Abstract: Reactivity Controlled Compression Ignition (RCCI) is a new advanced engine concept that uses a dual fuel mode of operation to achieve significant improvements in fuel economy and emissions output. The fuels used in this mode include a low- and high-reactivity fuel in varying proportions to control ignition timing. As such, understanding the interaction effects during autoignition of binary fuel blends is critical to optimizing these RCCI engines. In this work, we measure the autoignition delays of binary blends of dimethyl ether ($C_2H_6O$, DME) and methanol ($CH_4O$, MeOH) in a rapid compression machine. In these experiments, dimethyl ether and methanol function as the high- and low-reactivity fuels, respectively. We considered five fuel blends at varying blending ratios (by mole), including 100 % DME-0 % MeOH, 75 % DME-25 % MeOH, 50 % DME-50 % MeOH, 25 % DME-75 % MeOH, and 0 % DME-100 % MeOH. Experiments are conducted at an engine-relevant pressure of 30 bar, for the stoichiometric equivalence ratio. In addition, the experimental results are compared with simulations using a chemical kinetic model for DME/MeOH combustion generated by merging independent, well-validated models for DME and MeOH.

Keywords: chemical kinetics, rapid compression machine, binary fuel blends, advanced engines

1. Introduction

To reduce the environmental impact of combustion, future combustion processes must feature substantially reduced pollutant emissions while maintaining high efficiency. A promising concept in this respect is low-temperature combustion (LTC). As an outstanding representative of LTC technologies, the dual-fuel Reactivity Controlled Compression Ignition (RCCI) operation has great potential in terms of combustion controllability. The general principle of dual-fuel RCCI combustion requires two fuels with different reactivities, that is using a high reactivity fuel (such as diesel or dimethyl ether (DME)) to trigger the ignition and combustion of low-reactivity fuels (such as gasoline, methanol, ethanol, or butanol).

DME is considered an efficient alternative fuel for use in diesel engines because it has excellent autoignition characteristics. The low boiling point (248 K), low critical point (400 K), and high cetane number (> 55) of DME [1] [2] make it well suited for compression ignition engines. In addition, the high oxygen content of DME (34.8 % by mass) together with the absence of C-C bonds contributes to ultra-low soot formation during DME combustion [1].

The promoting effect of DME blending on fuels with poor autoignition qualities such as methane and propane is a promising feature with respect to the RCCI concept. Therefore, some research has
been conducted to reveal the promoting potential of DME. Several researchers [3-5] have studied the ignition delays of DME/methane blends in shock tubes. The results have shown that DME has a strong promoting effect on the autoignition of methane, even when the concentration of methane is much higher than that of DME. Further, Dames et al. [6] showed the promoting effect of DME in DME/propane blends using a rapid compression machine. The results of the work of Dames et al. [6] showed that propane combustion is promoted due to the large amount of radicals produced by low-temperature DME oxidation. These studies indicate the potential of DME as a combustion promoter together with fuels with poor auto-ignition qualities.

For dual-fuel RCCI operation, a lower reactivity fuel should be studied in combination with the high reactivity fuel. Methanol (MeOH) is well known as a widely used alcoholic alternative fuel, but when operated in a single fuel mode it tends to have poor autoignition quality [7]. Given the great potential of DME as a combustion promoter, we expect that DME can significantly improve the auto-ignition quality of methanol and the combination will be effective for dual-fuel RCCI operation.

In this work, we explore the autoignition characteristics of DME/MeOH binary blends. A set of ignition delay time data for DME/MeOH blends at different blending ratios over a wide range of temperature at engine relevant pressure conditions and the stoichiometric equivalence ratio is obtained in a rapid compression machine (RCM). In addition, we compile a chemical kinetic model for DME/MeOH combustion by merging independent models for the fuels. Simulations utilizing this model are compared to experimental results and good agreement is observed over the range of the experiments.

