



## An experimental and modeling study of the combustion of tetrahydrofuran



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### ABSTRACT

Tetrahydrofuran (THF) is a well suited starting point fuel to study the combustion chemistry of saturated cyclic esters that are being considered as promising bio-fuels. To better understand the combustion chemistry of THF, laminar low-pressure premixed flame structure, atmospheric adiabatic laminar burning velocities, and high-pressure ignition delay times were investigated. The structure of laminar premixed low-pressure (6.7 kPa) argon-diluted (78%) flames of THF were studied at three equivalence ratios (0.7, 1.0 and 1.3) using on-line gas chromatography analyses. The results consist of temperature and mole fraction profiles (about 40 species) measured as a function of the height above the burner. Ethylene, propene, formaldehyde, acetaldehyde, and dihydrofurans were observed as important intermediates. Aromatic species were detected in very low amounts. The adiabatic laminar burning velocities of THF–air mixtures were measured using the heat flux burner method at atmospheric pressure (initial temperatures from 298 to 398 K, at equivalence ratios from 0.55 to 1.60). The maximum burning velocity of THF was comparable to that of ethanol and diethyl ether. The ignition delay times of THF–oxygen–argon mixtures were measured behind reflected shock waves (temperatures from 1300 to 1700 K, pressures around 8.5 atm, mixtures containing 0.25–1% of fuel for equivalence ratios of 0.5–2.0). A new detailed kinetic model for THF combustion was developed using a combination of automatic generation (EXGAS), Evans–Polanyi correlations (for H-abstraction kinetic data), and CBS–QB3 theoretical calculations (for unimolecular initiation, H-abstraction and  $\beta$ -scission kinetic data). An overall good agreement between simulations and the present experimental results has been found. The main THF reaction pathways under flame conditions have been identified from flow rate analyses.

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### 1. Introduction

Today there is an increasing interest to shift from fossil fuels to bio-fuels. The use of bio-fuels allows a reduction of the dependence to petroleum-based fuels, and should limit the increase of the total amount of greenhouse gases in the atmosphere. Cyclic ethers of the family of tetrahydrofuran (THF, see molecule structure in Fig. 1), e.g. 2-methyltetrahydrofuran (MTHF) [1] and 2,5-dimethyltetrahydrofuran (DMTHF) [2], have the potential to become promising bio-fuels for internal combustion engines. These fuels have a lower

heating value ( $\sim 28.5$ – $29.5$  MJ/L), which is close to that of gasoline ( $\sim 31.6$  MJ/L), and higher than that of ethanol ( $\sim 21.3$  MJ/L) [3]. The THF family fuels are second generation bio-fuels and can be produced from non-edible biomass [4–7]. Some tests for MTHF as fuel in engine have been reported relatively early. In 1988, Rudolph and Thomas [8] have comparatively analyzed pollutant emissions from a spark-ignition engine using mixtures of gasoline with 10% of different potential liquid fuels. Their results show that the MTHF blend has power outputs and emissions of carbon monoxide, nitrogen oxides, and non-methane hydrocarbons close to unleaded gasoline. In 1999, MTHF has been approved by the USDOE as a component of *P*-series fuels for spark-ignition engine. The *P*-series fuels are blends of ethanol (25–40% by vol.), MTHF (20–35%), and  $C_5$  alkanes (25–40%), with butane (0–10%) added to blends, that would be used in severe cold-weather conditions to meet engine cold start requirements [9,10].

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In addition, THF and other saturated cyclic ethers have also been identified among the emissions produced during the low-temperature oxidation and auto-ignition of alkanes, this formation being due to isomerizations of alkylhydroperoxy radicals [11,12]. The subsequent reactions of these cyclic ethers can then influence the overall chemical kinetic mechanisms of the oxidation of alkanes. Therefore, a better understanding of saturated cyclic ether combustion chemistry, starting by that of THF, is necessary, and should be gained before actually using these fuels in engines.

The pyrolysis of THF was first experimentally studied in the 1950s [13,14] and then in 1986 by Lifshitz et al. [15] behind reflected shock waves (temperatures between 1070 and 1530 K at pressures around 3 bar). More recently Verdicchio et al. [16] have studied the unimolecular decompositions of THF using quantum chemistry and reaction rate theory. These computed reactions have been used in a pyrolysis model which satisfactorily reproduces the results of Lifshitz et al. [15] showing a determinant importance of the reactions involving carbenes and diradicals under these conditions.

