



Experimental and numerical study of a novel biofuel: 2-Butyltetrahydrofuran



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ABSTRACT

A novel lignocellulosic biofuel 2-butyltetrahydrofuran (2-BTHF) is investigated experimentally and numerically in the present study. Laminar burning velocities were measured in a combustion vessel. Ignition delay times were experimentally determined in a rapid compression machine and in a shock tube at high pressures covering a wide temperature range. A detailed chemical kinetic mechanism is proposed to describe the oxidation of 2-BTHF at both low and high temperatures. It is demonstrated that the model gives satisfactory results for the various experimental configurations. For a better understanding of the oxidation kinetics, the chemical model is further used to elucidate the reaction pathways of 2-BTHF. A comparison of its ignition behavior with other C₈ hydrocarbons is further presented and the impact of the tetrahydrofuranic ring on the fuel ignition characteristics is highlighted and analyzed.

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1. Introduction

Lignocellulose-derived biofuels nowadays attract major interest in the search for sustainable hydrocarbon-based transportation fuels. Tetrahydrofuranic fuels can be produced via novel lignocellulosic conversion routes based on selective catalytic transformations [1,2] and are in this respect of great interest for combustion research. The understanding of their physical and chemical properties as well as engine performance is crucial element thereof. Recently, Sudholt et al. [3] experimentally investigated the ignition characteristics of tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MTHF), 2-ethyltetrahydrofuran (2-ETHF), and 2-BTHF in form of derived cetane numbers (DCNs). It was found that the ignition propensity of tetrahydrofurans was highly sensitive to their side-chain lengths. While the THFs with short alkyl chain show inhibited auto-ignition reactivity and thus are suitable for spark-ignition engines, the long-chain 2-BTHF with a DCN of 45.5 meets the cetane number requirement for diesel fuels in the United States [3].

Several kinetic studies are available in the literature for short-chain tetrahydrofuranic species [4–11] and also for tetrahydropyran [11–13]. As they are promising candidates for gasoline replacements, these pioneering studies were limited to high-temperature combustion. Very recently, Vanhove et al. [14] and Antonov et al. [15] investigated the low temperature oxidation of tetrahydrofuran experimentally and numerically. Studies on long-chain tetrahydrofurans and their low-temperature ignition behavior are currently lacking in the literature. This leads unavoidably to the delay of their application in the transportation sector. Especially, missing chemical kinetic models hinder the understanding of their performance in combustion devices with the aid of computational fluid dynamic simulations.

The primary goal of this work is the first exploration of the combustion chemistry of the long-chain 2-BTHF at both low and high temperatures. For this, the laminar flame speeds of 2-BTHF were measured in a high-pressure combustion vessel, and its auto-ignition characteristics were investigated in a shock tube (ST) and in a rapid compression machine (RCM) for a variety of initial conditions. These experimental setups are described in Section 2. Section 3 presents the development of a detailed chemical mechanism including both low- and high-temperature kinetics. For the model development, the approach of reaction classes and rate rules

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is applied. Quantum chemistry calculations are conducted to obtain C–C bond dissociation energies (BDEs) of 2-BTHF and activation energies of the ring-opening reactions of fuel radicals. Following this, the model results are compared with the obtained experimental data in Section 4. Reaction pathway and sensitivity analyses are performed for a deeper understanding of the predicted 2-BTHF oxidation. The ignition characteristics of 2-BTHF are also compared to those of di-*n*-butyl ether (DnBE), *n*-octanol, and *n*-octane having identical carbon number in the molecular structures but different functional groups in Section 4.

2. Experimental facilities

This section describes the experimental facilities used in the present study. 2-BTHF with a purity of more than 97% has been supplied by the Institute for Technical and Macromolecular Chemistry at RWTH Aachen University. The purity was determined by nuclear magnetic resonance (NMR) spectroscopy analysis. Oxygen ($\geq 99.999\%$), argon ($\geq 99.996\%$), and nitrogen ($\geq 99.999\%$) were supplied by Westfalen AG and Praxair. Technical air with 21% oxygen and 79% nitrogen on a molar basis was used in experiments. For ST and RCM measurements, fuel/air mixtures were prepared in mixing vessels with a total pressure of almost 3 bar. For a maximum partial pressure of the fuel of about 50 mbar, a pre-heating of the facilities up to 90°C was sufficient to keep the fuel in the vapor phase. The mixtures were allowed to mix for at least 60 min in order to ensure homogeneous mixing via gaseous diffusion. For flame speed experiments, the mixing strategy of Halter et al. [16] was followed and the mixing process was performed in the combustion vessel. For all kinds of measurements, mixture composition was controlled by monitoring partial pressures and it was ensured that good reproducibility of experiments was achieved independent of the mixing times.

