

Insights into Oxidation Behavior of Potential Gasoline Additives: 2-Methylfuran and 2-Methyltetrahydrofuran

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Abstract

Ignition behavior of an unsaturated cyclic ether, 2-methylfuran (2-MF) and its blend with *n*-heptane (50/50 molar %) have been investigated in the present work. Two different experimental facilities shock tube and rapid compression machine were employed to measure the ignition delays for stoichiometric 2-MF/air and 2-MF/*n*-heptane/air mixtures at pressures of 10 and 20 bar, and temperatures between 650 K to 1200 K. A detailed chemical kinetic model including relevant high- and low-temperature oxidation chemistry for these fuels were formulated and utilized to back the experimental findings. A comparison of the ignition behavior of 2-MF with its saturated counterpart, 2-Methyltetrahydrofuran (2-MTHF) is further presented, and the impacts of unsaturation in the cyclic ether ring on fuel ignition characteristics are analyzed.

Introduction

Due to their superior physico-chemical properties [1] and possible production pathways from ligno-cellulosic biomass [2], various furans are identified as potential additives for spark-ignition (SI) engines. 2-MF is one of such candidates, which can be blended with gasoline without the risk of current engine design alterations [3]. The gasoline/2-MF blend offers several advantages such as reduction in hydrocarbon (HC) and carbon monoxide (CO) emissions [3] and high knock resistance [4]. A strong interest in this mono-alkylated unsaturated cyclic ether (2-MF) as a gasoline additive has resulted in many combustion studies [5-10]. These studies involve measurement of its various combustion properties in a variety of reactors [5-8]. Also, its combustion behavior has been investigated theoretically with the help of detailed chemical kinetic models [7-9] and quantum mechanical calculations [10].

Despite extensive research on its combustion behavior [5-10], 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 oxidation reactions. 2-MF is a stable unsaturated 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.

With this motivation, the main objective of this study is to investigate the ignition behavior of pure 2-MF as well as its blend with *n*-heptane, both experimentally and numerically. In order to shed light on the effect of saturated and unsaturated cyclic ether rings on the ignition delay time, the ignition behavior of 2-MF is compared with its saturated counterpart, 2-methyltetrahydrofuran (2-MTHF), with the help of the present study and literature sources.

Kinetic model development

The proposed chemical kinetic model, consisting of 883 species and 7872 reactions (forward and backward counted separately), was built hierarchically upon the C₀-C₄ base model of Blanquart et al. [11]. A sub-model of *n*-heptane, along with the C₅ and C₆ chemistry, was taken from the most recent optimized *n*-dodecane model of Cai et al. [12]. Regarding 2-MF specific reactions, a high-temperature specific sub-model was adopted from the 2,5-dimethylfuran (2,5-DMF) mechanism of Somers et al. [13]. The rate constants for several high-temperature specific reactions were revised based on the theoretical study of Somers et al. [9] and Tran et al. [8]. Additionally, a low-temperature specific sub-model of 2-MF was developed as a part of this research work and combined with the base mechanism. The main reaction pathways considered in the low-temperature specific 2-MF sub-model are as follows:

- A set of co-oxidation reactions between intermediate species formed in the oxidation of 2-MF and the species of *n*-heptane were included in the current model. The rate coefficients of these co-oxidation reactions were estimated on the basis of co-oxidation reactions of toluene and *n*-Heptane, explained in the work of Andrae et al. [14].
- Through his theoretical calculations, Davis et al. [10] revealed that the formed adduct, after addition of OH to 2-MF, can further decompose via hydrogen migration (HM), concerted elimination (CE), Waddington elimination (WE), and Waddington concerted elimination (WCE) reactions. In order to investigate the nature of radical addition to 2-MF all the proposed pathways of 2-MF/OH adducts, dominantly formed at α sites of the 2-MF ring were taken into account.

- In order to assess the importance of low-temperature specific chemistry, reaction of predominantly formed 2-MF radical with O_2 was incorporated. Rate parameters for this reaction were adopted from the quantum calculation work of Tran et al. [8].

