

Ignition Characteristics of 2,5-Dimethylfuran Compared with Gasoline and Ethanol

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ABSTRACT

2,5-dimethylfuran (DMF) and 2-methylfuran (MF) have attracted attention as new biofuels. To utilize furans as alternative fuels, fundamental studies on the combustion characteristics are required. In this study, the ignition delay times of DMF were measured using a rapid compression machine and compared with those of gasoline and ethanol. To investigate the effect of the addition of DMF to gasoline, the ignition delay times of DMF-gasoline surrogate fuel blends were also measured. The ignition delay times of DMF were longer than those of gasoline and shorter than those of ethanol. The simulation results using the DMF kinetic model were in reasonable agreement with those of the experiments.

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INTRODUCTION

Recently, furan and its derivatives, such as 2,5-dimethylfuran (DMF) and 2-methylfuran (MF), have been produced from non-food biomass using a catalytic strategy [1], which reduces the threat to food supply or biodiversity [2]. These fuels also provide certain advantages over ethanol, a major globally used biofuel, in terms of their physical and chemical properties, as shown in Table 1 [3, 4, 5]. The volumetric heating values of DMF and MF are similar to that of gasoline and 40% higher than that of ethanol. The research octane numbers (RON) of DMF and MF are higher than that of gasoline and lower than that of ethanol. Also, DMF and MF have lower aqueous solubilities; this character allows for easy fuel handling.

Engine experiments using direct-injection spark-ignition engines have indicated that DMF and MF are suitable gasoline alternatives because they have better or similar thermal efficiency and emission characteristics than gasoline [6, 7, 8, 9]. However, more studies on their fundamental combustion characteristics are required for adopting furan derivatives as fuels for spark ignition engines. Additionally, an evaluation of the effect of blending DMF and MF with gasolines is required because biofuel-gasoline-blended fuels are practically used.

Recently, the fundamental combustion characteristics of furans, such as the ignition delay time, laminar burning velocity, and intermediate species concentration were measured and their oxidation and soot formation mechanisms were investigated. Somers et al. measured the ignition delay times of DMF and constructed a chemical kinetic model in the wide temperature and pressure range using a shock tube [10]; they also studied the oxidation mechanism of MF [11] using the shock tube and a flat flame burner. The burning velocities of MF and DMF were measured using a spherical flame at atmospheric pressure [12,

13]. The intermediate species in lean as well as rich low-pressure premixed laminar MF flames were measured using tunable synchrotron vacuum ultraviolet photoionization-coupled molecular beam mass spectrometry [14]. The Battin-Leclerc group studied the oxidation mechanism of furan, MF, and DMF through intermediate species measurement, using molecular-beam mass sampling under premixed low-pressure flame conditions [15, 16, 17]. Elementary reaction studies of DMF [18] and MF [19] pyrolysis were also performed using the shock tube; analysis of the products of DMF pyrolysis was performed by synchrotron vacuum ultraviolet photoionization mass spectrometry [20]. The decomposition pathway of DMF was studied by ab initio calculation [21, 22]. Also, the formation of particulates and poly aromatic hydrocarbons during DMF and MF combustion was investigated using a counter-flow diffusion burner [23] and low-pressure rich laminar premixed flames [24]. However, there are very few studies on the ignition characteristics of furan and furan derivatives under lower temperature ($T < 1000$ K) conditions.

Therefore, our group has focused on the intermediate-and low-temperature ignition characteristics of furans. Previously, the ignition delay times of furan [25], MF, and MF-primary reference fuel (PRF) blends [26] were measured using a rapid compression machine (RCM) and their chemical kinetic mechanisms were investigated. In this study, the ignition delay times of DMF and DMF-PRF90 (PRF90 = n-heptane : iso-octane = 10vol% : 90vol%) blends were measured using the RCM, at an equivalence ratio of 1.0 and oxygen concentration of 16.4% and compared with those of ethanol, PRF90, and Japanese commercial gasoline. The measured ignition delay times were simulated using the detailed kinetic model of DMF constructed by Somers et al. [10] as well as a detailed kinetic model of DMF-PRF blends constructed by us.

