Oxidation of 2-methylfuran and 2-methylfuran/*n*-heptane blends: An experimental and modeling study

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ABSTRACT

There have been significant advances in understanding ignition behavior of oxygenated biofuels (mainly alcohols) and their blends with conventional fuel components. However, the oxidation behavior of ligno-cellulosic derived furanic compounds blended with hydrocarbons has received little attention. The present work is an experimental and numerical investigation of 2-methylfuran (2-MF) combustion and its blend with *n*-heptane. These results are compared with pure *n*-heptane results to better understand 2-MF reactivity. Ignition delay times of pure 2-MF and the 2-MF/*n*-heptane (50/50 2-MF/*n*-heptane molar %) blend in air were measured in three different facilities; a rapid compression machine and two different shock tubes. Experiments were performed in the temperature range of 861–913 K at a pressure of 20 bar for stoichiometric pure 2-MF. The ignition delay times of 2-MF/*n*-heptane blends were measured in the temperature range of 672–1207 K, at pressures of 10 and 20 bar, and at equivalence ratios of 0.5, 1.0, and 1.5. A comprehensive chemical kinetic model containing low- to high-temperature chemistry of 2-MF and *n*-heptane was formulated based on a combination of available 2-MF and *n*-heptane mechanisms and available theoretical studies on 2-MF form literature. The developed detailed kinetic model was validated against the ignition delay data measured in this work as well as against high-temperature shock tube ignition delay, flame speed, and flame species data from literature to ensure the competence of the model. The proposed mechanism predicts the measured and literature data to a reasonable extent. To elucidate fuel specific oxidation pathways, reaction path analyses were performed at various conditions. Furthermore, sensitivity analyses on the ignition delay times were conducted and the dominant reaction pathways in the oxidation of pure and binary mixtures at high, intermediate, and low temperatures were identified. It is found that the competition between *n*-heptane and 2-MF for ȮH radicals inhibits the consumption of *n*-heptane and promotes the consumption of 2-MF. This work provides the first insight into the global low-temperature oxidation behavior of a second generation furanic blended with a hydrocarbon.

1. Introduction

Hazardous effects of pollutant emissions from burning petro-diesel fuels have paved the way for development of cleaner combustion in engines. One probable way to address the challenge of emissions, is to blend oxygenated fuels with conventional fuel surrogates. Mixing of oxygenated fuels with hydrocarbons helps in reducing soot formation [1]. Among the available oxygenates, ethanol is widely used as an additive for gasoline and diesel fuels [2–7] and characterized as the most suitable additive for spark-ignition (SI) engines. However, the ethanol blending with conventional fuels also increases the formation of other toxic pollutants like formaldehyde and acetaldehyde [8,9]. Other drawbacks associated with the use of ethanol are its lower vapor pressure and miscibility in water [10]. Compared to ethanol, 2-methylfuran (2-MF) has been identified as a new potential lignocellulosic-derived biofuel [11]. Sudholt et al. [12] measured derived cetane numbers (DCNs) of several furanics and tetrahydrofuranics in an

ignition quality tester. Based on its very low DCN of 8.9, compared to *n*-heptane with a DCN of 53.8, 2-MF was proposed as a promising SI engine fuel. Combustion characteristics of 2-MF have been throughly investigated in SI engines [11,13–15]. These studies [11,13–15] reveal that 2-MF offers significant advantages over gasoline and ethanol such as a higher energy density, a higher research octane number (RON), and lower hydrocarbon emissions. Although formaldehyde was found to be a major intermediate of combustion of 2-MF, its emission is much lower from 2-MF than that from ethanol and gasoline. 2-MF is derived from waste cellulose [16], has lower boiling point, and higher vapor pressure than that of ethanol [10]. 2-MF is negligibly soluble in water unlike ethanol, and hence is not contaminated by absorbing water from the atmosphere.

Ever since lignocellulosic biofuel production came into the picture, many experimental and numerical studies of 2-MF and other alkylated furans have been performed [17–43]. Somers et al. [17] measured the laminar burning velocities (LBVs) of 2-MF/air mixtures as a function of equivalence ratio (Φ). The measurements were carried out at atmospheric pressure and in the temperature range of 298–398 K. LBVs were found to be controlled by the reaction of hydrogen with molecular oxygen at fuel rich conditions. On the other hand, under fuel lean conditions, oxidation of CO by $\dot{O}H$ radical to produce CO_2 and $\dot{H}$ radical was found equally important. In the same work, the ignition delay time measurements of 2-MF/O_2/Ar mixtures were performed in a shock tube at equivalence ratios of 0.5, 1.0, and 2.0, in the temperature range of 1200–1800 K, and at atmospheric pressure. H-abstraction from the side methyl group by $\dot{H}$ was found to be the most important pathway in this temperature regime. Further, Ma et al. [25,26] investigated low-pressure LBVs of 2-MF and 2-MF/iso-octane blends in a constant volume vessel with the help of high-speed schlieren photography at various temperatures and equivalence ratios. The LBVs of the blends were found to be somewhere in between those of pure 2-MF and pure iso-octane. The blended fuel flames were found to be less stable than iso-octane flames, but more stable than 2-MF flames at equivalence ratios lower than 1.0 at all tested temperatures.