2.1. Combustion vessel

Flame speed experiments were performed using a closed-vessel method combined with an optical Schlieren cinematography setup. The experimental setup has been described in detail by Beeckmann et al. [17]. The internal shape of the pressure vessel is spherical with an inner diameter of 100 mm; quartz windows with a diameter of 50 mm are positioned on opposite sides. The outward location of the propagating flame is imaged using a dual-field-lens Schlieren arrangement [18]. It is combined with a high-speed CMOS camera (LaVision High-SpeedStar 6). Images are taken with 25,000 frames per second, at 448×448 pixels, and a resolution of 10.29 pixel/mm. The Schlieren system consists of a pulsed high power LED as a light source and an adjustable power output. The LED, type Luminus CBT-120-G-C11-CJ-G6 [19], emits green light between 530 and 535 nm. Optical lenses are an aspheric condenser lens and three spherical lenses. Two pinholes with a diameter of 0.5 mm are used, and overexposure of the camera from flame radiation is prevented by an optical filter. A non-linear model has been utilized to extract the laminar flame speed, which has been discussed by Halter et al. [20] as well as by Kelley and Law [21]. Possible uncertainties in mixture preparation lead to an uncertainty of equivalence ratio of ± 0.02 , which corresponds to maximum uncertainties of 4% in flame speeds.

2.2. Rapid compression machine

The single piston RCM, which has been described in Ref. [22], was used to measure ignition delay times. This RCM consists of three main components, i.e. the pneumatically driven piston, the hydraulic braking, and control chamber with the reactor piston. The driver cylinder has an internal bore of 140 mm and that of

the reactor is 50 mm. The reactor volume can be varied through the interchange of the end walls. The cylindrical reactor chamber has six accessible ports for gas inlet/outlet valves, optical-, mass-sampling, and pressure measurements. The RCM is equipped with an external heating system covering the reactor chamber. The system is controlled and monitored by 13 type-T thermocouples mounted along the reactor wall. This allows the RCM to study various pre-compression temperatures, from ambient up to 423 K. Creved piston heads are used to suppress the formation of roll-up vortices. This ensures a homogeneous temperature field within the reactor core at the end of compression. The pressure within the RCM is measured using a recessed and silicon coated PCB113B24 sensor. The conditions after compression are calculated using the compression/expansion routine in the Gaseq code [23], based on the isentropic relationship between temperature and pressure. An uncertainty of $\pm 20\%$ is estimated for the measured ignition delay times. For more details, the reader is referred to previous work [22].

2.3. Shock tube

Ignition delay time measurements behind reflected shock waves were obtained in a rapid-screening shock tube. It is assembled of a 3 m long curved driver section and a 4.1 m driven section with an inner diameter of 63.5 mm. The two sections are separated through a double diaphragm chamber housing up to two pre-scored aluminum diaphragms. The incident shock velocities are measured over the last 1.0 m of the driven section using five uncoated PCB model 113B22 pressure transducers. An inhouse code based on the shock and detonation package toolbox [24] developed for the Cantera [25] code is used to determine the gas conditions behind the reflected shock. Accounting for possible uncertainties in the measurements of the initial temperatures and pressures, the shock velocities, and the thermodynamic data of the fuel/air mixtures, the uncertainties in the conditions behind the reflected shock are estimated for each experiment by solving the shock equations with the inhouse code. The maximum uncertainties in temperatures and pressures are determined as $\pm 0.5\%$ and $\pm 1.4\%$, respectively. Due to these uncertainties, an uncertainty of $\pm 20\%$ is estimated for the measured ignition delay times. A detailed description about the uncertainty estimation for experiments conducted in the applied shock tube can be found in Ref. [26].

3. Kinetic model development

A chemical kinetic model for 2-BTHF was developed using current understanding of combustion chemistry for a variety of structurally similar molecules, such as THF [4], 2-MTHF [8], 2,5-dimethyltetrahydrofuran (2,5-DMTHF) [9], and *n*-alkanes [27–29]. The molecular structure of 2-BTHF is shown in Fig. 1 including the notation of the atoms used below. Also provided are the C–H bond dissociation energies calculated at the CBS-QB3 level of theory by Sudholt et al. [3], along with the C–C BDEs of side-chain carbons calculated also at the CBS-QB3 level of theory as part of this work. The calculations were performed within the Gaussian09 suite of programs [30]. These calculated BDEs provide a global insight into fuel oxidation and were used to guide the kinetic modeling in this work. In general, the presence of an oxygen atom in a molecular structure affects the BDEs associated with the neighboring carbons [31,32]. Therefore, these carbon atoms are additionally labeled as α , β , and γ with respect to their positions relative to the oxygen atom. The C7–C9 atoms are not characterized specifically, as the effect of the O atom is minor on these sites.

In addition, barrier heights of the ring-opening reactions of fuel radicals were calculated. The barrier heights are defined as the energy differences between the transition state and the reactants

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