Table 1. Properties of MF, DMF, gasoline (Japanese JIS2 grade), and ethanol [3, 4, 5].

Fuel	MF	DMF	Gasoline	Ethanol
Molecular Formula	C ₅ H ₈ O	C ₆ H ₈ O	C ₂ -C ₁₄	C ₂ H ₆ O
RON	103	101	>89	111
MON	86	88	-	90
LHV [MJ/L]	28.5	33.7	34.6	21.1
Density @20 °C [mg/cm ³]	913.2	889.7	<783(15 °C)	790.9
Water Solubility	insoluble	insoluble	insoluble	highly soluble

EXPERIMENTS

Rapid Compression Machine

A RCM consisting of a driver piston, reactor piston, and driving air tank, as shown in Fig. 1, was used in this experiment. The reactor piston has a bore and stroke of 100 and 130 mm, respectively and is driven pneumatically. The compression time and compression ratio were 40 ± 2 ms and 14.1, respectively. The pressure measurement system and a gas inlet/outlet port are situated at the ends of the reaction cylinder. The reaction cylinder is covered with a heater, which is used for controlling the initial gas temperature. In this experiment, the initial gas temperature was set at 373 K. The gas mixtures were introduced into the preheated reaction cylinder from a stainless steel vessel, where the homogeneous gas mixtures were prepared, and compressed in one stroke without rebound.

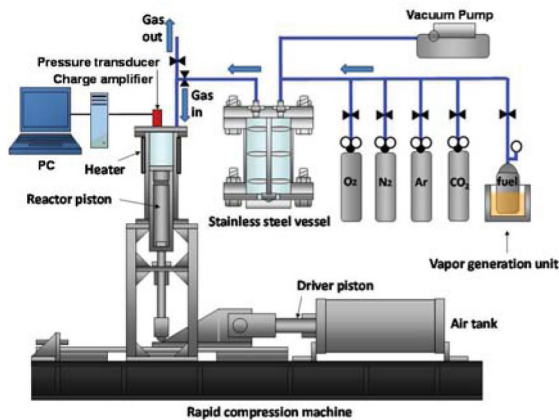


Fig. 1. Schematic diagram of the rapid compression machine with a stainless steel vessel for generating the premixed gas.

Homogeneous fuel/oxidizer gas mixtures were prepared in a stainless steel vessel using heaters and stirrers. Oxygen, nitrogen, carbon dioxide (CO₂), and argon (>99.99%, TAIYO NIPPON SANCO corporation) were used for gas mixture preparation. The gases and vaporized DMF (99%, ALDRICH) or DMF-PRF90 blends were filled manometrically in the vessel and stirred for 2 h. To avoid condensation, the vessel and flow lines for the gas mixture were heated at 373 K. For the preparation of commercial gasoline/oxidizer mixtures, gasoline was injected in the vessel using an injector situated at the top of the vessel, as shown in Fig. 2. Gasoline was injected into the vessel on a gravimetric basis [27]. The injector was controlled by the injector driver and pulse generator. The gasoline grade used was JIS2 (Japanese standard) with a RON and density (at 288 K) of 90.7 and 0.74 g/cm³, respectively.

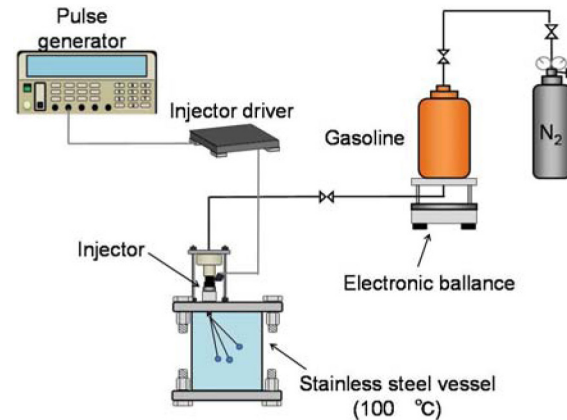


Fig. 2. Schematic diagram of the stainless steel vessel used for the preparation of commercial gasoline/oxidizer mixtures.

