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Experimental study of pollutants formation in laminar premixed flames of tetrahydrofuran family fuels

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Abstract

To better understand the combustion chemistry of tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MTHF) which has been considered as promising bio-fuel, the structure of their stoichiometric (φ=1.0) low-pressure laminar premixed flame has been investigated. The flames have been stabilized on a burner at a pressure of 50 Torr (6.7 kPa) using argon as dilutant (78 %), with a gas velocity at the burner of 59 cm s^{-1} at 293 K. The results consist of mole fraction profiles of about 40 species for the THF flame and 60 species for the MTHF flame identified and quantified as a function of the height above the burner by probe sampling followed by on-line gas chromatography analyses. An analysis and comparison of the combustion of these fuels was performed regarding the mole fraction of the products.

Keywords

Tetrahydrofuran, 2-methyltetrahydrofuran, laminar premixed flame, bio-fuels, combustion chemistry, gas chromatography.

1. Introduction

At present an increasing interest is noted to shift from fossil fuels to bio-fuels. The use of bio-fuels allows a reduction of the dependence on petroleum-based fuels. Moreover burning bio-fuel should not lead to an increase of the total amount of greenhouse gases in the atmosphere.

Cyclic ethers of tetrahydrofuran (THF) family, e.g. 2-methyltetrahydrofuran (MTHF) and 2,5-dimethyltetrahydrofuran (DMTHF) have been considered as promising bio-fuel compounds for adding to gasoline fuel. They have a high lower heating value (~28.5-29.5 MJ/L), which is close to that of furan family fuels (~27.7-30.0 MJ/L) and of gasoline (~31.6MJ/L), and higher than that of ethanol (~21.3 MJ/L) (see Table 1). MTHF has good antiknock characteristics, and satisfactory performance when mixed in a 10% blend with gasoline in conventional internal combustion engine (Wallington et al., 1990). The THF family fuels can be produced from non-edible biomass (Yang and Sen, 2010), (Lange et al., 2012), (Tran et al., 2012). Some tests for MTHF as fuel on engine have been reported. Rudolph and Thomas (in 1988) have comparatively analyzed pollutant emissions from a spark-ignition engine performed on mixtures of gasoline with 10% potential liquid fuels, including ethanol, methanol, methyl *t*-butyl ether (MTBE), and MTHF. The result has shown that the fuel blend containing 10% MTHF has power outputs and carbon monoxide, nitrogen oxides, and non-methane hydrocarbons emissions that most closely resemble unleaded gasoline. MTHF has been approved by the USDOE as a component of P-series fuels for spark-ignition engine, which were firstly developed by Dr. Stephen Paul of Princeton University and awarded Patent number 5697987 by the United States Patent and Trademark Office on December 16, 1997. The P-series fuels are blends of ethanol (25-40 % by vol.), MTHF (20-35 %), and pentanes plus (C≥5; 25-40 %), with butane (0-10 %) added to blends that would be used in severe cold-weather conditions to meet engine cold start requirements (Paul, 1997), (Paul, 1998), (DOE, 1999).

Furthermore, THF, MTHF, DMTHF and other saturated cyclic ethers have been also identified among the emissions produced during the combustion and auto-ignition of alkanes and alkenes by isomerization of alkylhydroperoxy radicals (Leppard, 1987), (Leppard, 1989), (Herbinet et al., 2011a), (Herbinet et al., 2011b). The subsequent reactions of these cyclic ethers can then influence the overall chemical kinetics mechanisms of alkanes and alkenes combustion.

Table 1: Properties of THF family and other selected fuels (Thewes et al., 2011), (Tran et al., 2012), (Simmie, 2012).

Fuels	Chemical Formula	Density (kg/l)	Boiling Point (K)	LHV[a] (MJ/L)	LHV[a] (MJ/Kg)	AIT[a] (K)	RON/MON[a]	CN[a]
THF	C_4H_8O	0.89	339.2	--	--	594	--	--
MTHF	$C_5H_{10}O$	0.85	353.4	28.5	33.5	--	86/72	~15
DMTHF	$C_6H_{12}O$	0.83	364.1	29.5	35.5	--	82 /--	--
Ethanol	C_2H_5OH	0.79	351.6	21.3	26.8	763	120/99	5-8
n-Butanol	C_4H_9OH	0.81	355.9	26.8	33.1	703	96/78	--
MF[b]	C_5H_6O	0.91	336.0	27.7	30.4	--	100.7 /82.4	--
DMF[b]	C_6H_8O	0.89	366.5	30.0	33.7	559	119 /--	--
Diesel[c]	C_8-C_{25} HC	0.84	443-633	36.1	43.0	~533	--	40-55
Gasoline[c]	C_4-C_{14} HC	0.74	303-473	31.6	42.7	~723	95/85	--

[a] LHV: Lower Heating Value (LCV- Lower Calorific Value); RON: Research Octane Number; MON: Motor Octane Number; CN: Cetane Number; AIT: Autoignition Temperature. [b] MF: 2-methylfuran; DMF: 2,5-dimethylfuran [c] Fuel standard.

Therefore, the fundamental understanding of their combustion chemistry is really wishful, and need to be done before using MTHF and DMTHF as a fuel in practice. THF is well suited as a model fuel to study more about the combustion chemistry of saturated cyclic ethers, especially of its derivatives. Very early, the pyrolysis of THF has been studied by Klute and Walters (in 1946), Mcdonald et al. (in 1951), and Lifshitz et al. (in 1986). The later suggested two main possible decomposition pathways of THF which give: (i) ethylene and $(CH_2)_2O$ bi-radical, and (ii) propene and formaldehyde with a rate constant of four times lower than the first one. The low-temperature (493 K) oxidation of THF has been investigated by Molera et al. (in1988), in a static reactor. A motored engine study on auto-ignition chemistry of acyclic and cyclic ethers, including MTBE, ethyl *t*-butyl ether-ETBE, methyl *t*-amyl ether-TAME, THF, MTHF, and tetrahydropyran, has been performed by Leppard (in 1991). The chemical mechanisms responsible for auto-ignition of both ether classes are detailed, compared, and used to explain the differences in antiknock characteristics of the two ether classes. The author explained that, due to a dominance of very reactive alkoxy-carbonyl radicals produced by low-temperature oxygen-addition chemistry in the cyclic ethers auto-ignition, octane number of the cyclic ethers is significantly lower than that of acyclic ethers. Later, the ignition delay times and oxidation of THF have been studied by Dagaut et al. (in 1998), in a single-pulse shock tube and in a jet-stirred reactor, respectively, under a range of conditions of 202-1013 kPa, $0.5 \leq \varphi \leq 2.0$, 800-1800 K. On the basis of these experimental data, a detailed reaction mechanism with 71 species and 484 reaction was proposed and used to describe the ignition and the oxidation of THF. This study has shown that a large amount of aldehydes (formaldehyde, acetaldehyde, and propanal) were produced during the THF oxidation. Recently, Kasper et al. (in 2011) investigated the structure of laminar premixed low-pressure THF flames using photoionization (PI) and electron-ionization (EI) molecular-beam mass spectrometry (MBMS). About 60 intermediates were measured and analyzed, but several assumptions have been given for species identification. Large uncertainties in mole fraction values were considered, especially for minor species, and species assignment at some mass (*m/z*) remained ambiguous and uncertain. Very recently, the kinetics and thermochemistry of THF, MTHF and DMTHF have been theoretically investigated by Simmie (in 2012). From bond dissociation energies (BDE) calculated in this study and their previous paper (Simmie and Curran, 2009), we present in Fig. 1 the structure of THF, MTHF, and DMTHF, compared to that of furan, MF, and DMF. This figure shows that ring C-H and C2-C6 bonds of THF family fuels are much weaker than those of furan family fuels, while C6-H bonds (in methyl group) have an inverse trend. In MTHF and DMTHF molecules, C2-C6 bond has the lowest BDE. In the saturated cyclic ethers, the remoteness from the heterocyclic O atom strengthens the C-H bond and the presence of methyl group slightly weakens the C2-H bond, while it is not significantly affected in the unsaturated cyclic ethers.

