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Ignition delay times of low alkylfurans at high pressures using a rapid compression machine

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Abstract

Auto-ignition behavior of 2-ethylfuran (EF) was investigated in the low to intermediate temperature range (766–1013 K) over equivalence ratios of 0.5, 1.0, and 2.0 at 16 and 30 bar using a rapid compression machine. Equivalence ratio was varied by changing the mole fractions of O_2 while fixing the fuel fraction. The fuel did not show "negative temperature coefficient (NTC)" or two stage ignition behavior in the present measuring range. Simulations were conducted on the basis of the alkylfuran mechanism of Somers et al. (2013) [1], in which the EF sub-mechanism is not fully developed. Optimization of the EF sub-mechanism was attempted. Results show that the modified mechanism shows better agreement with our measurements and other data in the literature. Comparison of the reactivity of EF with that of 2-methyl furan (MF) and 2, 5-dimethyl furan (DMF) under various equivalence ratios was conducted and results show that the relative reactivity of the three furanic fuels depends complicatedly on both equivalence ratio and temperature, which was further interpreted by examining the ignition kinetics. As DMF is more branched, H-abstractions contribute most to the fuel consumption. For EF and MF, OH-additions at C2 and C5 positions dominate the reaction pathways. From reaction flux analyses, the reactions involving alkyl side chains of alkylfurans are analogous with those of alkylbenzenes at low to intermediate temperature oxidation conditions. Moreover, large amount of alkylfurans go through OH-addition reactions on the ring, which is not observed in the reaction pathways of alkylbenzenes.

Keywords: Ignition delay times; Ethylfuran; Low temperature; Alkylfurans

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1. Introduction

Alkylfurans have recently received increasing attention from the combustion field, since they can be produced in large quantities from lignocellulosic biomass [2,3]. DMF (2, 5-dimethylfuran) and

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MF (2-methylfuran) possess similar energy densities and research octane numbers with commercial gasoline [4]. The application potential of alkylfurans in internal combustion engines has been evaluated. Sudholt et al. [5] reported the DCNs (derived cetane numbers) of alkylfurans: DMF (10.9) > EF (10.2) > MF (8.9). Daniel et al. [6] investigated the influence of operating parameters on the combustion and emissions of DMF. When applied in spark-ignition engines, DMF [7] and MF [8] possess similar indicated specific fuel consumption and indicated efficiency with gasoline, and the emissions are lower except for NOx. For compression–ignition engines, the addition of DMF could effectively prolong ignition delay times, resulting in higher NOx emissions [9]. Homogeneous charge compression ignition (HCCI) combustion is a combustion concept realizing compression-engine like high thermal efficiency without abundant NOx or soot emissions [10]. As there is no direct control strategy for the beginning of auto-ignition, fuel modification altering the auto-ignition chemistry of the fuel mixture thus effectively influences the combustion phase [11]. Research toward fundamental combustion characteristics of low alkylfurans facilitates their HCCI application.

Experimentally, species profiles of DMF, MF, and furan have been measured to reflect their laminar premixed flame structures and interpret the influence of possessing different numbers of methyl side-chains [12–14]. Comparisons among laminar flame speeds of DMF [15], MF [16], iso-octane, and ethanol has been conducted. Tian et al. [17] concluded that the deviation between the laminar burning velocities of DMF and iso-octane is within 10% at the equivalence ratios of 0.9–1.1.

High temperature ignition delay times of DMF have been measured by Somers et al. [1] and Sirjean et al. [18]. Two kinetic models have been developed respectively, yielding reasonable agreement with their shock tube data. With respect to MF, Somers et al. [19] measured the ignition delay times and constructed a kinetic model. Thereafter, Wei et al. [20] extended the ignition delay times for MF to a wider pressure range and modified the mechanism of Somers et al. [19]. In addition to DMF and MF, EF is another alkylfuran of combustion research interest, possessing a side chain C–C bond. Moreover, the weaker allylic C–H bond and side chain C–C bond would results in easier H-abstractions at allylic sites or bond scission at the side chain C–C bond, contributing to its reactivity. Eldeeb and Akih-Kumgeh [21,22] conducted systematic investigation toward high temperature combustion kinetics of low alkylfurans in “air” conditions. From their comparison, DMF is the least reactive, while MF is the most reactive. Furthermore, EF ignites easier than DMF, and they contribute the higher reactivity to the ethyl radicals and more favorable sites for abstraction and decomposition reactions. Xu et al. [23] has compared the ignition delay times of DMF, MF, and furan under a constant fuel load, indicating that substituted furans possess higher reactivity.

However, research toward low to intermediate temperature ignition of low alkylfurans has not been sufficiently explored. This study firstly aims to provide the ignition delay times of EF at low to intermediate temperatures and high pressures over various equivalence ratios. Moreover, previous stoichiometric MF ignition data [24] has been complemented with different equivalence ratios. In addition, investigation on the effects of different methyl side chain numbers, alkyl side chain lengths, and isomers was conducted by comparing the ignition behaviors of EF, MF, and DMF. Finally, the sub-mechanism of EF in Somers et al. [1] was updated and validated against the measured ignition delay times and other literature data. Kinetic analyses based on the updated mechanism were applied to interpret the relative reactivity of the three furanic fuels.

2. Methodology

The ignition delay times of low alkylfurans were measured using the RCM at Tsinghua University, see details in Di et al. [25]. The RCM comprises five components: the high pressure air tank, the drive section, the driven section, the test section, and the hydraulic section. A creviced piston is employed to ensure the homogeneous temperature distribution in the test section. The length of the test section is variable to study different compression ratios. The gas mixture is prepared in a stainless steel tank according to their partial pressures. The partial pressures of MF and EF were kept below 0.0025 bar to avoid fuel condensation [26,27]. Composition of gas mixtures are tabulated in Table S1.

The effective pressure and temperature were adopted to define experimental conditions. The effective pressure is defined as the integral average of the end-of-compression pressure and the lowest pressure due to heat loss before ignition.

$$\mathrm{P_{eff}} = \frac{1}{(t_{P_{\min}} - t_{P_{\max}})} \int_{t_{P_{\max}}}^{t_{P_{\min}}} \mathrm{P\,dt} \tag{1}$$

The effective temperature is calculated thusly using isentropic compression integral:

$$\int_{\mathrm{T_0}}^{\mathrm{T_{eff}}} \frac{\gamma}{\gamma - 1} \mathrm{d}\ln T = \ln\left(\frac{P_{\mathrm{eff}}}{P_0}\right) \tag{2}$$

where T_0 is the initial temperature, P_0 is the initial pressure, γ is the specific heat ratio of the gas mixture. The experimental ignition delay times were deduced from pressure traces and defined as the time interval between end-of-compression and the steepest pressure rise, as shown in Fig. 1.

Simulation was conducted using the SENKIN code of the ChemkinIIsoftware, the maximum