presents the profiles of reactants (C2H5OH, CH4, Ar, O2) and shows that ethanol is completely consumed close to the burner, at 2.5 mm height (Figure 4a), while some methane remains up to 3.5 mm (Figure 4b). The reason for this difference is the laminar flame speed for methane/oxygen mixture is slower than that for ethanol/oxygen mixture [29], implying that the pure methane flame front is further from the burner.

It can be seen from Figure 4c that there is very slight difference in O2 mole fraction for the three flames, which reveals that the consumption rate of oxygen has little variation for various flames in this experiment and there is a small fraction of O2 in the post flame region.

There is also very slight difference in Ar mole fraction for the three flames (Figure 4d).

**FIGURE 4**

Mole fraction profiles of major species, including CO2, H2O, H2 and CO, are shown in Figure 5.

**FIGURE 5**

The mole fraction profile of CO2 is shown in Figure 5a. The CO2 is the main green house effect gas and will be controlled by future emission legislated regulations. The mole fraction of CO2 formed in pure ethanol flame is the highest and in pure methane flame is the lowest. The increase of CO2 mole fraction in the pure ethanol flame is mainly due to the increase of C/H ratio (see table 1). There is only slight difference in H2O mole fraction for the three flames (Figure 5b).

In the pure ethanol flame, the profiles of H2 display a marked maximum at 2.5 mm height, which is at 3.0 mm in the doped flame and in the pure methane flame. It can be seen from Figure 5c that there is a small fraction of hydrogen in the post flame region.

In the doped flame and in the pure methane flame, the profiles of CO (Figure 5d) display a marked maximum at 3.5 mm height, which is at 3.0 mm in the pure ethanol flame. The maximum mole fraction of CO formed in the pure ethanol flame is the highest and in the pure methane flame is the lowest. The increase of CO mole fraction in the pure ethanol flame is mainly due to the increase of C/H ratio. The CO formation occurs as an essential intermediate step in the process of oxidation of
fueles, leading to the final product CO₂ by the reaction: CO + OH → CO₂ + H. It can be seen from Figure 5d that there is a small fraction of CO in the post flame region.

Mole fraction profiles of intermediates CH₄, C₂H₆, C₂H₄, and C₂H₂ are shown in Figure 6.

**FIGURE 6**

In the pure ethanol flame, CH₄ is an abundant intermediate, formed from the radical CH₃ and consumed to give this same radical. The profile of CH₄ (Figure 6a) have a peak near 2 mm (peak mole fraction of 2700 ppm).

For C₂ (non-oxygenated) species, the most important are C₂H₆ in the pure methane flame (peak mole fraction of 1000 ppm), C₂H₄ in the pure ethanol flame (peak mole fraction of 5000 ppm) and in the doped flame (peak mole fraction of 2000 ppm). C₂H₅ is formed first in the pure methane flame (peaks around 1.8 mm) and in the doped flame (peaks around 1.8 mm) (Figure 6b), while C₂H₄ is formed first in the pure ethanol flame (peaks around 2 mm) (Figure 6c). From the description above, there are differences in the most important and first formation of C₂ species in the three flames. These differences can be explained as follows. High temperature chemical kinetic models show clearly that there are two well-known pathways for methane oxidation, i.e., C₁ and C₂ pathways: the C₁ pathway being the dominating one [30], [31]. In the C₂ pathway, two CH₃ radicals combine to produce C₂H₆ and C₂H₅. C₂H₅ forms C₂H₄ by reacting with H and OH radicals, and C₂H₄ finally leads to the formation of C₂H₂ through intermediate species C₂H₃ and C₂H₅. Therefore, in the pure methane flame, C₂H₅ is the most abundant C₂ species and is produced first. While in ethanol flame, C₂H₄ is formed essentially from ethanol by the following decomposition reaction: C₂H₅OH (+M) → C₂H₄ + H₂O (+M) or via the CH₂CH₂OH (hydroxylethyl) radical: CH₂CH₂OH (+M) → C₂H₄ + OH (+M) [10], [18]. CH₂CH₂OH radicals are obtained from ethanol by H-abstractions. Therefore, in the pure ethanol flame, C₂H₄ is the most abundant C₂ (non-oxygenated) species and is produced first.