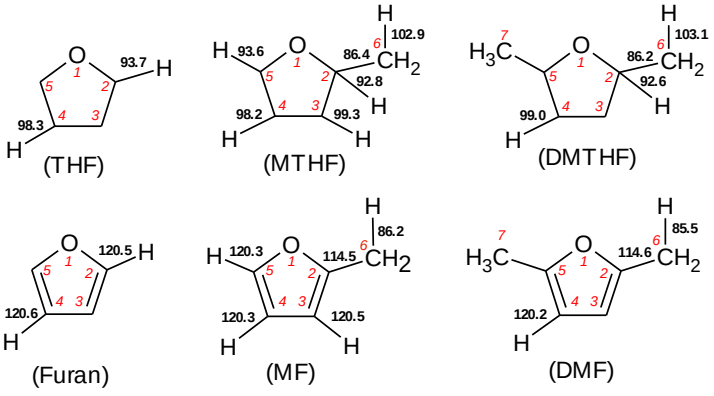


Figure 1. Structure of THF, MTHF, and DMTHF, compared with furan, MF, and DMF. Italic number near the atom: atom label; bold numbers: bond energy (in kcal mol^{-1}) (Simmie and Curran, 2009), (Simmie, 2012).

From the above bibliography, we find that information about the combustion properties of THF is very little in flame condition, and there is no report on MTHF and DMTHF combustion in laminar premixed low-pressure flame as well as in other fundamental devices (excluding engine configuration), which provide a stringent test for kinetic reaction models. In addition, to our knowledge, an experimental analysis of the two fuels THF and MTHF under the same laminar premixed flame conditions, which allows to compare between them, has not been published prior to the present study. In the present work, as part of a continuing effort to enrich experimental data and to improve the knowledge on the combustion chemistry of THF family fuels, we report experimental data of low-pressure premixed THF and MTHF flames with Ar dilution of 78%, pressure of 50 Torr (6.7 kPa), and an equivalence ratio φ=1.0, using on-line gas chromatography (GC) analyses.

2. Methods

The experimental setup has been developed in the LRGP to study stable species profiles in a laminar premixed flat flame at low-pressure and has been described previously (Pousse et al., 2009). Briefly, all flames were stabilized on a McKenna burner (diameter 60 mm, water-cooled) housed in a vacuum chamber which is maintained at 50 Torr (6.7 kPa). The burner is cooled with water at a constant temperature of 333 K.

Oxygen (99.5% pure) and argon (99.995% pure) were provided by Messer. Liquid fuels: THF (>99.7 % pure) and MTHF (>99.0 % pure), were supplied by VWR and Sigma-Aldrich, respectively. Liquid fuel was contained in a metallic vessel pressurized with argon. After each load of liquid fuel, argon bubbling and vacuum pumping were performed in order to remove traces of dissolved oxygen. Liquid fuel was mixed with argon and then evaporated by passing through a CEM (Controlled Evaporator and Mixer). The temperature of this CEM was set at 373 K. Liquid and gas flow rates were measured by using mass flow controllers provided by BronKhorst®, with a mass flow accuracy of ± 0.5%.

Analyses were made by GC with a heated (at 423 K) online connection to a quartz probe. The quartz probe had an upper diameter of 6 mm and was tipped by a small cone with a 100 µm diameter orifice at the tip and an angle to the vertical of 22°. Three types of columns were used: Carbosphere, HP-Molsieve, and HP-Plot Q, and two types of detectors: flame ionization detection (FID) coupled with a methanizer and thermal conductivity detection (TCD). The Carbosphere column with argon as carrier gas was used to analyze O_2 and H_2 by TCD. The HP-Molsieve column with helium as carrier gas was used to analyze CH_4 and C_2H_4 by FID and Ar by TCD. The HP-Plot Q column with helium as carrier gas was used to analyze all hydrocarbon species from C_2 and oxygenated species by FID. Additionally, this column was used also to analyze H_2O by TCD. In usual gas chromatography, CO and CO_2 can only be detected by TCD, and formaldehyde cannot be measured by FID. Here, CO, CO_2, as well as formaldehyde were passed through the methanizer, were converted to methane, and could then be detected by FID which is more sensitive (by a factor of 100) than TCD. Stable species were identified by the determination of their individual retention times and by mass spectrometry (GC/MS). Calibrations were made directly using cold-gas mixtures. The calibration factors were estimated using the effective carbon number (ECN) method for species for which a direct calibration procedure was not possible. The calculated uncertainties of the mole fraction measurements of the quantified species were ~5% for the major compounds and ~10% for minor products (<100 ppm). The FID detection threshold was about 0.5 ppm, while the TCD

detection limit was about 50 ppm for H_2O, H_2 and O_2. Note that in the present experiments, furan and acrolein peaks were not separated by GC. However their individual mole fraction values were deduced using additional aid of their signals ratio in GC-MS. This process could give an uncertainty up to 20% in their absolute mole fraction values. The uncertainty for these two species is, however, identical in all measured flames and a relative comparison of trends between the flames can thus be performed with a significantly higher precision.

Flames of THF and MTHF were investigated under the same conditions, pressure of 50 Torr (6.7 kPa) with a dilution of 78 %, a gas velocity of 69 cm s^{-1} at 333 K, an equivalence ratio φ=1, a C/O and C/H ratios of 0.33 and 0.5, respectively. The initial operating conditions of these flames are presented in Table 2.