Experimental results and model validation

Figures 1a and 1b present the experimental results obtained in rapid compression machine (RCM) and shock tubes (STs) for pure 2-MF and the 2-MF/*n*-heptane blend, respectively. Note that a detailed description of the RCM used for the low-temperature measurements, has been described in detail previously [15]. In order to assess the facility-to-facility variation in the shock tube (ST) experimental data, ST measurements were carried out at the same conditions in two different facilities, PCFC RWTH Aachen ST facility and SWL RWTH Aachen ST facility. A detailed description on design features of both STs has been provided in previous studies [16-17].

Fig. 1a presents numerically computed ignition delays compared to the newly measured ignition delay results of stoichiometric 2-MF/oxidizer/diluent mixtures at $P = 20$ bar, the ST ignition delays measured by Uygun et al. [6] at $P = 40$ bar, and those measured by Sudholt et al. [5] at a pressure of 20 bar in an RCM. Numerical simulations at constant volume are shown as line plots, while simulations including ST and RCM facility effects are represented by dotted lines. The newly measured RCM data set matches well with the data set of Sudholt et al. [5]. The predicted ignition delays compare well with the experimental values with the exception of those below 890 K (1.12 1/K). Both ST and RCM data sets are over predicted by the model at lower temperature regimes.

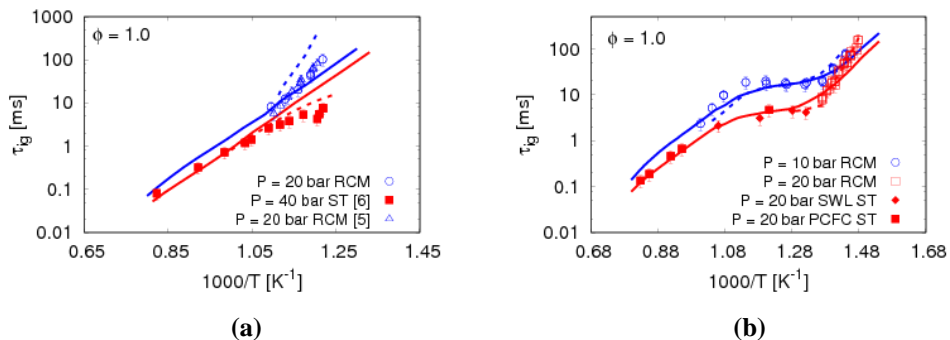


Figure 1. Ignition delay times in RCM and in ST. Figure (a) pure 2-MF;
(b) 2-MF/*n*-heptane blend.

Figure 1b shows the measured and the calculated ignition delays of 2-MF/*n*-heptane blends at pressures of 10 bar and 20 bar. It should be noted that due to non-ideal bursting of diaphragms in ST, a pressure rise was observed for longer ignition

delay times. This rate of pressure change (dp/dt) is different for both ST facilities, 5 %/ms and 8 %/ms for SWL and PCFC, respectively. It can be seen from Fig. 1b that experimental measurements from both the facilities agree very well; furthermore, SWL ST measurements are at lower temperatures, hence longer ignition delays, in comparison to the PCFC ST measurements. Since the pressure rise mainly occurs for longer ignition delays, numerical simulations for ST data were performed using the observed dp/dt of 5 % in SWL ST. The model accurately predicts the ST and the RCM ignition delay data at the pressure of 20 bar. However, data points obtained in the RCM at the pressure of 10 bar are under-predicted in the temperature range of 833 - 926 K (1.20 – 1.08 1/K). Unlike pure 2-MF, the blend of 2-MF/*n*-heptane exhibits a negative temperature coefficient (NTC), which is reproduced by the model as well.

Comparison with saturated mono-alkyl furan, 2-methyltetrahydrofuran

In order to see the effect of saturated and unsaturated cyclic ether ring on ignition delay time, ignition delays of 2-MF are compared with those of 2-MTHF [18-19] in Fig. 2. 2-MTHF is saturated counterpart of 2-MF and has only one structural difference that is the absence of double bonds in the cyclic ring. Yet, a higher reactivity of 2-MTHF compared with 2-MF is evident from Fig. 2. The ignition delay times of 2-MF and 2-MTHF are consistent with their cetane numbers, calculated by Sudholt et al. [1], which are representative of temperatures of 788 to 841 K at a pressure of 21.1 bar [20]. The reported cetane number of 2-MF (8.9) is much less than that of 2-MTHF (22.0), and hence its reactivity is lower at these conditions.