The maximum concentration of C₂H₂ (Figure 6d) and C₂H₄ (Figure 6c) which are significantly increased in the doped flame compared to the pure methane flame, even reaches a higher level in the pure ethanol flame. The highest concentration of C₂H₆ (Figure 6b) is almost similar in both pure ethanol and pure methane flames, and is slightly reinforced in the doped flame. Additionally, the similarity of C₂H₆ concentration in the pure ethanol and pure methane flames can be explained as follows. C₂H₆ is produced by combination of two CH₃ radicals. The C/H ratio of the pure ethanol flame is the highest leading to high mole fraction of intermediate C₂H₆. However, CH₃ is the most important intermediate radical in methane combustion.

The maximum concentration of C₂H₄ is proportional to the C/H, C/O ratios of the fresh initial gases. Indeed, in Figure 6c, we observe that the concentration of C₂H₄ in the pure ethanol flame is the highest (5000 ppm), followed by the doped flame (2000 ppm), and finally the pure methane flame (500 ppm).

C₂H₂ is considered as the most representative soot precursor in a variety of hydrocarbon fuel flames because it yields benzene, which is the first step toward the production of soot [32]. The maximum concentration of C₂H₂ is also proportional to the C/H, C/O ratios of the fresh initial gases. Figure 6d shows that the concentration of C₂H₂ in the pure ethanol flame is the highest (1300 ppm), followed by the doped flame (550 ppm), and finally the pure methane flame (150 ppm).

Figure 7 presents the profiles of the C₃ species including C₃H₆ (Figure 7a), C₃H₅ (Figure 7b), pC₃H₄ (Figure 7c), and aC₃H₄ (Figure 7d). These figures show that a very small amount of C₃ products is also observed in the pure methane flame.

**FIGURE 7**
In the three flames, C₃H₆ and C₃H₈ reach the highest concentration first around 1.8 mm above the burner, while the maxima of pC₃H₄ and pC₃H₄ are around 2.5 mm. These figures show that a very small amount of these products is also observed in the pure methane flame and the concentration of pC₃H₄ and pC₃H₄ is lower than the limit of detection of the gas chromatograph. The peak mole fraction of C₃H₆, which is the most important C₃ species in the pure ethanol flame, is 105 ppm, while that in the pure methane flame and doped flame is 26 ppm and 54 ppm, respectively.

The concentration of C₃ species in the pure ethanol flame is the largest, followed by the doped flame, and finally the pure methane flame, i.e. the maximum concentration of C₃ product is also proportional to the C/H, C/O ratios of the fresh initial gases.

Figure 8 displays the profiles of light oxygenated species: formaldehyde (CH₂O) and acetaldehyde (CH₃HCO).

**FIGURE 8**

The aldehydes, hazardous air pollutants, are produced promptly in these flames and reach their maximum concentration close to the burner, around 1.5 mm for CH₂O (Figure 8a) and around 1.0 mm for CH₃HCO (Figure 8b).

The concentration of aldehydes in the pure ethanol flame is the highest, followed by the doped flame, and finally the pure methane flame. CH₃HCO is not detected in the pure methane flame.

**In ethanol flame**, the two radicals (CH₃CHOH, CH₃CH₂O) initially formed by H-abstraction from the ethanol generate CH₃HCO via following reactions:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{O} + \text{M} &= \text{CH}_3\text{HCO} + \text{H} + \text{M} & [18] \\
\text{CH}_3\text{CH}_2\text{O} + \text{O}_2 &= \text{CH}_3\text{HCO} + \text{HO}_2 & [33] \\
\text{CH}_3\text{CH}_2\text{O} + \text{OH} &= \text{CH}_3\text{HCO} + \text{H}_2\text{O} & [18] \\
\text{CH}_3\text{CHOH} + \text{M} &= \text{CH}_3\text{HCO} + \text{H} + \text{M} & [15] \\
\text{CH}_3\text{CHOH} + \text{O}_2 &= \text{CH}_3\text{HCO} + \text{HO}_2 & [15] \\
\text{CH}_3\text{CHOH} + \text{O} &= \text{CH}_3\text{HCO} + \text{OH} & [18] \\
\text{CH}_3\text{CHOH} + \text{HO}_2 &= \text{CH}_3\text{HCO} + \text{OH} + \text{OH} & [18] \\
\text{CH}_3\text{CHOH} + \text{OH} &= \text{CH}_3\text{HCO} + \text{H}_2\text{O} & [18].
\end{align*}
\]

Production of CH₂O can also be rationalized from this scheme through the C-C β-scission of the CH₃CH₂O radical (CH₃CH₂O + M → CH₃ + CH₂O + M) [18]. These reaction paths show how large aldehyde emissions may be expected from ethanol combustion. The results of this study confirm that acetaldehyde formation during ethanol combustion is important. Acetaldehyde is the main intermediate species formed in the flame front (the peak mole fraction is 7500 ppm).