Table 2. Flame conditions

Flame name	φ*	Gas flow (NL/min)			C/O	C/H	Pressure (Torr)	Dilution* (%)	Flow velocity at T=293 K (cm s^{-1})
		Fuel	O_2	Ar					
THF flame	1.0	0.234	1.29	4.56	0.33	0.5	50	78	59
MTHF flame	1.0	0.187	1.31	4.64	0.33	0.5	50	78	59

*Dilution=Ar/(Ar+O_2); φ-equivalence ratio.

3. Results and Discussion

The carbon (C), hydrogen (H), and oxygen (O) balances were checked in all two flames. The quantified mole fraction of argon allowed taking into account the change in the total mole number along the flame profiles. The difference between inlet and outlet is ~3-4 % for C, ~5-9 % for O and H. About 40 and 60 species were identified and quantified in the THF and MTHF flames, respectively. However, only some selected important species will be presented and discussed in the following paragraphs. Figures 2-10 present the mole fraction profiles of chemical species (major and intermediate) as a function of distance above the burner *h*. The reaction zone peaks at ~1-3 mm above the burner.

Figure 2 shows the major species profiles, including reactants (THF, MTHF and O_2), diluent (Ar), and main products (CO, CO_2, H_2O, and H_2) in both THF and MTHF flames. This figure shows that THF is completely consumed at height 2.0 mm, but at height 2.5 mm for MTHF. A significant mole fraction of O_2 (~2×10^{-2}) remains in the post flame region. The main final products are, to a large extent, CO_2 and H_2O. The profiles of CO display a marked maximum at height 2.5 mm (~9.5×10^{-2}) in the THF flame and at height 3.0 mm (8.7×10^{-2}) in the MTHF flame. It can be seen that there is also a remaining mole fraction of CO (~5×10^{-2}) and H_2 (~$1\text{-}1.5\times10^{-2}$) in the post flame region. The maximum mole fraction of the main products is quite comparable between the THF and MTHF flames. This observation is logical with the similar C/O and C/H ratios in both flames conditions (see Table 2). The major as well as intermediate species profiles show that the THF flame front is closer to the burner compared to the MTHF flame, reflecting a higher adiabatic burning velocities of THF (~41 cm s^{-1} at 298 K, φ=1.0, compared to ~37 cm s^{-1} for MTHF (Monge et al., 2012)).

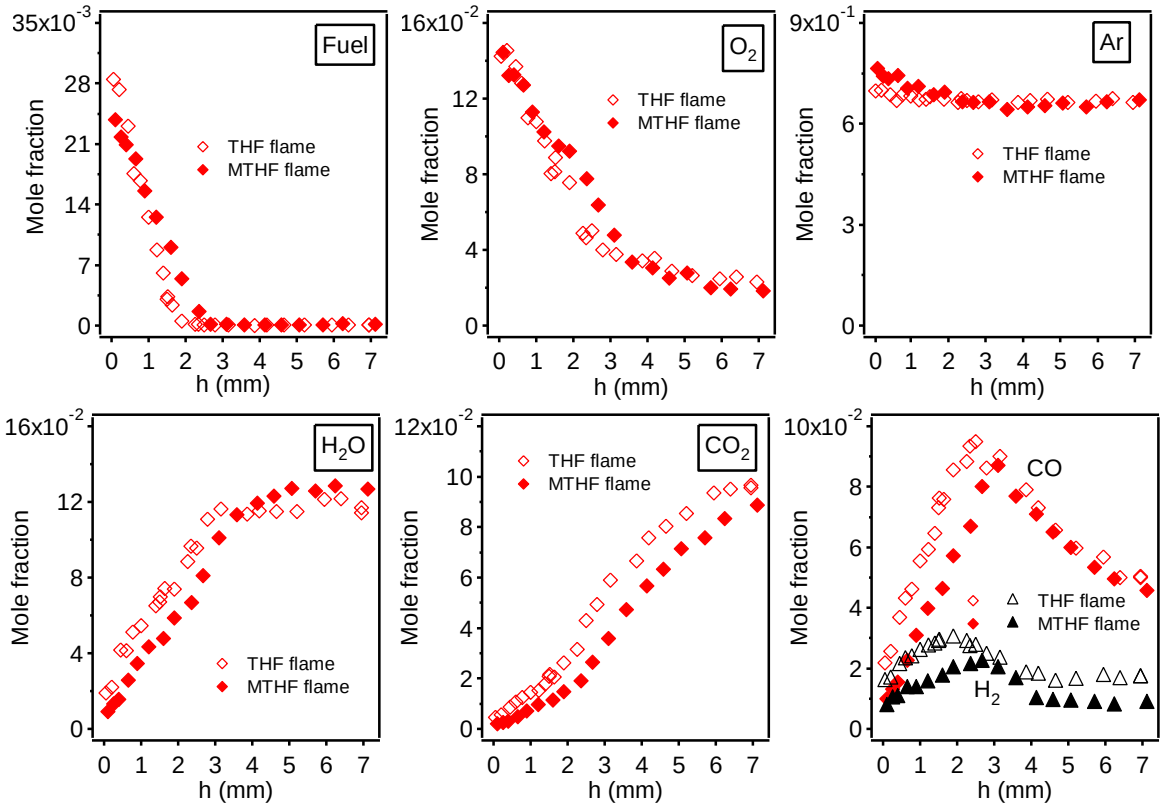
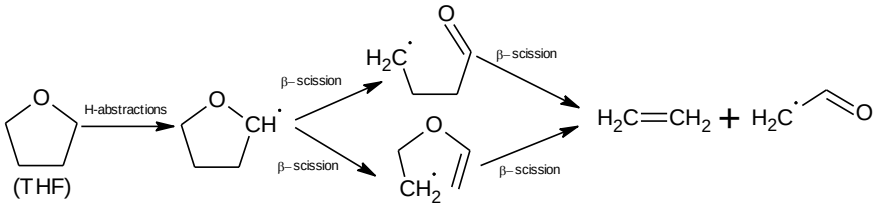


Figure 2. Major species

Figure 3 displays the mole fraction profiles of C_1-C_2 hydrocarbon intermediates, including methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), and ethane (C_2H_6). In the THF flame, the maximum mole fractions of these C_2 intermediates are quite comparable to those in the MTHF flame. Ethylene is the most abundant one of all intermediates in both flames, with maximum mole fractions of ~12×10^{-3} and ~11×10^{-3} in the THF and MTHF flames, respectively. Note that for unsaturated cyclic ethers such as furan family fuels (Tian et al., 2011), acetylene is the most abundant one. As discussed by Kasper et al. (2011) and very recently by Simmie (2012), ethylene can be directly formed from fuels (THF and MTHF) through H-abstractions followed by β-scission steps (see reaction pathways rp1, rp2a, rp2b, and rp2c).