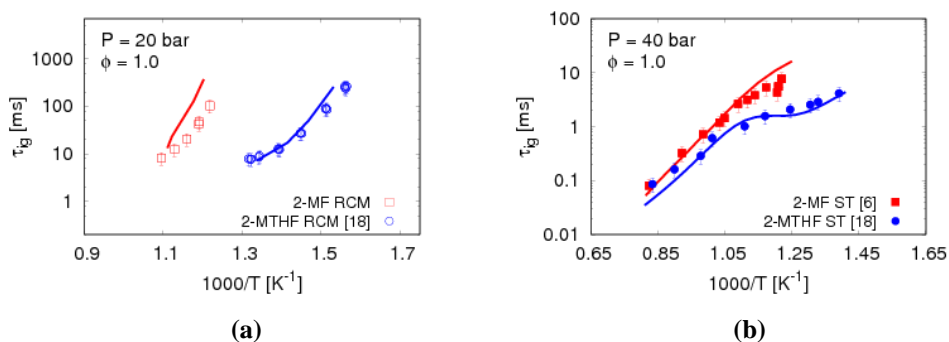


Figure 2. Comparison between 2-MF and 2-MTHF ignition delays. Figure (a) in RCM at 20 bar; (b) in ST at 40 bar.

In order to assess the impact of the fuel's molecular structure on the reactivity, a comparative reaction path analysis of 2-MF and 2-MTHF was performed (Fig. 3). It can be seen from Fig. 3 that due to presence of a stable unsaturated ring in 2-MF, H-abstraction from the ring carbons are restricted, and methyl side chain is the

main site for the abstraction reactions. Also, a large amount of the 2-MF is decomposed by its addition reactions with OH radical. Comparatively, in 2-MTHF, abstraction mainly takes place at α -ring carbon sites. The resulting fuel radical in 2-MF further reacts with HO₂ and leads to the formation of one OH radical. However, 2-MTHF fuel radicals either undergo β -scission reaction or O₂ addition reaction. 2-MTHF and O₂ adducts mainly lead to low temperature degenerate branching pathways, which results in its higher reactivity.

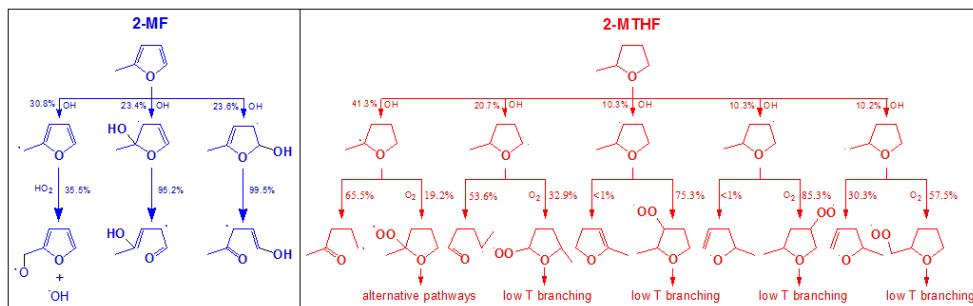


Figure 3. Comparison between main reaction pathways of 2-MF with those of 2-MTHF at 20 bar, 750 K, $\phi = 1$, and at 30 % fuel consumption.

Conclusions

This work presents a chemical kinetic investigation on the oxidation of 2-MF and its blend with *n*-heptane. A detailed chemical kinetic model was developed based on the literature understanding of furan chemistry. Low- to high-temperature ignition delay measurements were performed in RCM and STs. Overall a satisfactory agreement between experiments and numerical simulations has been observed. In comparison to 2-MTHF, the unsaturated ring structure in 2-MF results in inhibited fuel reactivity, hence longer ignition delay times.

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