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Experiments and modeling of the autoignition of methyl pentanoate at low to intermediate temperatures and elevated pressures in a rapid compression machine

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ABSTRACT

Methyl valerate ($C_6H_{12}O_2$, methyl pentanoate) is a methyl ester and a relevant surrogate component for biodiesel. In this work, we present ignition delays of methyl valerate measured using a rapid compression machine at a range of engine-relevant temperature, pressure, and equivalence ratio conditions. The conditions we have studied include equivalence ratios from 0.25 to 2.0, temperatures between 680 K and 1050 K, and pressures of 15 bar and 30 bar. The ignition delay data demonstrate a negative temperature coefficient region in the temperature range of 720–800 K for both $\phi = 2.0$, 15 bar and $\phi = 1.0$, 30 bar, with two-stage ignition apparent over the narrower temperature ranges of 720–760 K for 15 bar and 740–760 K at 30 bar. In addition, the experimental ignition delay data are compared with simulations using an existing chemical kinetic model from the literature. The simulations with the literature model under-predict the data by factors between 2 and 10 over the entire range of the experimental data. In addition, a new chemical kinetic model is developed using the Reaction Mechanism Generator (RMG) software. The agreement between the experimental data and the RMG model is also not satisfactory. To help determine the possible reasons for the disagreement, a path analysis of both models is completed. It is found that improvements to both the reaction pathways and thermodynamic properties are required. Further directions for future improvement of the methyl valerate model are discussed.

1. Introduction

For transportation applications, biodiesel is an important constituent in improving environmental friendliness of fuels. This is due to its renewability when produced from sustainable agricultural crops and its ability to reduce emissions relative to petroleum-derived fuels [1]. Biodiesel typically consists of long-chain methyl ester molecules, with typical compositions of C_{14} to C_{20} [1]. Recognizing that the large molecular size of the methyl esters within biodiesel fuel makes creating and using detailed chemical kinetic models challenging [2], it is desired to study their combustion chemistry by studying simpler methyl ester molecules.

A recent review paper summarizes the work on methyl esters relevant to biodiesel combustion [3]; the following summary focuses on ignition delay measurements, since these are the focus of this paper. Autoignition of methyl butanoate (MB, $C_5H_{10}O_2$) has been well-studied in both shock tube and rapid compression machine experiments [4–10]. The prevalence of MB data in the literature is largely due to the early identification of MB as a potential surrogate fuel for biodiesel [11]. However, the literature experiments have shown that MB may not be an appropriate surrogate for biodiesel, due to its lack of negative temperature coefficient (NTC) behavior, a requirement for a suitable biodiesel surrogate [3].

Methyl esters larger than MB, such as methyl valerate (MV, $C_6H_{12}O_2$, methyl pentanoate), have also been studied as possible biodiesel surrogates. Hadj-Ali et al. [9] used a rapid compression machine (RCM) to study the autoignition of several methyl esters including MV. Although MV exhibited two-stage ignition in this study, little additional research has been done on its low-temperature chemistry. Korobeinichev et al. [12] studied MV in premixed laminar flames and extended a detailed high temperature chemical kinetic model to include MV and methyl hexanoate. Dmitriev et al. [13] added MV to n-heptane/toluene fuel blends to determine the resulting intermediate species in premixed flames using a flat burner at 1 atm and an equivalence ratio of 1.75. The addition of MV helped reduce soot forming intermediates including benzene, cyclopentadienyl, acetylene, propargyl, and vinylacetylene [13]. Hayes and Burgess [14] computationally examined the peroxy radical isomerization reactions for MV to better understand the

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low temperature reaction pathways. Finally, Diévart et al. [15] used diffusion flames in the counterflow configuration to determine extinction limits for a number of methyl esters, including MV, and validated a detailed kinetic model with the experimental data.

This work provides additional data for the autoignition of MV. Data is collected in a RCM under engine relevant conditions spanning from 15 bar to 30 bar, equivalence ratios (ϕ) from 0.25 to 2.0, and temperatures from 680 K to 1050 K. The NTC region of MV is mapped out to provide additional information on the fidelity of using MV as a biodiesel surrogate and insights into the autoignition chemistry of large methyl esters.

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 [16] 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 (P_0), initial temperature (T_0), and specific heat ratio of the experiments. The piston in the reaction chamber is machined with a specially designed crevice to suppress the roll-up vortex effect and promote homogeneous conditions in the reactor during and after compression [17].

The primary diagnostic on the RCM is the in-cylinder pressure measured by a Kistler 6125C dynamic transducer that is compensated for thermal shock. The transducer is coupled to a Kistler 5010B charge amplifier. The voltage output of the charge amplifier is recorded by a National Instruments 9125 analog input device connected to a cDAQ 9178 chassis. The voltage is sampled at a rate of either 50 kHz or 100 kHz by a LabView VI and processed by a Python package called UConnRCMPy [18]. Version 3.0.5 of UConnRCMPy [19], 3.6 of Python, 2.3.0 of Cantera [20], 1.13.0 of NumPy [21], 0.19.0 of SciPy [22], and 2.0.1 of Matplotlib [23] are used in the analysis in this paper.

