



# Experimental and modeling study of the pyrolysis and combustion of 2-methyl-tetrahydrofuran



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## ARTICLE INFO

### Article history:

Received 2 May 2016

Revised 10 June 2016

Accepted 15 November 2016

Available online 9 December 2016

### Keywords:

Bio-fuel

2-Methyl-tetrahydrofuran

Pyrolysis

Laminar premixed flame

Detailed kinetic model

## ABSTRACT

Saturated cyclic ethers are being proposed as next-generation bio-derived fuels. However, their pyrolysis and combustion chemistry has not been well established. In this work, the pyrolysis and combustion chemistry of 2-methyl-tetrahydrofuran (MTHF) was investigated through experiments and detailed kinetic modeling. Pyrolysis experiments were performed in a dedicated plug flow reactor at 170 kPa, temperatures between 900 and 1100 K and a N<sub>2</sub> (diluent) to MTHF molar ratio of 10. The combustion chemistry of MTHF was investigated by measuring mole fraction profiles of stable species in premixed flat flames at 6.7 kPa and equivalence ratios 0.7, 1.0 and 1.3 and by determining laminar burning velocities of MTHF/air flat flames with unburned gas temperatures of 298, 358 and 398 K and equivalence ratios between 0.6 and 1.6. Furthermore, a kinetic model for pyrolysis and combustion of MTHF was developed, which contains a detailed description of the reactions of MTHF and its derived radicals with the aid of new high-level theoretical calculations. Model calculated mole fraction profiles and laminar burning velocities are in relatively good agreement with the obtained experimental data. At the applied pyrolysis conditions, unimolecular decomposition of MTHF by scission of the methyl group and concerted ring opening to 4-penten-1-ol dominates over scission of the ring bonds; the latter reactions were significant in tetrahydrofuran pyrolysis. MTHF is mainly consumed by hydrogen abstraction reactions. Subsequent decomposition of the resulting radicals by  $\beta$ -scission results in the observed product spectrum including small alkenes, formaldehyde, acetaldehyde and ketene. In the studied flames, unimolecular ring opening of MTHF is insignificant and consumption of MTHF through radical chemistry dominates. Recombination of 2-oxo-ethyl and 2-oxo-propyl, primary radicals in MTHF decomposition, with hydrogen atoms and carbon-centered radicals results in a wide range of oxygenated molecules.

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## 1. Introduction

There is an increased demand for a sustainable production of chemicals and fuels. Currently, a lot of effort is dedicated to the conversion of lignocellulosic biomass through catalytic, fermentative and pyrolytic processes. These conversion routes result in a wide variety of molecules that may be processed further into other high-value chemicals, so-called platform molecules, or that can be used directly, for example as bio-fuel.

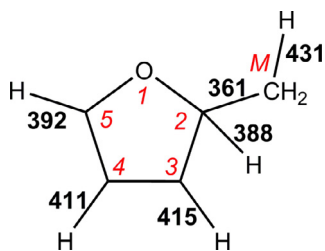
Recently, several production routes to saturated cyclic ethers, such as 2-methyl-tetrahydrofuran (MTHF) and 2,5-dimethyl-tetrahydrofuran (DMTHF), have been proposed [1–3]. This class of molecules has lower heating values that range between  $\sim 28.5 \text{ MJ l}^{-1}$  and  $29.5 \text{ MJ l}^{-1}$ , which are close to those of furans ( $\sim 27.7\text{--}30.0 \text{ MJ l}^{-1}$ ) and of gasoline ( $\sim 31.6 \text{ MJ l}^{-1}$ ), but clearly higher than that of ethanol ( $\sim 21.3 \text{ MJ l}^{-1}$ ). MTHF has good anti-knock characteristics (RON=86, MON=73), and satisfactory performance when mixed with gasoline in a conventional internal combustion engine [4–7].

The potential of cyclic ethers to serve as next-generation bio-derived fuels has triggered several fundamental studies that aim at understanding their combustion chemistry. Tetrahydrofuran (THF), the simplest five-membered cyclic ether, has received most attention. Verdicchio et al. investigated the unimolecular

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**Fig. 1.** Structure of MTHF with atom labels (red italic) and bond energy in  $\text{kJ mol}^{-1}$  [14] (black bold). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

decomposition of THF using quantum chemical methods [8]. The calculations show that biradical and carbene intermediates play an important role in the initial ring-opening steps, but that a concerted molecular channel is also active. Model simulations with a kinetic model based on the mentioned *ab initio* study are in good agreement with shock tube experiments [9]. Tran et al. expanded the model to describe the combustion chemistry of THF. The model was validated with data obtained from premixed flames and shock tube measurements [10]. Kasper et al. investigated the structure of laminar premixed low-pressure THF flames using photoionization (PI) and electron-ionization (EI) molecular-beam mass spectrometry (MBMS) [11]. THF oxidation and ignition has been studied in jet-stirred reactors and a rapid compression machine [12, 13]. The available experimental data and developed kinetic models of the aforementioned studies indicate that THF decomposition is dominated by radical chemistry as soon a radical pool is established.