2. Experimental Methods

The RCM used in this study is a single piston arrangement and is pneumatically driven and hydraulically stopped. The device has been described in detail previously [8] and will be described here briefly for reference. The end of compression (EOC) temperature and pressure (\(T_C\) and \(P_C\) respectively), are independently changed by varying the overall compression ratio, initial pressure, and initial temperature of the experiments. The primary diagnostic on the RCM is the in-cylinder pressure. The pressure data is processed by a Python package called UConnRCMPy [9], which calculates \(P_C\), \(T_C\), and the ignition delay(s). The definition of the ignition delay is shown in Fig. 1. The time of the EOC is defined as the maximum of the pressure trace prior to the start of ignition and the ignition delay is defined as the time from the EOC until local maxima in the first time derivative of the pressure.

In addition to the reactive experiments, non-reactive experiments are conducted to determine the influence of machine-specific behavior on the experimental conditions and permit the calculation of the EOC temperature via the isentropic relations between pressure and temperature [10]. The EOC temperature is calculated by the procedure described in Section 3.1.

The RCM is equipped with heaters to control the initial temperature of the mixture. After filling in the components to the mixing tanks, the heaters are switched on and the system is allowed 1.5 h to come to steady state. The mixing tanks are also equipped with magnetic stir bars so the reactants are well mixed for the duration of the experiments.

The mixtures considered in this study are shown in Table 1. The “% DME” and “% MeOH” columns indicate the molar percent of each component in the fuel blend. Mixtures are prepared in stainless steel mixing tanks. The proportions of reactants in the mixture are determined by
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Figure 1: Definition of the ignition delay used in this work. The experiment in this figure was conducted for a 25% DME blend with \( P_0 = 1.1528 \text{bar}, \ T_0 = 338 \text{K}, \ P_C = 29.98 \text{bar}, \ T_C = 748 \text{K}, \) and \( \tau = (35.39 \pm 1.93) \text{ms}. \)

specifying the absolute mass of the methanol in the mixture (if present), the equivalence ratio, the oxidizer composition (in this study, \( \text{O}_2 \) and \( \text{N}_2 \) in the ratio of 1 : 3.76 are used throughout), and the molar ratio of DME/MeOH in the fuel blend. Since MeOH is a liquid at room temperature and pressure, it is injected into the mixing tank through a septum. Proportions of DME, \( \text{O}_2 \), and \( \text{N}_2 \) are added manometrically at room temperature.

Table 1: Mixtures considered in this work

| % DME | % MeOH | Mole Fraction (purity) |
|-------|--------|------------------------|
|       |        | DME (99.7%) | MeOH (100.00%) | \( \text{O}_2 \) (99.994%) | \( \text{N}_2 \) (99.999%) |
| 100   | 0      | 0.0654       | 0.0000         | 0.1963       | 0.7383       |
| 75    | 25     | 0.0556       | 0.0185         | 0.1945       | 0.7314       |
| 50    | 50     | 0.0427       | 0.0427         | 0.1921       | 0.7225       |
| 25    | 75     | 0.0252       | 0.0756         | 0.1889       | 0.7103       |
| 0     | 100    | 0.0000       | 0.1229         | 0.1843       | 0.6928       |

3. Computational Methods

To the best of our knowledge, there are no chemical kinetic models for the combustion of binary blends of DME and MeOH available in the literature. Therefore, we compile a kinetic model in this work by combining two independent models. The kinetics for DME are taken from the work of Burke et al. [3] while the kinetics for MeOH are taken from the work of Burke et al. [11].
To combine the two models, duplicate reactions and species were taken from the Burke et al. [3] model; however, the models were produced by the same research group approximately one year apart, so we do not expect many differences in the common chemistry. In the work of Dames et al. [6], it was found that for combined models of high-reactivity fuels such as DME and low-reactivity fuels such as propane, cross-reactions between the fuels do not strongly affect the ignition delay and the fuels instead interact through radical species such as OH. Therefore, we do not consider any cross-reactions between the high- and low-reactivity fuels in this study (DME and MeOH, respectively).