(rp1)

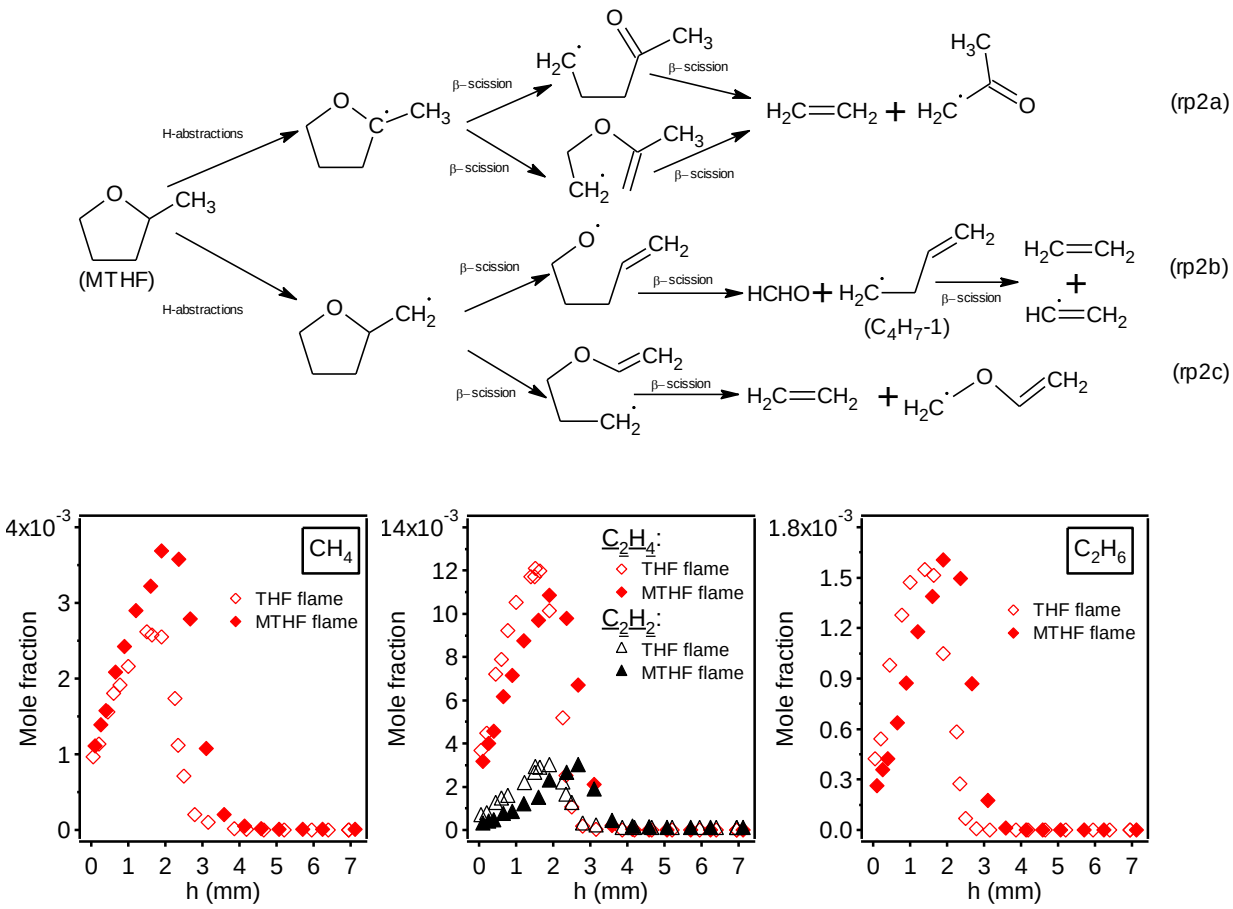


Figure 3. C_1-C_2 hydrocarbon intermediates

Under the same conditions, the ethylene and acetylene mole fractions reach higher levels in the THF and MTHF flames than those in the ethanol flame reported by Tran et al. (2013) (by a factor of ~2.3). In the THF flame published by Kasper et al. (2011) (φ=1.0, 15 Torr, and dilution ~ 28 %), the mole fractions of ethylene, acetylene, and methane are ~2-3 times higher than those in the present THF flame.

Figure 4 presents the profiles of C_3 hydrocarbon intermediates, including propyne (pC_3H_4), allene (aC_3H_4), propene (C_3H_6), and propane (C_3H_8). Unsaturated C_3 species (aC_3H_4, pC_3H_4, and C_3H_6) were detected with a much higher mole fraction in the MTHF flame than those in the THF flame, but saturated C_3 (C_3H_8) has an inverse trend, its mole fraction is higher in the THF flame. Among these C_3 intermediates, C_3H_6 is the most abundant one, with maximum mole fractions of ~13×10^{-4} (at h=1.2 mm) and ~35×10^{-4} (at h=1.7 mm) in the THF and the MTHF flames, respectively. Kasper et al. (2011) and Dagaut et al. (1998) found also this trend in their studies. However, in the stoichiometric THF flame of Kasper et al. (2011), the mole fraction of all these C_3 intermediates were measured with higher absolute values than those in the present THF flame (by a factor of ~2-3.5 for C_3H_6 and C_3H_8, and of ~9-11 for aC_3H_4 and pC_3H_4). This too large difference for aC_3H_4 and pC_3H_4 could be caused by the low signal-to-noise ratios of the PI-MBMS or by the difference of dilution ratio.