Continuing the series of experimental measurements, Wei et al. [18], Uygun et al. [19], Eldeeb and Akih-Kumgeh [20], and Xu et al. [21], measured ignition delay times of 2-MF behind reflected shock waves at Φ ranging from 0.25 to 2.0, in the pressure range of 1.2–40 bar, and the temperature range of 800–2010 K, with oxygen concentrations up to 20 %. The measured data was simulated using the high-temperature 2-MF model of Somers et al. [17]. The results demonstrate the pressure and dilution ratio dependence of measured 2-MF ignition delay times, which decreases with increasing pressure and decreasing dilution ratio. Concerning intermediate-temperature ignition delay measurements, Sudholt et al. [22] and Xu et al. [23] reported 2-MF experimental data in rapid compression machines at a temperature range of 824–1030 K. Sudholt et al. [22] compared the RCM ignition delays of 2-MF with furan, 2-ethylfuran, and 2-butylfuran. The reactivity of alkylated furans was found to increase with increasing side chain length. Xu et al. [23] compared the RCM ignition delays of 2-MF with those of 2,5-dimethylfuran (2,5-DMF) and reported a comparable reactivity of 2-MF and 2,5-DMF under the studied conditions. A cross-over temperature was observed, below which 2,5-DMF reactivity was shown to be slightly higher and vice versa.

Furthermore, Tran et al. [24], in their series of works on furanics addressed the combustion of 2-MF in a premixed low-pressure flame for stoichiometric and fuel rich mixtures. Mole fractions of a large number of reactants, products, and intermediates were identified and quantified in combination with electron-ionization molecular-beam mass spectrometry (EI-MBMS) and gas chromatography (GC) at pressures of 20 and 40 mbar. In addition to the experimental work, a chemical kinetic mechanism of 2-MF was developed and validated [24]. Under measured conditions, ipso-addition yielding furan and H-addition to the side chain carbon were identified as the main consumption pathways of 2-MF. Later, Cheng et al. [27] also reported the species profile measurements of 2-MF/O_2/Ar mixtures in a laminar flat flame burner. Recently, Alexandrino et al. [44] and Tran et al. [45] measured species profiles of 2-MF in a plug flow and a laminar flow reactor, respectively. A chemical kinetic model of 2-MF was also developed in the work of Tran et al. [45], based on theoretically calculated rate parameters of several reactions. High concentrations of several toxic species, such as formaldehyde, acrolein, methyl vinyl ketone, furfural, and phenol, were detected and experimental observations were backed with numerical simulations.

From a chemical kinetic perspective, several studies were performed to understand the pyrolysis behavior of 2-MF. Grela et al. [28] and Lifshitz et al. [29–31] studied the decomposition of 2-MF experimentally in a heated flow reactor and in a single pulse shock tube, respectively. Later, Liu et al. [32,33] and Sendt et al. [34] studied the pyrolysis of 2-MF theoretically with the help of ab-initio quantum chemical methods. Several ab-initio calculations [34–36] were also performed to calculate formation enthalpies, bond dissociation energies (BDEs), and rate parameters for a range of unimolecular decomposition reactions, confirming the presence of considerably weak C–H bonds on the alkyl side-chain. The presence of weak C–H bonds in 2-MF and 2,5-DMF offers an important site for abstraction by free radicals and are a key source of reactive hydrogen atoms. In the theoretical study of Somers et al. [37], the rate parameters and thermodynamic parameters of high-temperature specific reactions like β-scission, unimolecular decomposition, and H-abstraction by $\dot{H}$ and $\dot{C}H_3$ were presented. Concerning low-temperature oxidation, Davis and Sarathy [46], in their computational work on 2-MF, gave insight on the low-temperature alkene specific reaction pathways like Waddington elimination and Waddington concerted elimination reactions.

Despite extensive development at high to moderate temperatures [17–37], the chemical kinetics of 2-MF oxidation at lower combustion temperatures are not well known. There remains a need to characterize the combustion behavior of 2-MF at low temperatures because phenomena such as knock in SI engines and ignition in compression ignition (CI) engines are influenced by low-temperature reactions. 2-MF is a stable furanic compound, and that limits its reactivity at low temperatures, but practical engine applications would blend 2-MF with a hydrocarbon base fuel. The presence of more reactive species (*n*-alkanes) in blends could initiate the oxidation of 2-MF at low temperatures. A similar approach was used by Zhang et al. [47] to study the low-temperature oxidation of toluene by blending it with dimethyl ether.

With this motivation, the present work focuses on both experimental and numerical results for 2-MF and 2-MF/*n*-heptane mixtures at various conditions. As per the author's knowledge, this is the first work providing insight into the low-temperature combustion behavior of 2-MF blended with hydrocarbons. Briefly, the sections of this paper include the following. Section 2 represents the experimental facilities used to measure the ignition delay times, followed by the development of the detailed kinetic model in Section 3. The sections thereafter, include a comprehensive assessment of the model performance against measured experimental data as well as literature data. Then, a comparison of ignition characteristics of pure 2-MF with blended mixtures of 2-MF/*n*-heptane and pure *n*-heptane is presented, followed by a detailed chemical kinetic analysis of 2-MF and the 2-MF/*n*-heptane blend oxidation.