The compression stroke of the RCM brings the fuel/oxidizer mixture to the EOC conditions, and for suitable thermodynamic states, the mixture will ignite after a delay period. The definitions of the ignition delays are 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 delays are defined as the time from the EOC until local maxima in the first time derivative of the pressure. Each experimental condition is repeated at least five times to ensure repeatability of the data. As there is some random scatter present in the data, the standard deviation (σ) of the ignition delays from the runs at a given condition is computed. Typically, σ is less than 10% of the mean values of the overall ignition delay (τ) and the first stage ignition delay (τ_1).

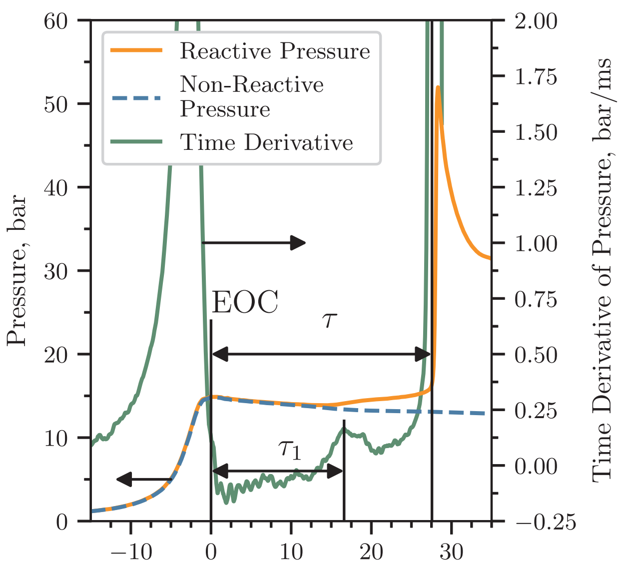

Fig. 1. Definition of the ignition delays used in this work. The experiment in this figure is conducted for a ϕ = 2.0 mixture with Ar/(N_2 + Ar) = 0.5, P_0 = 0.7806 bar, T_0 = 373 K, P_C = 14.92 bar, T_C = 720 K, τ = (27.56 ± 0.89) ms, and τ_1 = (16.60 ± 0.46) ms. The non-reacting pressure trace by replacing O_2 with N_2 is also shown for reference.

In addition to the reactive experiments, non-reactive experiments are conducted by replacing O_2 with N_2 to determine the influence of machine-specific behavior on the experimental conditions (see Fig. 1) and permit the calculation of the EOC temperature via the isentropic relations between pressure and temperature [24]. The EOC temperature is calculated by the procedure described in Section 3.

The mixtures considered in this study are shown in Table 1. Four equivalence ratios of MV in "air" are considered. While O_2 is kept at 21% by mole in the oxidizer, the ratio of Ar:N_2 in the oxidizer is varied to adjust the temperatures reached at the EOC. Two P_C conditions are studied in this work, 15 bar and 30 bar, representing engine-relevant conditions. For the ϕ = 2.0 condition, only P_C = 15 bar is considered because we could not achieve T_C values low enough that the ignition during the compression stroke could be prevented.

Mixtures are prepared in stainless steel mixing tanks, 17 L and 15 L in size. The proportions of reactants in the mixture are determined by specifying the absolute mass of the fuel, the equivalence ratio, and the ratio of Ar:N_2 in the oxidizer. Mixtures are made by first vacuuming the mixing tanks to an ultimate pressure less than 5 Torr. Since MV is a liquid with a relatively small vapor pressure at room temperature and pressure, it is measured gravimetrically to within 0.01 g of the specified value. The fuel is injected into the mixing tank through a septum. Proportions of O_2, Ar, and N_2 are added manometrically at room temperature and the total pressure is measured by an Omega Engineering MMA100V10T2D0T4A6 type static pressure transducer. The same transducer is used to measure the pressure of the reactant mixture prior to an experiment.

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. Previous work has shown this procedure to completely vaporize the fuel and prevent fuel cracking during the heating process [25–27].

The initial temperature is chosen such that the saturated vapor pressure (P_{sat}) of the fuel at the initial temperature is at least twice the partial pressure of the fuel in the mixing tank. The Antoine equation

$$\log_{10}P_{sat} = A - \frac{B}{T - C} \tag{1}$$

is used to model the saturated vapor pressure of MV as a function of temperature (T), where A, B, and C are substance-specific coefficients, given in units of K and kPa. Coefficients for Eq. (1) are given in the literature by Ortega et al. [28], Camacho et al. [29], and Stephenson et al. [30]. Unfortunately, the values of the coefficients are different among all three references. Therefore, coefficients for use in Eq. (1) are determined in this work by least squares fitting of the data of Ortega et al. [28], van Genderen et al. [31], and Verevkin and Emel'yanenko [32] using the `curve_fit()` function of SciPy [22] version 0.19.0. Fig. 2 shows that the coefficients fitted with this procedure give good agreement with the experimental data; values for the coefficients computed in this work and reported in the literature works are given in Table 2. The data and code used to calculate the coefficients are provided in the Supplementary Material.

3. Computational methods

3.1. RCM modeling

The Python 3.6 interface of Cantera [20] version 2.3.0 is used for all simulations in this work. Detailed descriptions of the use of Cantera for