A few studies on the combustion of THF have also been carried out. The low-temperature (493 K) oxidation of THF was investigated by Molera et al. [17], in a static reactor. A motored engine study of auto-ignition chemistry of acyclic and cyclic ethers, including THF, was performed by Leppard [18]. The chemical mechanisms responsible for auto-ignition of both ether classes are detailed and can be used to explain the differences in antiknock characteristics. Ignition delay times and oxidation of THF have been studied by Dagaut et al. [19] behind reflected shock waves and in a jet-stirred reactor (JSR), respectively (temperatures from 800 to 1800 K, pressures from 202 to 1013 kPa, equivalence ratio ( $\phi$ ) from 0.5 to 2). On the basis of these results, a detailed reaction mechanism with 71 species and 484 reactions was proposed. The JSR study showed that a large amount of aldehydes (formaldehyde, acetaldehyde, and propanal) were produced during the THF oxidation. Recently, Kasper et al. [20] have 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 including radicals have been

measured and analyzed. Finally Uygun et al. [21] have studied ignition delay times of THF in a high pressure shock tube at temperatures from 691 to 1100 K and pressures of 20 and 40 bar for stoichiometric mixtures. No model has been proposed to support these two recent experimental work [20,21]. Theoretical calculations have also been performed [2,22] to study the kinetics and thermochemistry of THF and its derivatives.

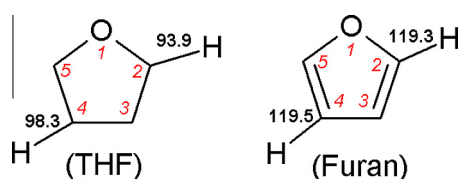
The main experimental studies published in the literature on the pyrolysis and combustion of THF are summarized in Table 1. In the present work, as part of a continuing effort to improve the knowledge on the combustion chemistry of this cyclic ether, we report experimental data obtained in premixed flames and in shock tube. These data consist of: (i) temperature and mole fraction profiles of chemical species measured in low-pressure premixed THF flames including isomer identification, (ii) laminar burning velocities obtained under atmospheric pressure using the heat flux method, and (iii) ignition delay times measured in a shock tube behind reflected shock waves at temperatures higher than those investigated by Uygun et al. [21]. A new detailed kinetic model for THF combustion has been developed using a combination of automatic generation (EXGAS), Evans–Polanyi correlation, and CBS-QB3 theoretical calculations in order to represent the present high-temperature experimental results. This model includes the unimolecular initiations recently studied by Verdicchio et al. [16].

## 2. Experimental and simulation methods

The combustion chemistry of THF was studied in low-pressure and atmospheric flat flames, and in a shock tube. THF liquid fuel (>99.7% pure) was supplied by VWR. This section presents the experimental and simulation methods used in the present study. In the flame experiments, gas flow rates (of oxygen, argon and nitrogen) were measured using Bronkhorst High-Tech Mass Flow Controllers (MFC) and flow rates of liquid THF were measured using Bronkhorst mini-CORI-FLOW Mass Flow Controller connected to a Controlled Evaporator Mixer (CEM). The liquid fuel was mixed with inert gas and then evaporated by passing through the CEM set at 373 K. The gas and liquid mass flow accuracy was  $\pm 0.5\%$ .

### 2.1. Low-pressure premixed flat flame structure

Three flames, fuel-lean ( $\phi = 0.7$ ), stoichiometric ( $\phi = 1.0$ ), and fuel-rich ( $\phi = 1.3$ ), were investigated at 50 Torr (6.7 kPa) with an argon dilution of 78%. The experimental setup developed in LRGP to study stable species profiles in a laminar premixed flat flame at low-pressure has been described previously [23–25]. Briefly, all flames are stabilized on a McKenna burner (diameter of 60 mm) housed in a vacuum chamber. The burner is cooled with



**Fig. 1.** Structure of THF compared with that of furan. Italic number near the atom: atom label; bold numbers: calculated bond energy (in kcal mol<sup>-1</sup>) from the thermochemical data of molecules and radicals calculated theoretically at the CBS-QB3 level of theory in present and work [52].

**Table 1**

Recent main studies on the pyrolysis and combustion of THF.

Reactor	Operating conditions			Ref.
	<i>T</i> (K)	<i>P</i> (kPa)	$\phi$	
ST	1070–1530	178–1018	Pyrolysis	Lifshitz et al. [15]
SR	493	21	2.75	Molera et al. [17]
ICE	400 <sup>a</sup> ; 827 <sup>b</sup>	80 <sup>a</sup> ; 1200 <sup>b</sup>	0.95–1.0	Leppard [18]
ST	1000–180	200–500	0.5–2.0	Dagaut et al. [19]
JSR	800–1100	1000	0.5–1.0	(a 71 species and 484 reactions model has been proposed)
FF	500–2300	2.0–3.3	1.0–1.75	Kasper et al. [20]
ST	691–1100	2000–5000	1.0	Uygun et al. [21]

SR – static reactor; ST – shock tube; ICE – internal combustion engine; JSR – jet-stirred reactor; FF – flat flame.

<sup>a</sup> In admission collector.

<sup>b</sup> Maximal value in cylinder at compression ratio of 8.7.

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