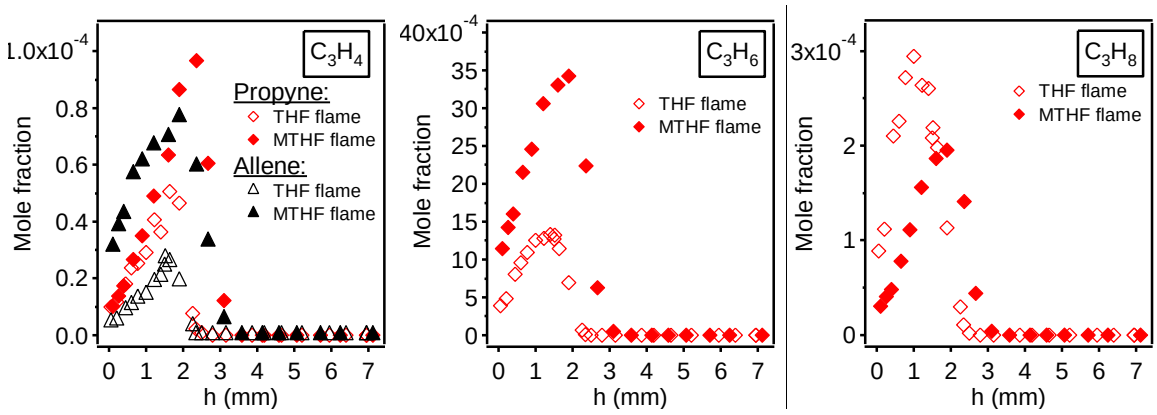
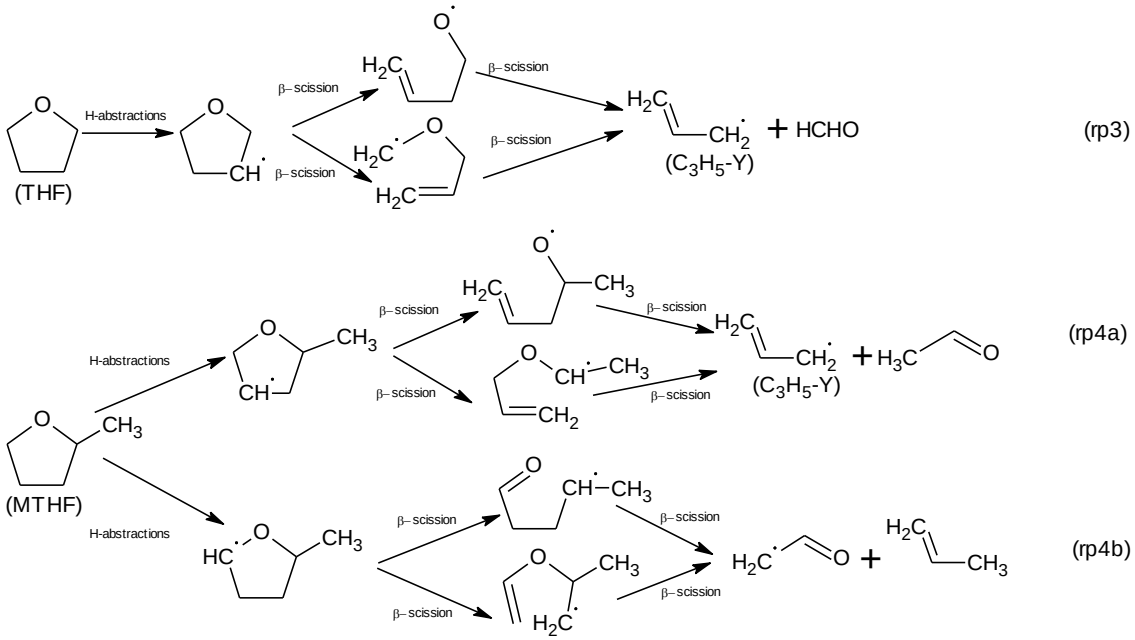


Figure 4. C_3 hydrocarbon intermediates

As discussed by Simmie (2012), propene can be yielded by a combination of an H-atom and an allyl radical (C_3H_5-Y) which can be produced in a few H-abstraction and β-scission steps from THF and MTHF (see reaction pathways rp3 and rp4a). In addition, propene can be formed directly from MTHF through reaction pathway (rp4b) which should be a more important source of this C_3 alkene. Probably due to this reason, C_3H_6 mole fraction reaches a higher level in the MTHF flame than that in the THF flame (Fig. 4).



Figures 5-6 presents the C_4-C_6 hydrocarbon intermediates, including three isomers of C_4H_6 - 1,3-butadiene (1,3-C_4H_6), 1,2-butadiene (1,2-C_4H_6), and 2-butyne (2-C_4H_6), three isomers of C_4H_8 - 1-butene (1-C_4H_8), 2-butene (2-C_4H_8) and i-butene (i-C_4H_8), three isomers of C_5H_{10} - 1-pentene (1-C_5H_{10}), 2-pentene (2-C_5H_{10}), and 2-methyl-2-butene (Fig. 5), and two cyclic species - 1,3-cyclopentadiene (1,3-C_5H_6) and benzene (C_6H_6) (Fig. 6). Among C_4H_6 isomers, the mole fraction of 1,3-butadiene is the largest one with maximum value of ~5.4×10^{-4} in the THF flame, and with a larger value (~7.8×10^{-4}) in the MTHF flame. Its mole fraction is much larger than those of 1,2-butadiene and 2-butyne. For C_4H_8 isomers, 1-butene is the most abundant one (contribution of ~95% to the three C_4H_8 isomers), with a

maximum mole fraction of ~4×10^{-4} in the THF flame being 2 times lower than that in the MTHF flame (~8.3×10^{-4}). However, the mole fraction of butane (n-C_4H_{10}, not shown in Fig. 5) reaches a higher level in the THF flame than that in the MTHF flame, with mole fractions of 2.5×10^{-4} and 0.74×10^{-4}, respectively. Other C_4 (not shown in Fig. 5), e.g. diacetylene (C_4H_2) and *iso*-butane (iC_4H_{10}) were detected with a mole fraction lower than 10 ppm in both flames. Among all these C_4 species, 1-butene is the most abundant one followed by butane in the THF flame, but by 1,3-butadiene in the MTHF flame. Kasper et al. (2011) have detected butane, 1-butene, 2-butene, and 1,3-butadiene as well in their THF flames using photoionization MBMS. 1-Butene, 1,3-butadiene and diacetylene were also identified in the THF thermal decomposition performed by Lifshitz et al. (1986). Only 1-butene has been identified and quantified in the THF oxidation study of Dagaut et al. (1998), using GC analysis.

In the THF flame, 1-butene can be formed by a combination of methyl radical (CH_3) and allyl radical (C_3H_5-Y) which can be produced through a few H-abstraction and β-scission steps from THF as shown in reaction pathway rp3 (Simmie, 2012). In the case of the MTHF flame, a similar pattern of 1-butene formation can be considered (via the formation of C_3H_5-Y in reaction pathway rp4a), but other sources of 1-butene can be also considered: combinations of a H-atom with a but-3-en-1-yl radical (C_4H_7-1) or with a resonance stabilized but-1-en-3-yl radical (C_4H_7-Y). These two C_4H_7-1 and C_4H_7-Y radicals can be yielded directly from the MTHF decompositions (see rp2b and rp5, respectively) (Simmie, 2012).