The pyrolysis and combustion chemistry of alkylated cyclic ethers is less well established. A theoretical study by Simmie provides thermochemistry for THF, MTHF, DMTHF and the derived radicals, and kinetic data for a selection of hydrogen abstraction and radical decomposition reactions [14]. Other quantum chemical studies have focused on hydrogen abstraction from MTHF and DMTHF by hydroperoxy radicals [15] and intramolecular hydrogen abstraction of the various peroxy radicals formed from 3-methyl-tetrahydrofuran [16]. Fuel rich ( $\varphi = 1.7$ ), low pressure, premixed laminar MTHF flames were investigated by Moshhammer et al. [17]. Reaction products were identified and quantified using molecular beam mass spectrometry with electron ionization and synchrotron-based tunable VUV photoionization. A kinetic model was developed using the theoretical study by Simmie [14] and analogy with other molecules.

This work aims to improve the understanding of the pyrolysis and combustion chemistry of MTHF, see Fig. 1. Firstly, the experimental database for MTHF reactions is expanded in several ways. The pyrolysis chemistry is investigated in a tubular plug flow reactor. Furthermore, temperature and mole fraction profiles are measured in three low-pressure premixed flames while laminar burning velocities are obtained at atmospheric pressure using the heat flux method. Secondly, a new detailed kinetic model for MTHF pyrolysis and combustion has been developed. Kinetic data related to the decomposition of MTHF has been calculated using the CBS-QB3 level of theory. Thirdly, predictions of the new kinetic model are compared to the obtained experimental data. Reaction path and sensitivity analyses are performed to better understand the MTHF chemistry. The proposed kinetic model is meant to serve as a building block for biomass pyrolysis and gasification processes as the cyclic ether structure is present in some biomass model compounds.

## 2. Experimental and computational methods

The pyrolysis chemistry of MTHF was studied in a plug flow reactor. The combustion chemistry was studied using premixed, lam-

inar flames. A detailed description of the experimental setups used in this study has been given elsewhere [18–23]. Only the main features of the experimental and analytical methods used are summarized below. Operating conditions are listed in Table 1.

### 2.1. Tubular flow reactor for pyrolysis

MTHF (Sigma Aldrich, state purity +99%) is fed to an evaporator kept at 573 K using a Coriolis flow meter controlled pump. Nitrogen (Air Liquide, purity +99.999%) is used as diluent and its flow rate is controlled using a Coriolis mass flow controller. It is heated to the same temperature as MTHF and both gasses are mixed ( $V_{\text{pre-mixing zone}} = 5 \cdot 10^{-4} \text{ m}^3$ ) before entering the reactor.

The tubular reactor has an internal diameter of 6 mm and is 1.475 m long. The reactor is placed in an electrically heated furnace. In total, eight thermocouples are positioned along the reactor length, measuring the gas temperature. The reactor consists of four separate sections and the temperature in each section is controlled by a thermocouple. Type K thermocouples were used. Uncertainty on temperature reading is  $\pm 2.2 \text{ }^\circ\text{C}$  or 0.75% of reading in  $^\circ\text{C}$ , whichever is greater, based on American Society for Testing Materials (ASTM) specifications for calibration accuracy. Two manometers, positioned at the inlet and outlet of the reactor, measure the pressure. The pressure was kept fixed at 0.17 MPa using a valve positioned downstream of the reactor. The pressure drop across the reactor was found to be negligible ( $< 0.001 \text{ MPa}$ ).

Products and unconverted feed are identified and quantified online, downstream of the reactor, using several dedicated gas chromatographs. The reactor effluent is first sent to a heated sampling system kept at 573 K to avoid condensation. A part of the mixture is injected on a refinery gas analyzer (RGA) after removal of the condensable fraction. This chromatograph is able to calculate the flow rate of all permanent gases using two thermal conductivity detectors (TCD) and  $\text{C}_4$  hydrocarbons using a flame ionization detector (FID) based on the fixed flow rate of  $\text{N}_2$ , i.e. primary internal standard. A different fraction of the effluent is injected on a two dimensional gas chromatograph (GC $\times$ GC) and a light oxygenates analyzer (LOA) through heated transfer lines, without prior condensation. The flow rate of water, formaldehyde and methanol are calculated using the LOA, equipped with a TCD, with propene, identified and quantified on the RGA, as secondary internal standard. The GC $\times$ GC allows identification, using a time-of-flight mass spectrometer (TOF-MS), and quantification, using a FID, of all hydrocarbons and oxygenated molecules that have two or more carbon atoms. Methane, identified and quantified on the RGA, acts as secondary internal standard. This methodology allows online analysis of the complete product spectrum and avoids separate gas-phase and condensate analysis. A more detailed description of data quantification can be found elsewhere [24].

The procedure described above allowed closing C, H and O molar balances within 5%. Several repeat experiments were performed and the average uncertainty on product mole fraction is 5%, in line with previous experiments.

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

The flow rates of oxygen (Messer, purity +99.995%) and argon (Messer, purity +99.999%), the diluent, are controlled by two mass flow controllers (Bronkhorst). The flow rate of liquid MTHF (Sigma Aldrich, purity +99%) is regulated using a mass flow controller connected to an evaporator/mixer (Bronkhorst). There, MTHF is evaporated and mixed with argon. Subsequently, the gaseous stream is mixed with oxygen and fed to a McKenna burner (60 mm diameter) housed in a vacuum chamber. The temperature of the burner is kept at 333 K using water cooling.

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