An experimental and modeling study of dimethyl ether/methanol blends autoignition at low temperature

Hongfu Wang [a,b], Ruozhou Fang [a], Bryan W. Weber [a,*], Chih-Jen Sung [a]

[a] *Department of Mechanical Engineering, University of Connecticut, Storrs, CT, USA*
[b] *School of Mechanical and Electrical Engineering, Nanchang University, Jiangxi Province, PR China*

ARTICLE INFO

ABSTRACT

New rapid compression machine (RCM) ignition delay data for dimethyl ether (DME), methanol (MeOH), and their blends are acquired at engine-relevant conditions ($T = 600$ K–890 K, $P = 15$ bar and 30 bar, and equivalence ratios of $\phi = 0.5$, 1.0, and 2.0 in synthetic dry air). The data are then used to validate a detailed DME/MeOH model in conjunction with literature RCM and shock tube data for DME and MeOH. This detailed DME/MeOH model, constructed by systematically merging literature models for the combustion of the individual fuel constituents, is capable of accurately predicting the experimental ignition delay data at a wide range of temperatures and pressures. The experiments and simulations both show a non-linear promoting effect of DME addition on MeOH autoignition. Additional analyses are performed using the merged DME/MeOH model to gain deeper insight into the binary fuel blend autoignition, especially the promoting effect of DME on MeOH. It is found that the unimolecular decomposition of HO_2CH_2OCHO plays an essential role in low temperature DME/MeOH blend autoignition. The accumulation of HO_2CH_2OCHO before the first-stage ignition and later quick consumption not only triggers the first-stage ignition, but also causes the non-linear promoting effect by accumulating to higher levels at higher DME blending ratios. These analyses suggest the rate parameters of HO_2CH_2OCHO unimolecular decomposition are critical to accurately predict the first-stage and overall ignition delay times as well as the first-stage heat release profile for low temperature DME/MeOH oxidation.

© 2018 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

The environmental impact of combustion as well as the future fossil fuel supply issue has spurred the global community to develop advanced combustion technologies and alternative fuels that feature substantially reduced pollutant emissions while maintaining high efficiency. One such potential technology is dual-fuel reactivity-controlled compression ignition (RCCI), which has been shown to have low pollutant emissions and high thermal efficiency [1–4]. The basic principle of dual-fuel RCCI combustion requires two fuels with different reactivities, where the ignition of the low-reactivity fuel (such as gasoline, methane, or methanol) is triggered by the high-reactivity fuel (such as diesel or dimethyl ether). Among these potential fuels, dimethyl ether (DME) and methanol (MeOH) have been identified as possible alternative, non-fossil-based-fuels for using in RCCI engines.

DME is a good candidate for RCCI not only because of its reduced particulate matter (PM) emissions and potentially renew-able supplies [5] compared to traditional fuels, but also because it has a strong promoting effect on ignition of low-reactivity fuels. DME has a high cetane number (>55) which makes it well suited for compression ignition [6], while the absence of a carbon-carbon bond in the DME molecule and its high oxygen content by mass significantly limits soot formation during DME combustion [7]. Chen et al. [8] and Kajitani et al. [9] found that DME has lower NO_x emissions than diesel, while Arcoumanis et al. [5] found that the unburned hydrocarbon emissions are also lower than diesel. Although the current production of DME is largely from fossil fuels, DME has great potential to be produced by renewable sources, mostly from MeOH and syngas using appropriate catalysts [10,11]. In recognition of these aspects, DME ignition has been well-studied in the literature [12–30].

Another important feature of DME is its promoting effect on low-reactivity fuels over a wide range of conditions. For instance, a detailed study performed by Chen et al. [12] on DME/methane blends showed that DME addition can increase the laminar flame speed of methane, while the works of Burke et al. [13], Tang et al. [14], and Jiang et al. [15] demonstrated reduced ignition delays of methane and n-butane with DME addition over a wide range of engine-relevant conditions. Furthermore, Dames et al. [16] found

that at low temperature (< 1000 K) DME can promote propane combustion via low temperature DME oxidation, which produces hydroxyl radicals (•OH). The shock tube experimental/modeling work of Hu et al. [17] on DME/propane also showed that the promoting effect of DME at high temperature (1100–1500 K) is achieved by providing a radical pool.

MeOH is also considered a promising fuel for dual-fuel RCCI combustion because it is a clean-burning alcoholic alternative fuel [31] and has the potential to be renewably produced by carbonaceous feedstock such as wood or CO_2 recycling [32]. MeOH has a relatively low reactivity over a wide range of engine-relevant conditions. Several ignition delay studies have been performed to explore the autoignition properties of MeOH [33–39]. As DME can promote the ignition of low-reactivity fuels, MeOH can be mixed with DME as a dual-fuel blend suitable for RCCI operation. Several practical studies [40–44] have shown that DME can promote MeOH combustion and shorten the ignition delay time in internal combustion engines. In particular, Yao et al. [40] demonstrated that an internal combustion engine operated with DME/MeOH blends can reach its highest indicated thermal efficiency with DME percentage (the percentage of energy released from DME in total energy) of 60–76%. However, to the best of the authors' knowledge, fundamental autoignition studies conducted for DME/MeOH fuel blends are limited.