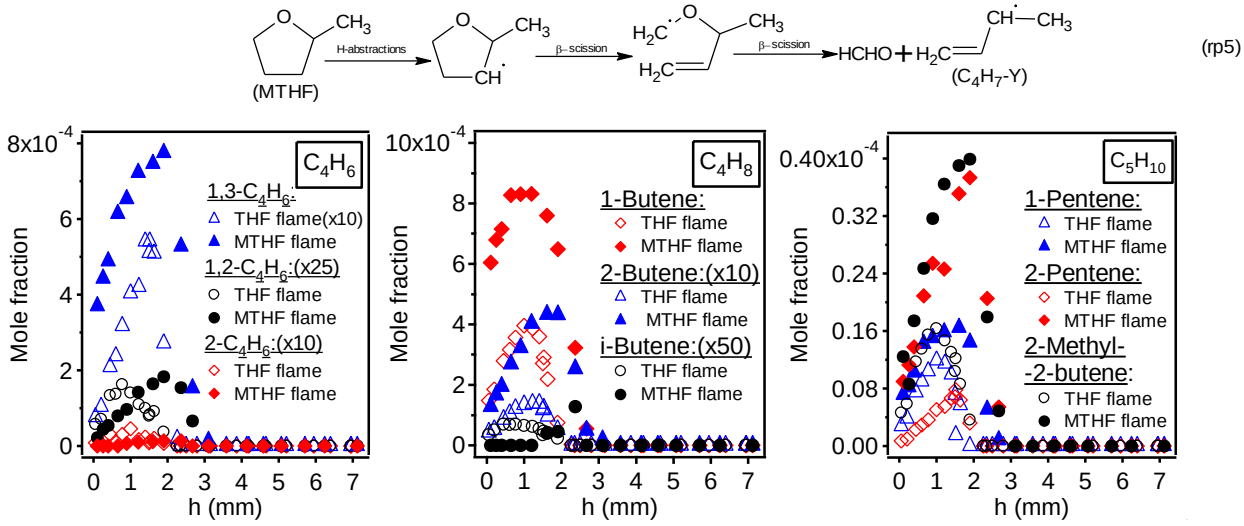


Figure 5. C_4-C_5 hydrocarbon intermediates

For the three C_5H_{10} isomers, the contributions of 2-methyl-2-butene, 1-pentene, and 2-pentene are ~45%, ~33%, and ~22%, respectively, in the THF flame, and are 43%, 18%, and 40%, respectively, in the MTHF flame. We can see the same isomers identification, but their contributions and mole fraction values are different between the THF and MTHF flames. In the THF flame, 2-methyl-2-butene is the most abundant species (mole fraction of 0.16×10^{-4}) in the three C_5H_{10} isomers, while in the MTHF flame, the mole fractions of 2-methyl-2-butene (~0.4×10^{-4}) and 2-pentene (0.37×10^{-4}) are quite comparable. In the THF flame of Kasper et al. (2011), 1-pentene was also detected, but 2-pentene has been omitted and 2-methyl-2-butene was not seen. These C_5 species have not been presented in the THF oxidation study of Dagaut et al. (1998).

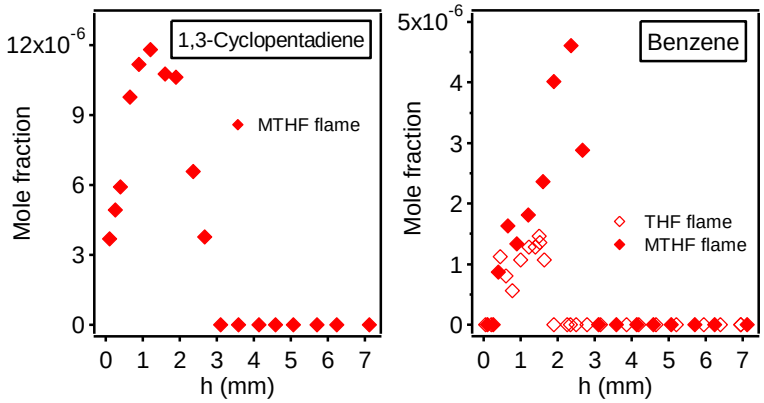


Figure 6. Cyclic hydrocarbon intermediates

The cyclic hydrocarbon intermediates (Fig. 6) were detected with small mole fractions, only 12 ppm for 1,3-cyclopentadiene (1,3-C_5H_6) in the MTHF flame, 1.5 and 4.6 ppm for benzene (C_6H_6) in the THF and MTHF flames, respectively.

Several oxygenated intermediates were detected in both THF and MTHF flames, feature of the combustion of oxygenated fuels. Only some important selected species are presented in the present paper as seen in Figs.7-10. Figure 7 displays the mole fraction profiles of C_1-C_2 oxygenated intermediates, including formaldehyde (HCHO), two C_2H_4O isomers - acetaldehyde (CH_3CHO) and ethylene oxide (cy-C_2H_4O), ketene (C_2H_2O), and dimethyl ether (C_2H_6O; DME). Formaldehyde, toxic and cancerogenic, is measured with the largest mole fraction and quite comparable between the THF and MTHF flames (maximum of ~2.9×10^{-3} and ~3.3×10^{-3}, respectively). Acetaldehyde is also found in large amounts in the MTHF flame with a maximum mole fraction of ~1.2×10^{-3}, but with a much lower mole fraction (~0.26×10^{-3}) in the THF flame. Under the similar conditions, the ethanol flame reported by Tran et al. (2013) emitted a much larger mole fraction of acetaldehyde (5.5×10^{-3} at φ=1.0) compared to the present flames, while the mole fraction of formaldehyde in the ethanol flame (2.8×10^{-3} at φ=1.0) is quite comparable to that in both THF and MTHF flames. Note that acetaldehyde and formaldehyde mole fractions reach higher levels in the stoichiometric THF flame reported by Kasper et al. (2011) than those in the present THF flame (by a factor of ~3). However, the ratio of formaldehyde to acetaldehyde (~10) is similar for the two studies at φ=1.

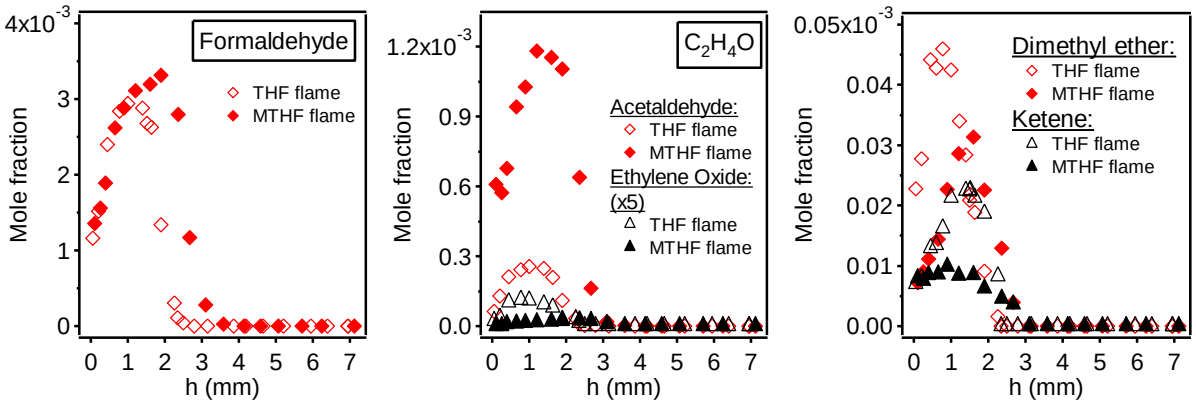
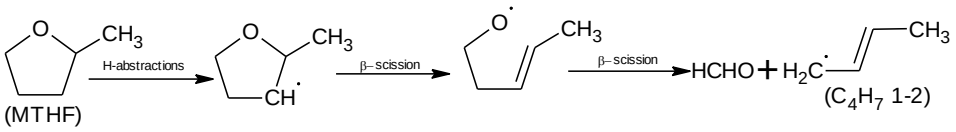


Figure 7. C_1-C_2 oxygenated intermediates

Mole fraction of other C_2 species (Fig. 7) - ethylene oxide, ketene, and dimethyl ether- reach lower levels (less than 50 ppm). Since ethylene oxide and ketene are very reactive, there is possibly a larger uncertainty in their mole fractions. Note that ethylene oxide and dimethyl ether were not found in both earlier studies of Kasper et al. (2011) and Dagaut et al. (1998). In the study of Dagaut et al. (1998), only three oxygenated intermediates (formaldehyde, acetaldehyde, and propanal) were measured; others such as dihydrofurans were detected at trace levels.