**In the methane flame**, formaldehyde is essentially formed from CH₃ and C₂H₃ radicals [31] by the following reactions:

\[
\begin{align*}
\text{CH}_3 + \text{O} &= \text{CH}_2\text{O} + \text{H} \\
\text{CH}_3 + \text{O}_2 &= \text{CH}_2\text{O} + \text{OH} \\
\text{C}_2\text{H}_3 + \text{O}_2 &= \text{CH}_2\text{O} + \text{CHO}
\end{align*}
\]
CONCLUSION
This paper presents new experimental results about the structure of three low-pressure stoichiometric laminar premixed flames: a pure flame methane, a pure ethanol flame, and a methane flame doped by 30% of ethanol. Profiles of temperature and mole fraction of 17 stable species from C_0 to C_3 have been obtained. Among these 17 species, there are 2 oxygenated compounds and the reactants. A comparison between the profiles of temperature and of mole fraction is also presented. This comparison shows that, in general, mole fraction of all species (except reactants and C_3H_6) in the pure ethanol flame is the highest, followed by the doped flame, and finally the pure methane flame. The reaction paths consuming the organic reactant (depending on the nature of fuel) and the H/C, C/O ratios of the fresh initial gases have allowed us to identify the origin of differences among these flames.

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REFERENCES


Table 1. Flame inlet conditions.

<table>
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<tr>
<th>Flame Name</th>
<th>Φ</th>
<th>Mole fraction</th>
<th>Total flow rate at 20°C (cm/s)</th>
<th>Dilution (%)</th>
<th>C/O</th>
<th>C/H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ethanol</td>
<td>CH₄</td>
<td>O₂</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>Pure ethanol flame</td>
<td>1.0</td>
<td>0.06840</td>
<td>0</td>
<td>0.20437</td>
<td>0.72722</td>
<td>57</td>
</tr>
<tr>
<td>Doped flame*</td>
<td>1.0</td>
<td>0.02072</td>
<td>0.06907</td>
<td>0.20076</td>
<td>0.70945</td>
<td>57</td>
</tr>
<tr>
<td>Pure methane flame</td>
<td>1.0</td>
<td>0</td>
<td>0.09910</td>
<td>0.19888</td>
<td>0.70202</td>
<td>57</td>
</tr>
</tbody>
</table>

Φ - equivalence ratio; C/H - Carbon/Hydrogen ratio; C/O - Carbon/Oxygen ratio

* = ethanol/methane mixture flame.
FIGURE CAPTIONS

Figure 1: World fuel ethanol production by country.

Figure 2: Scheme of the apparatus of low-pressure laminar premixed flame.

Figure 3: Flame temperature profiles: without (a) and with (b) the sampling probe.

Figure 4: Mole fractions profiles of reactants C₂H₅OH, CH₄, O₂, Ar.

Figure 5: Mole fraction profiles of major species CO₂, H₂O, H₂, CO.

Figure 6: Mole fractions profiles of CH₄ (intermediate) and C₂ species.

Figure 7: Mole fractions profiles of C₃ species.

Figure 8: Mole fraction profiles of oxygenate intermediates.
Figure 1: World fuel ethanol production by country (adapted from [6])

![World fuel ethanol production by country](image)

Figure 2: Scheme of the apparatus of low-pressure laminar premixed flame. The thick lines correspond to the heated lines.

![Scheme of the apparatus of low-pressure laminar premixed flame](image)
Figure 3: Temperature profiles: without (a) and with (b) the sampling probe.
Figure 4: Mole fraction profiles of reactants C$_2$H$_5$OH, CH$_4$, O$_2$, Ar.
Figure 5: Mole fraction profiles of major species CO$_2$, H$_2$O, H$_2$, CO
Figure 6: Mole fractions profiles of CH₄ (intermediate) and C₂ species

a) CH₄ (intermediate)

b) C₂H₆

c) C₂H₄

d) C₂H₂
Figure 7: Mole fractions profiles of C₃ species

a) C₃H₈

b) C₃H₆

c) pC₃H₄

d) aC₃H₄
Figure 8: Mole fraction profiles of oxygenate intermediates

a) 

Mole fraction profiles for CH$_2$O with different flames: Ethanol/Methane mixture flame, Pure ethanol flame, Pure methane flame.

b) 

Mole fraction profiles for CH$_3$HCO with different flames: Ethanol/Methane mixture flame, Pure ethanol flame, Pure methane flame.