Thus, the main objective of this work is to obtain fundamental autoignition data for blends of DME/MeOH under engine-relevant conditions. This dataset is collected over the temperature range from 600 K to 890 K, pressures of 15 bar and 30 bar, and $\phi = 0.5$, 1.0, and 2.0 in dry synthetic air. These data are compared to a chemical kinetic model developed in this work following the methodology of Dames et al. [16]. Dames et al. [16] demonstrated that it is not necessary to consider cross-reactions of fuel fragments during combustion of high-/low-reactivity fuel blends and that simple addition and de-duplication of separately validated models is sufficient to produce a combined model that can satisfactorily reproduce fundamental combustion experimental data. Since chemical kinetic models for both DME [13,25–30] and MeOH [39,44–46] have been well developed previously, individual DME and MeOH sub-models can be selected from the existing models and merged by the technique described by Dames et al. [16]. In addition to comparison with experimental data, this merged model is used to further understand the autoignition chemistry of DME/MeOH fuel blends.

2. Experimental specifications

A rapid compression machine (RCM) is used to perform ignition delay measurements in this study. The detailed description of this RCM can be found in the works of Mittal and Sung [47,48] and only a brief overview will be given here. The RCM consists of a heated reaction chamber, a piston arrangement, a hydraulic motion control chamber, and a driving tank. The piston arrangement is pneumatically driven and hydraulically stopped. The overall compression ratio is adjusted by varying the stroke length and/or clearance height. The reaction chamber is filled by premixed fuel-oxidizer mixture, which is rapidly compressed by the piston to reach a desired elevated pressure and temperature condition. The end of compression (EOC) pressure (P_C) and temperature (T_C) are adjusted independently by changing the overall compression ratio, initial temperature (T_0), and initial pressure (P_0). The piston has a specially-designed crevice to suppress the vortex roll-up effect and ensure homogeneity during and after compression. The reaction chamber, mixing tank, and connection manifold are equipped with heaters that are controlled by a thermocouple/meter-relay-heater loop using T_0 as the set point (298 K–393 K herein).

A high frequency piezo-electrical pressure transducer (Kistler 6125C) is installed on the reaction chamber to record the in-
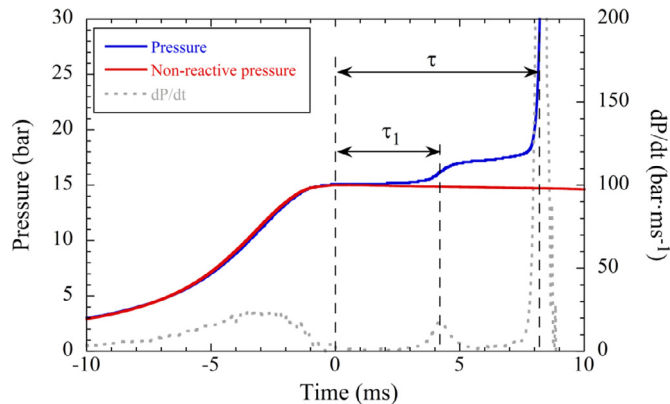
Fig. 1. Representative experimental pressure trace demonstrating the definitions of the first-stage ignition delay (τ_1) and the overall ignition delay (τ) with 50/50 DME/MeOH/air mixture, $\phi = 1$, $P_C = 15$ bar, $T_C = 694$ K. Time "0" denotes the end of compression.

cylinder pressure at a sampling rate of 100 kHz. A charge amplifier (Kistler 5010B) together with a National Instruments data acquisition device (NI 9215) is used to capture the signal from the transducer. The captured signal is converted to a pressure trace and processed by a Python package called UConnRCMPy [49] to determine the overall ignition delay (τ) and first-stage ignition delay (τ_1). The τ and τ_1 are defined as the time from the EOC to the respective maximum of the first order time derivative of pressure, as shown in Fig. 1. In addition, at least five consecutive experiments are taken for each experimental condition to ensure repeatability, and one representative pressure trace is selected to represent each test condition. The typical scatters of τ and τ_1 are less than 15% of the reported values.

The fuel-oxidizer mixture is prepared in a pre-vacuumed stainless steel mixing tank at room temperature. Since MeOH is liquid at room temperature, a glass syringe is used to inject MeOH into the mixing tank first. Then gas phase components (DME, O_2, and N_2) are filled into the mixing tank to their target pressure in sequence. Sufficient time interval is given between filling of two consecutive gases to minimize the influence of the small (~ 5 K) temperature change in the mixing tank caused by filling the previous gas. The molar ratio of O_2 and N_2 is kept at 1:3.76 throughout this study. The mixing tank is equipped with heaters and a magnetic stirrer to preheat the mixture and ensure the homogeneity of the mixture. After filling all reactants, the heaters and stirrer are switched on and kept running for at least two hours before beginning experiments to completely vaporize the liquid fuel, ensure a homogeneous mixture, and stabilize the preheat temperature. The molar proportions of the investigated mixtures are summarized in Table 1. High purity fuels and gases are used in this study: DME ($> 99.7\%$) and MeOH ($> 99.9\%$) are purchased from Sigma-Aldrich; O_2 ($> 99.994\%$) and N_2 ($> 99.999\%$) are obtained from Airgas.

In addition to reactive experiments, non-reactive experiments are performed by replacing O_2 in the original reactive mixture by N_2. An example non-reactive pressure trace can be seen in Fig. 1. For each reactive experimental test condition, a non-reactive pressure is measured at the same machine settings to characterize the machine-specific effect during compression and the induction period. The non-reactive pressure trace can also be used to distinguish whether heat release happened during the compression stroke in the reactive case. If the EOC pressures of the non-reactive and reactive pressure traces closely match each other, then there is negligible heat release during the compression stroke. The temperature at the EOC (T_C) is deduced from the measured pressure trace by applying the "adiabatic core hypothesis" [50]. Under this hypothesis, the heat loss from the reaction chamber only occurs