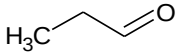
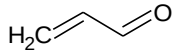
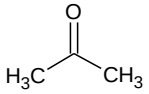
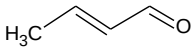
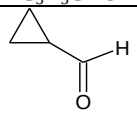
Simmie (2012) has shown that formaldehyde can be produced directly from the THF and MTHF decompositions via H-abstractions followed by few β-scission reactions as seen in (rp3) for THF, and in (rp2b), (rp5), and (rp6) for MTHF. However, formaldehyde formation can also be usually dominated by other different reactions in the flames. In the THF and MTHF flames, acetaldehyde can be formed via the formation of formylmethyl radical (2-oxomethyl, $CH_2{-}CH{=}O$) through the reaction pathways (rp1) and (rp4b), followed by a H termination reaction. However, in the case of MTHF, acetaldehyde can be formed directly in the fuel decomposition via other route (see rp4a).



(rp6)

Other aldehydes, e.g. propanal (C_2H_5CHO), acrolein (C_2H_3CHO; Fig. 8), 2-butenal (C_3H_5CHO; Fig. 9) and cyclopropanecarboxaldehyde (cy-C_4H_6O; Fig. 10) were also detected in the two THF and MTHF flames. The structure of some C_3-C_4 oxygenated intermediates is given in Table 3. The mole fraction of propanal (~18-20×10^{-5}) and acrolein (~10-11×10^{-5}) reach higher levels than those of 2-butenal and cyclopropanecarboxaldehyde, and are quite comparable between the THF and MTHF flames. The mole fraction of 2-butenal (Fig. 9) in the THF flame (~0.6×10^{-5}) are much lower than that in the MTHF flame (~3.9×10^{-5}), while cyclopropanecarboxaldehyde (Fig.10) has an inverse trend, is much higher in the THF flame (5.2×10^{-5} compared to ~1.8×10^{-5} in the MTHF flame).

Table 3. Formulae of some C_3-C_4 oxygenated intermediates

Species	Formula
Propanal	 C_2H_5CHO
Acrolein	 C_2H_3CHO
Acetone	 CH_3COCH_3
2-Butenal	 C_3H_5CHO
Cyclopropane-carboxaldehyde	 cy-C_4H_6O
Furan	C_4H_4O
2,3-Dihydrofuran	2,3-DHF; C_4H_6O
2,5-Dihydrofuran	2,5-DHF; C_4H_6O

In comparison with the studies of Kasper et al. (2011) and Dagaut et al. (1998), the acetaldehyde/propanal ratio - approximately ~1-1.5 - is quite comparable at φ=1, despite the individual propanal and acetaldehyde mole fractions are different between the three studies. 2-Butenal was also identified in the THF flame reported by Kasper et al. (2011). The presence of cyclopropanecarboxaldehyde, as mentioned by Kasper et al. (2011) can neither be confirmed nor excluded

based on the flame-sampled PIE curves because a complicated convolution of signals at *m/z* = 70. However, this species is well identified and quantified in the present THF and MTHF flames (Fig. 10). The possible formation of this species and of 2-butenal from 2,3-dihydrofuran has been reported by Lifshitz et al. (1989) and (Dubnikova and Lifshitz, 2002), and will be presented below.

The same picture with acetaldehyde and 2-butenal, acetone was measured with a much larger mole fraction in the MTHF flame than in the THF flame (Fig. 8); e.g. MTHF: X(acetone)=10×10^{-5} and THF: X(acetone)=1.4×10^{-5}, reflecting the effect of methyl group in MTHF molecule on its combustion chemistry.

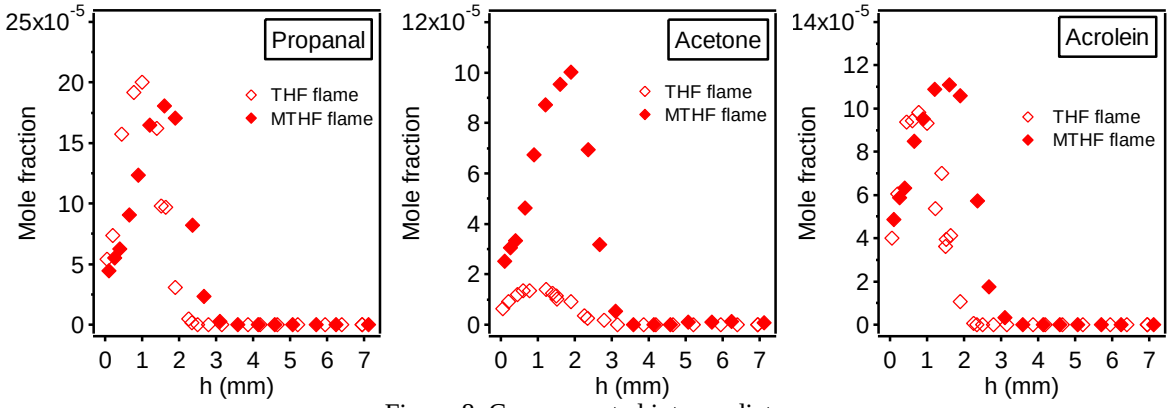


Figure 8. C_3 oxygenated intermediates

Several cyclic ethers, such as 2,3-dihydrofuran (2,3-DHF), 2,5-dihydrofuran (2,5-DHF), furan (Fig. 9), THF (intermediate in the MTHF flame) and MTHF (intermediate in the THF flame; Fig. 10), were identified and quantified in the THF and MTHF flames. Figure 9 shows that 2,3-dihydrofuran, 2,5-dihydrofuran, and furan were found in much higher mole fractions in the THF flame than in the MTHF flame. The 2,3-dihydrofuran is 5-10 times more abundant than 2,5-dihydrofuran, and its mole fraction reaches maximum 11.2×10^{-5} at h=0.6 mm in the THF flame and 2.0×10^{-5} at h=1.2 mm in the MTHF flame. These two dihydrofurans can be formed directly from fuel in the THF flame via the formation of cyclic radicals C_4H_7O followed by an elimination of a H-atom (Simmie, 2012), (Kasper et al., 2011). As discussed by Lifshitz et al. (1989) and Dubnikova and Lifshitz (2002), the isomerization of 2,3-dihydrofuran can produce 2-butenal and cyclopropanecarboxaldehyde which subsequently isomerizes to 2-butenal, as seen in reaction pathway rp7.