Test Conditions and Estimation of Compressed Temperature

Ignition delay times of DMF, DMF-PRF90 blends (DMF : PRF90 = 30vol% : 70vol%), ethanol-PRF90 blends (Ethanol : PRF90 = 30vol% : 70vol%), and commercial gasoline were measured in temperature and pressure ranges of 692-930 K and 2.14-2.76 MPa, respectively. As the initial gas temperature was set at 373 K, the compressed temperature and pressure were controlled by varying the proportion of inert gases (nitrogen, argon, and CO₂). The equivalence ratio was set at 1.0.

The compressed gas temperature (T_c) was calculated, based on the adiabatic core hypothesis, using the following equation [28].

$$\int_{T_0}^{T_c} \frac{\gamma}{\gamma - 1} \frac{dT}{T} = \ln\left(\frac{P_c}{P_0}\right) \quad (1)$$

where P_c , T_0 , and P_0 are the compressed pressure, initial temperature, and initial pressure, respectively, and γ is the ratio of specific heats. The γ of DMF was estimated using the previously reported thermodynamic parameters [10]. The γ of commercial gasoline was estimated using the thermodynamic parameters of the gasoline surrogate species and the ratio of their contents, as shown in the Simulations section.

Definition of Ignition Delay Time

The ignition delay time is defined as the time interval between the end of compression (derivative of pressure equals zero) and the occurrence of the maximum rate of pressure rise, when the single stage ignition occurred. In the case of two-stage ignition, the first and second ignition delay times are defined similarly. Typical pressure profiles of single stage ignition (DMF ignition) and two-stage ignition (commercial gasoline ignition) are shown in Fig. 3.

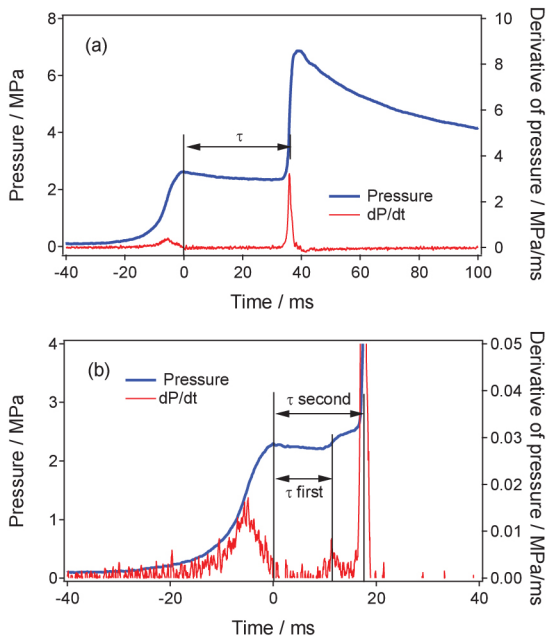


Fig. 3. Definition of ignition delay time. (a) Single stage ignition (DMF, $\phi = 1.0$, $P = 2.64$ MPa, $T = 876$ K), (b) two-stage ignition (Commercial gasoline, $\phi = 1.0$, $P = 2.29$ MPa, $T = 756$ K)

