Experimental study of 2,5-dimethylfuran and 2-methylfuran in a rapid compression machine: Comparison of the ignition delay times and reactivity at low to intermediate temperature

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ABSTRACT

In this work, low to intermediate temperature autoignition behaviors of DMF (2,5-dimethylfuran) were investigated at pressures of 16 and 30 bar, temperatures from 737 to 1143 K, and equivalence ratios of 0.5, 0.75, 1.0, and 2.0 for different fuel concentrations using a rapid compression machine. Ignition delay times of 1% MF (2-methylfuran) stoichiometric mixture was measured at 16 and 30 bar in order to compare its combustion chemistry with DMF. Two mechanisms were employed to predict experimental ignition data. The mechanism of Somers et al. (2013, 2014) shows reasonable agreement with experimental results when some modifications are incorporated. Both experiments and numerical simulations show that the reactivity of DMF and MF is similar in the low to intermediate temperature range. However, the ignition delay time of MF is slightly more sensitive to temperature, compared to DMF, and a crossover temperature T_{c2} was observed, below which DMF preserves a slightly higher reactivity. Kinetic analysis by examining the reaction flux and the sensitivity coefficients at temperatures close to T_{c2} were conducted to interpret the dominant reaction kinetics of the ignition delay times of DMF and MF. Finally, comparisons between the ignition delay times of DMF and PRF (primary reference fuel) components (*iso*-octane, toluene, and *n*-heptane) was also conducted due to the interests of its practical applications, based on PRF ignition data in literature.

1. Introduction

Depletion of fossil fuels and air pollution caused by fossil fuels combustion raise more public concerns over the application of alternative fuels to replace gasoline. DMF (2,5-dimethylfuran), which have been reported recently to be produced from non-food biomass [1–5] is one of the most promising alternative fuel candidates. Similar to DMF, MF (2-methylfuran) is also a second generation biofuel that can be produced from lignocellulosic biomass [6, 7]. In addition, the energy density and RON (Research Octane Number) of DMF and MF are close to those of commercial gasoline, which renders its application in internal combustion engines more attractive, either by SI (spark ignition) or CI (compression ignition) engines.

Studies on performance and emissions of DMF fueled SI engines have been extensively reported. Zhong et al. [8] compared the combustion characteristics of DMF, gasoline, and ethanol in a single cylinder SI engine. Daniel et al. [9–11] studied the effect of operating parameters on the SI engine performance of DMF, gasoline, and ethanol. Studies on MF fueled spark ignition engine performance have been conducted by Wang et al. [12] recently. Their results indicate that the combustion performance of DMF and MF is similar with that of gasoline, and better emissions are observed except for NOx. For CI engines, Zhang et al. [13] and Chen et al. [14] compared the performance of DMF/diesel blend and gasoline/diesel blend. Their results show that the addition of DMF prolongs ignition delay times and results in higher NOx emissions, and the engine need to be run on a higher EGR (exhaust gas recirculation) ratio.

The above practical engine investigations have demonstrated the flexibility of DMF and MF in conventional engines. HCCI (homogeneous charge compression ignition) mode maintains the merits of high combustion efficiency and low NOx and PM emissions

Table 1
Alkylfuran ignition delay time studies in literature using shock tubes.

Fuel	Mixture	ϕ	P (bar)	T (K)	Ref.
DMF	Diluted	0.25–1.0	1 and 4	1300–1831	[26]
DMF	Diluted	0.5–2.0	1	1350–1800	[28]
DMF	Diluted	1.0	20 and 80	820–1210	[28]
MF	Diluted	0.5–2.0	1	1200 1800	[27]
MF	Diluted	0.25–2.0	1.25–10.65	1120–1700	[32]
DMF and MF	In air	0.5–2.0	2–12	977–1570	[29]
MF	In air	1.0	40	780–1100	[33]
DMF and DMF/ *iso*-octane	In air	0.5–2.0	5–12	1009–1392	[30]

Table 2
Test mixture composition.

Fuel	ϕ	Fuel concentration	P (bar)
DMF	0.5, 0.75, 1.0, 2.0	1%	16 and 30
	1.0	0.5% and 2.0%	16
MF	1.0	1%	16 and 30

[15–17]. The understanding of the chemical kinetics of alkylfurans would help meet economic and emission legislations in the future and facilitate their application in HCCI combustion as there is no extra method to control auto-ignition.