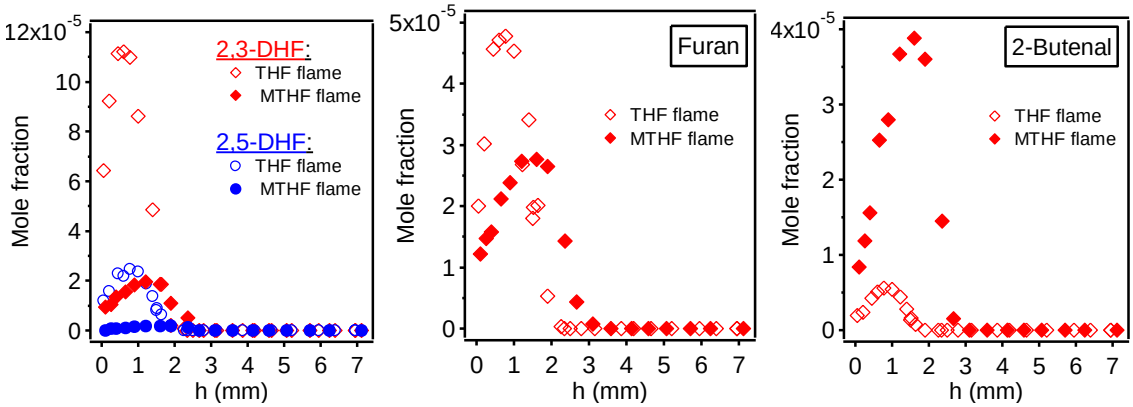


Figure 9. C_4 oxygenated intermediates

The peak mole fraction of furan (Fig. 9) is 4.8×10^{-5} at h=0.8 mm in the THF flame, and is 2.8×10^{-5} at h=1.6 mm in the MTHF flame. These peak position and maximum mole fraction value indicate a possible formation of furan from 2,3-dihydrofuran, especially evident in the THF flame.

Mole fractions of THF and MTHF (Fig. 10) formed in the MTHF and THF flames, respectively, are quite low (only ~1.4×10^{-5} for THF and 2.1×10^{-5} for MTHF). Addition of a methyl radical to the C2-position of the THF-ring seems the most likely process for the MTHF formation. Kasper et al. (2011) have also detected MTHF in their THF flames.

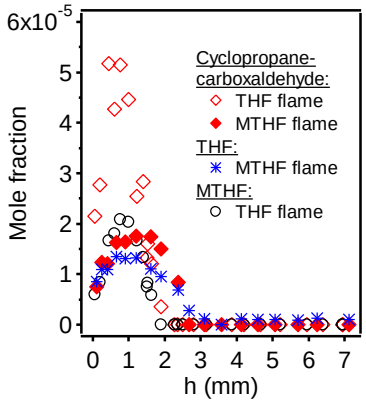
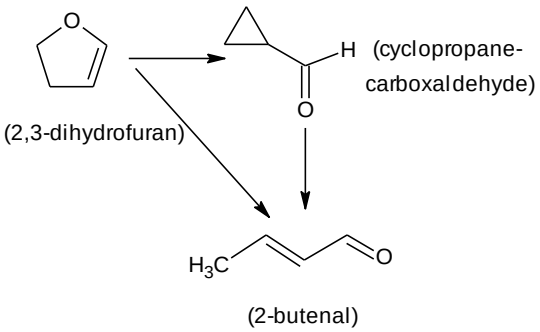


Figure 10. Cyclopropanecarboxaldehyde, THF and MTHF intermediates



(rp7)

Note that, a number of other oxygenated species were also detected in the MTHF flame, such as 2-butanone (mole fraction of ~26×10^{-5}), 4-pentenal (~10.6×10^{-5}), methyl furan (~3.5×10^{-5}), 2-butenone (~2.8×10^{-5}), ethyl acetone (~2.1×10^{-5}), pentanal (~1.9×10^{-5}), butanal (~1.1×10^{-5}), and methyl propanal (~0.3×10^{-5}), while in the THF flame, these species were either not detected or detected at trace levels only.

4. Conclusions

This paper presents new experimental results about the chemical structure of low-pressure laminar premixed flame of THF and MTHF, under the same conditions: φ=1.0, Ar dilution of 78%, pressure of 50 Torr (6.7 kPa), C/O=0.33, and C/H= 0.5. On-line GC and GC-MS were used. About 40 and 60 stable species were identified and quantified as a function of burner distance in the THF and MTHF flames, respectively. A number of selected important species have been presented, discussed and compared to those in previous studies reported in the literature. Among all intermediate species measured for the two tetrahydrofuranic fuels flames, the production of ethylene is the largest and comparable between the two fuels. Note that for unsaturated cyclic ethers as furan family fuels acetylene is the most abundant one as reported in the literature.

Due to the different structure of these molecules, the combustion chemistry of THF and MTHF present some differences. Indeed, the profile positions of the major and intermediate species show that the THF flame front is closer to the burner compared to the MTHF flame, reflecting a higher laminar flame speed of THF. The mole fractions of C_3H_4 isomers, C_3H_6, C_4H_8 isomers, C_5H_8 isomers, 1,3-C_4H_6, 1,3-C_5H_6, C_5H_{10} isomers, C_6H_6, acetaldehyde, acetone, and 2-butenal reach higher levels in the MTHF flame than those in the THF flame, while the mole fraction of C_3H_8, oxide

ethylene, ketene, DME, 2,3- and 2,5-dihydrofuran, furan, and cyclopropanecarboxaldehyde have inverse trends. Other species were found in comparable mole fractions between the THF and MTHF flames.

The comparison of the present results and that obtained for the combustion of ethanol previously studied under similar conditions shows that the combustion of tetrahydrofuranic fuels emits a much lower mole fraction of acetaldehyde, compared to the ethanol combustion, while formaldehyde emission is quite comparable in both fuels classes.

The obtained experimental results provide database for the analysis of intermediates in flames, which will be used to develop a new mechanism for tetrahydrofuranic fuels combustion. Despite the structure of laminar premixed low-pressure THF flames investigated using MBMS has been reported in the literature, it should be noted that the information from another independent quantitative measurement such as GC was very valuable to confirm species identifications and to unambiguously identify the respective isomers. To our knowledge, the present study is the first work on the MTHF flame. This is also the first experimental analysis of the two tetrahydrofuranic fuels under the same conditions.

Acknowledgements

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