3.1 RCM Modeling

All of the simulations in this work use the Python interface for Cantera 2.3.0 [12]. Two types of simulations are considered. The first is used to calculate \( T_C \). Detailed descriptions of the use of Cantera for these simulations can be found in the work of Weber and Sung [13] and Dames et al. [6]; a brief overview is given here. As mentioned in Section 2, non-reactive experiments are conducted to characterize the machine-specific effects on the experimental conditions in the RCM. This pressure trace is used to compute a volume trace by assuming that the reactants undergo a reversible, adiabatic, constant composition (i.e., isentropic) compression during the compression stroke and an isentropic expansion after the EOC. The volume trace is applied to a non-reactive simulation conducted in an \texttt{IdealGasReactor} in Cantera [12] and the temperature at the end of compression is reported as \( T_C \).

The second type of simulation uses a constant-volume, adiabatic reactor. This method does not consider the effect of the compression stroke and post-compression heat loss present in the experiments and the initial conditions in the simulation are set equal to the EOC conditions in the experiment. The ignition delay is defined as the time required for the simulated temperature to increase by 400 K over the initial temperature in the simulation.

4. Results and Discussion

Ignition delay results for the mixtures listed in Table 1 are shown in Fig. 2 for the stoichiometric equivalence ratio and \( P_C = 30 \text{ bar} \). In the following, we use the shorthand of specifying the molar percent of DME in the fuel blend to indicate the blending condition.

It can be seen in Fig. 2 that the 100 % DME case (0 % MeOH) is the most reactive while the 0 % DME case (100 % MeOH) is the least reactive. Interestingly, the change in reactivity as MeOH is added to DME appears to be non-linear with respect to the molar percent of MeOH added. In other words, the change in ignition delay at a fixed \( T_C \) is smaller going from 100 % DME to 50 % DME than going from 50 % DME to 0 % DME.

This is also demonstrated by Fig. 3 which shows the \( T_C \) values for ignition delays near 20 ms at the range of mixtures considered in this study. As the % DME decreases in the blend, the temperature required to achieve the same ignition delay increases. However, the temperature increase from 100 % to 50 % DME is much smaller than the increase from 50 % to 0 % DME.

Also shown on Fig. 2 are constant volume, adiabatic simulations computed according to the procedure laid out in Section 3.1. In general, the agreement between the model and the experiments is quite good over the entire range of the experiments. It can be seen in Fig. 2 that at low temperatures
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Figure 2: Ignition delays of blends of DME and MeOH as a function of inverse temperature, for an equivalence ratio of $\phi = 1.0$ and $P_C = 30$ bar. Constant volume, adiabatic simulations are shown as the solid lines.

Figure 3: $T_C$ values for ignition delays near 20 ms at the range of blends considered in this study

for a given mixture composition the ignition delay tends to be under-predicted, while at the higher temperatures the ignition delay is over-predicted.

As discussed by Mittal et al. [14], this is likely due in part to the modeling procedure used in this work. In general, we expect constant volume simulations to have shorter ignition delays than the experiments for long ignition delays because they do not include the effect of post-compression heat loss; conducting simulations that include the post-compression heat loss are very likely to improve agreement in this region. Furthermore, for short ignition delays, we expect constant volume simulations to over-predict the experimental ignition delay because they do not include the effect of radical pool buildup during the compression stroke. Therefore, conducting simulations that include the compression stroke are very likely to improve the agreement for short ignition delays.

5. Conclusions

In this study, we have measured ignition delays for binary blends of dimethyl ether and methanol for engine-relevant pressure, temperature, and equivalence ratio conditions using a heated rapid compression machine. The ignition delay results show that pure DME is more reactive than pure MeOH, and that the increase in ignition delay as DME is replaced by MeOH is non-linear as a function of the blending fraction. The ignition delays are also compared to a chemical kinetic model compiled by combining independent models for the two fuels. This model does not consider cross reactions between DME and MeOH. Nonetheless, the model gives quite good agreement with the data, supporting the hypothesis that the fuels do not interact via cross reactions but instead through common radicals such as OH. In addition, this further demonstrates that models for low-reactivity fuels such as methanol and high-reactivity fuels such as DME can be constructed by

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simple concatenation and deduplication of their respective independent models.

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