Extensive fundamental studies emphasizing on the chemical kinetics of alkylfurans have been conducted, and we only give a brief review on related works. A consecutive low pressure flame studies on laminar premixed DMF, MF, and furan/O_2/Ar mixtures have been conducted by Liu et al. [18], Togbé et al. [19], and Tran et al. [20]. Relevant kinetic mechanism was constructed, and the effects of methyl branches on the flame structures were then interpreted. Wu et al. [21–24] conducted systematic study on the laminar flame propagation characteristics of DMF/air mixtures using a constant volume combustion chamber. Tian et al. [25] concluded that the difference of DMF and gasoline laminar burning velocities is within 10% when equivalence ratio falls in 0.9–1.1. With regard to ignition delay times. The low pressure ignition delay times of DMF were measured by Sirjean et al. [26] and used to validate their newly constructed DMF mechanism. Somers et al. [27] measured atmospheric ignition delay times of MF, and the ignition delay times of DMF at atmospheric pressure and high pressures (20 and 80 bar) were also provided [28]. A kinetic mechanism has been constructed and validated against species profiles, laminar flame speeds, and ignition delay times, which shows fairly good agreements. Air diluted ignition delay times of alkylfurans have been measured by Eldeeb et al. [29,30]. Among the three alkylfurans, MF shows a higher reactivity than DMF, and the reactivity of furan is the lowest. Moreover, DMF is relatively unreactive compared with *iso*-octane under their circumstances, and the newly combined mechanism of *iso*-octane (Mehl et al. [31]) and DMF (Somers et al. [28]) could give good agreement with ignition delay times of both fuels.

Table 1 summarizes the related fundamental combustion study on DMF and MF. Compared with the high temperature kinetics study of DMF, the low to intermediate temperature research towards DMF auto-ignition characteristics is relatively insufficiently explored, in terms of experimental data and kinetic modeling, while the low to intermediate is temperature range ignition kinetics is more relevant with compression ignition in engines. Thus our first objective is to extend previous ignition delay time study of DMF and MF to a wider range of equivalence ratios, pressures, and fuel concentrations. The new experimental data were compared with model predictions, and modifications were made to improve model performance in the low to intermediate temperature range. In addition, the structural difference between DMF and MF makes us to investigate the effect of side chain numbers. The reactivity of DMF and MF is compared in the low to intermediate temperature range. Kinetic analysis was further conducted to interpret the key reaction pathways and dominant reactions. Furthermore, to elucidate the potential engine applications of the fuel, comparison between DMF, PRF (primary reference fuel) components, and biofuels (*n*-butanol and DME (dimethyl ether)) was carried out based on literature data.

2. Experimental specifications

2.1. Setup and procedures

Ignition delay times of DMF and MF were measured using the rapid compression machine of Tsinghua University (TU-RCM). The TU-RCM consists of five components: the high pressure air tank, the drive section, the hydraulic section, the driven section, and the test section, see details in Refs. [34,35]. The length-variable text section permits convenient change of the compression ratio. The test section is equipped with pressure transducer (KISLER6125C) together with a charge amplifier (KISLER 5018A). A creviced piston is employed to ensure a quasi-homogeneous temperature distribution after compression.

The mixture is prepared in a stainless steel tank according to the partial pressure of each component. The purities of DMF and MF are 99% and 98%, respectively. A relative manometer (DPG400 omega) with an accuracy of 10^{-5} MPa was used to measure the partial pressure of the fuel. The vapor pressure of DMF is 7.07 kPa at 295.3 K [36] and that of MF is 18.9 kPa at 293 K [37]. It is noted that the partial pressure of each fuel is assured to be less than 1/3 of its saturated pressure so as to avoid condensation effect. Ar and N_2 were selected as dilution gas. At least one hour is waited to achieve homogeneous mixing after charging the mixing tank. Since DMF is not very reactive at low temperatures, the lowest ignition temperature was carefully examined for different equivalence ratios and fuel concentrations at 16 bar. The lowest ignition temperature is achieved at the lowest compression ratio, and the Ar/N_2 ratio is then determined. Besides, the highest temperature of present study is limited by the shortest ignition delay times can be validly extracted from the pressure trace. For a certain mixture composition, the end-of-compression gas temperature and pressure are varied by varying the length of the test section and thus the compression ratio. Experiments were conducted at least 3 min after finishing charging the reaction chamber, letting the mixtures to reach the equilibrium state. The corresponding unreactive mixture experiments were conducted by replace O_2 with the same mole fraction of N_2 to obtain volume-time profiles. The test mixture composition is shown in Table 2.

2.2. Definition of ignition delay times and test conditions

Figure 1 shows a typical pressure histories for the ignition of DMF/O_2/N_2/Ar mixture (solid line) and the corresponding unreactive mixtures (dash line) where O_2 were replace with N_2. It is seen that the test section pressure increases sharply when the piston approaches the top dead center and it reaches a maximum ($P_{max} = 29.81$ bar) at the end of compression stroke. Then the piston is locked at the top dad center, while the test section pressure slightly decreases. This is caused by the heat loss to the test section walls. Thus using the peak top dead center pressure P_{max} and T_{max} is not a reasonable way to demonstrate the test condition. Here the effective pressure P_{eff} and temperature T_{eff}, as adopted by Walton et al. [38] is used, as calculated in Eqs. (1) and (2). The mixture ignite at $\tau_{ing} = 166.3$ ms, as manifested by the steep increase in the pressure history. The effective pressure is obtained from the experimental pressure trace and is the integral average