SIMULATIONS

The ignition delay times of DMF were simulated using the detailed kinetic model of DMF, consisting of 545 species and 2768 reactions, constructed by Somers et al. [10]. This model was constructed using the ignition delay times obtained, using the shock tube, in the 820–1210 K temperature range at 2 and 8 MPa, and in the 1350–1800 K temperature range at atmospheric pressure. The model also predicts the laminar burning velocity of DMF. The DMF-PRF model was constructed using the DMF and PRF models [29]. The ignition delay times of commercial gasoline were simulated using a gasoline surrogate model constructed by Hashimoto et al. [30]. The surrogate species were n-heptane, iso-octane, iso-octene, methylcyclohexane, toluene, ethanol, and ethyltertiarybutylether (ETBE). In this calculation, the contents of n-heptane, iso-octane, iso-octene, methylcyclohexane, and toluene were set to 14%, 35%, 11%, 6%, and 34%, respectively, which were determined by analyzing the contents of the commercial gasoline used in this experiment. The simulation starts from the point in time where compression ends. The compression temperature was estimated, based on the adiabatic core hypothesis [28], using the measured pressure profiles. Heat loss was also considered for reproducing the experimental pressure profiles of fuel/buffer gas mixtures under each temperature and pressure condition. The experimental pressure profile of the PRF90/ N_2 mixture at 800 K and 2.6 MPa is shown in Fig. 4. The simulated ignition

delay time is defined as the time interval between the start of calculation and the time when the rate of pressure rise is maximum. The CHEMKIN-PRO package [31] was used to perform the simulations.

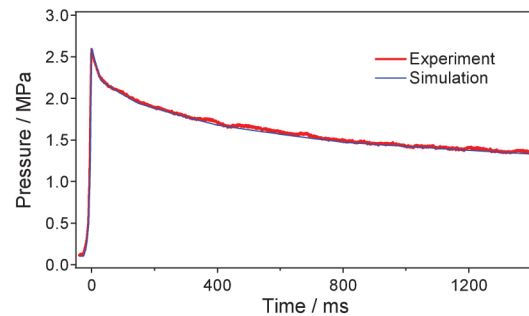


Fig. 4. Red line shows the experimental pressure profile of the PRF90/buffer gas mixture ($\phi = 1.0$, $P = 2.6$ MPa, $T = 800$ K) and blue line shows the simulated pressure profile after accounting for heat loss.

RESULTS AND DISCUSSION

Ignition Delay Times Of Dmf

Typical pressure profiles of DMF, commercial gasoline, and ethanol at 875 K and 2.7 MPa are shown in Fig. 5. Under this temperature condition, single stage ignitions are observed with no dependence on fuel species. When the ignition occurred, the pressure profiles of DMF and ethanol showed a single-stage pressure rise over the entire temperature and pressure range. These results indicate that the oxidation mechanism in DMF has no low-temperature chemistry such as RO_2 isomerization to form QOOH and O_2 addition to QOOH.

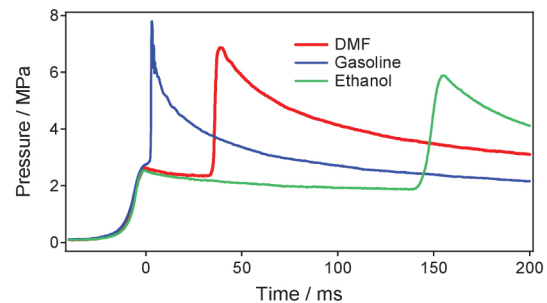


Fig. 5. Experimental pressure profiles of DMF, commercial gasoline and ethanol ($\phi = 1.0$, $P = 2.7$ MPa, $T = 875$ K).

The pressure profiles of commercial gasoline and PRF90 are shown in Fig. 6. Different characteristics are observed depending on the temperature. The pressure profiles of commercial gasoline and PRF90 show a single-stage pressure rise in the higher temperature conditions, while a two-stage pressure rise is exhibited in both profiles in the lower temperature conditions. At around 760 K, the second stage ignition delay of commercial gasoline is nearly same as that of PRF90, while the first stage ignition delay of commercial gasoline is longer than that of PRF90.