



# Autoignition of methyl propanoate and its comparisons with methyl ethanoate and methyl butanoate



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## ABSTRACT

This work reports an experimental and computational study on the autoignition characteristics of methyl propanoate under high pressure and low-to-intermediate temperature conditions. Comparisons to its next higher and lower methyl esters are also presented. The methyl propanoate experiments have been conducted using a rapid compression machine over compressed pressure and temperature ranges of 15–45 bar and 899–1103 K, respectively, as well as covering both stoichiometric and fuel lean conditions. In addition, the performance of four chemical kinetic models reported in the literature is assessed by comparing the experimental ignition delay times to numerical simulations. Sensitivity analysis is also performed to identify important reactions influencing the model predictions for ignition delay times. Further, we provide a comparison between the experimental ignition delay times of methyl propanoate and its next higher and lower homologs, namely methyl butanoate and methyl ethanoate, under selected conditions. An unusual trend in the autoignition response with respect to the carbon number is observed among methyl ethanoate and methyl propanoate. Methyl ethanoate is found to be more reactive than methyl propanoate in the low-temperature regime of 850–950 K despite having a lower carbon number, with a crossover in reactivity above 950 K. Methyl butanoate is the most reactive among the three esters investigated which is consistent with the notion of increase in reactivity with increasing carbon number. This experimental and computational investigation provides insights into the homogenous autoignition chemistry associated with small unsaturated methyl ester compounds under engine relevant conditions.

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## 1. Introduction

Long chain esters are the key constituents in bio-derived fuels. It is therefore important to develop a fundamental understanding of this class of fuels to facilitate their clean and efficient utilization in transportation engines. The detailed understanding of combustion kinetics of large carbon number fuels is greatly facilitated by a systematic approach that also includes the low carbon number fuels of the same class. This follows from the hierarchical nature of detailed chemical kinetic models. The autoignition response is a fundamental global target used to determine the suitability of a fuel type for use in advanced internal combustion engines. In addition, ignition delay times are used to validate the low-to-intermediate temperature sub-mechanisms present in detailed kinetic models. Low carbon number neat constituents are therefore a logical starting point in the process of developing an understanding of real fuels.

There has been an increased interest in understanding the fundamental combustion properties of small esters. Wang et al. [1] studied the oxidation of seven different compounds including small methyl and ethyl esters in the counterflow flame configuration under atmospheric pressure conditions. Another study by Wang et al. [2] examined three model bio-diesel fuels composed of methyl butanoate, methyl crotonate, and methyl decanoate under both laminar premixed and non-premixed flame conditions using the atmospheric pressure counterflow configuration. A review by Hansen et al. [3] discussed the application of the molecular beam mass spectrometry technique to understand the combustion chemistry of methyl esters, among other types of oxygenated and non-oxygenated hydrocarbon fuels. The oxidation of ethyl acetate in flame environment using microprobe sampling and gas chromatography has been studied by Gasnot et al. [4]. Ethyl butanoate has also been the subject of an experimental and modeling study in a laminar plug flow reactor by Bennadji et al. [5]. Using the photoionization mass spectrometry technique, Zhao et al. [6] investigated the pyrolysis of methyl propanoate in a laminar flow reactor at 30 Torr and within the temperature range of 1000–1500 K, and also reported a pyrolysis reaction mechanism.

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A study by Diévar et al. [7] examined the chemical kinetic characteristics of small methyl esters in non-premixed flame extinction. By recording the species time history for O, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub>O using laser absorption techniques, high temperature pyrolysis of methyl and ethyl propanoate was studied behind reflected shocks at a pressure of 1.5 atm and in the temperature range of 1250–1750 K by Farooq et al. [8]. Another study by Farooq et al. [9] examined the pyrolysis kinetics for methyl butanoate behind reflected shocks at a pressure of 1.5 atm and a temperature range of 1200–1800 K. An experimental and computational study on the decomposition pathways for methyl esters using the shock tube apparatus was also reported by Farooq et al. [10].

By comparison, there are very limited experimental studies on the ignition delay times of small methyl esters. HadjAli et al. [11] studied the autoignition of a series of C<sub>4</sub>–C<sub>8</sub> fatty acid methyl esters using a rapid compression machine in the temperature range of 650–850 K, and at pressures in the range of 4–20 bar. Akh-Kumgeh and Bergthorson [12] investigated C<sub>1</sub>–C<sub>4</sub> alkanolic acid methyl esters for structure reactivity trends using a high temperature shock tube apparatus and quantum chemical calculations. A detailed review of the combustion kinetics of methyl and ethyl esters including modeling and experiments can be found in the review article by Coniglio et al. [13]. The studies on the oxidation of methyl esters reported in the literature are mostly limited to the low pressure and high temperature conditions. As such, this work seeks to expand and fill in the gaps in the understanding of oxidation characteristics of small methyl esters in the complementary thermodynamic conditions corresponding to elevated pressure and low-to-intermediate temperature.

## 2. Experimental specifications

### 2.1. Apparatus and procedure

The ignition delay times of methyl propanoate and methyl ethanoate have been obtained using a rapid compression machine (RCM), which mimics a single compression stroke of a reciprocating internal combustion engine. A fixed mass of premixed fuel/oxidizer mixture is brought to an elevated pressure and temperature condition at the compression top dead center, starting from initial conditions corresponding to a charge at much lower pressure and temperature. This change in thermodynamic conditions of the premixed fuel/oxidizer mixture is brought about in a very short time interval of approximately 30 ms, and the compression process is nearly adiabatic. The current RCM uses a creviced piston design that provides for a uniform temperature field in the compressed gas over an experimental duration by minimizing the influence of roll-up vortex due to piston motion [14]. The high pressure and temperature conditions in an RCM can be maintained for time intervals of the order of 100 ms [14]. The temperature at the end of compression is estimated using the adiabatic core hypothesis which relates the initial pressure and temperature ( $P_0$  and  $T_0$ , respectively) to the final compressed pressure and temperature ( $P_C$  and  $T_C$ , respectively) by the relation  $\int_{T_0}^{T_C} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln \left[ \frac{P_C}{P_0} \right]$ . Here  $\gamma$  is the ratio of specific heats of the compressed gas and is a function of the temperature of the gas. The quantities  $P_0$  and  $P_C$  are recorded by two different pressure transducers. The compression top dead center pressure,  $P_C$ , can be controlled by either varying the compression ratio or the initial charge pressure ( $P_0$ ). Similarly, the temperature at the end of compression can be varied by changing either the initial charge temperature ( $T_0$ ), the compression ratio, or the mixture specific heat. The oxidizer used in the current experiments consists of ‘argon-air’ with argon in place of nitrogen and an argon to oxygen ratio of 3.76:1 by mole. Experimental results for three different methyl propanoate/oxidizer mixtures corresponding to equivalence ratios of  $\phi = 0.25, 0.5$ , and 1.0 are

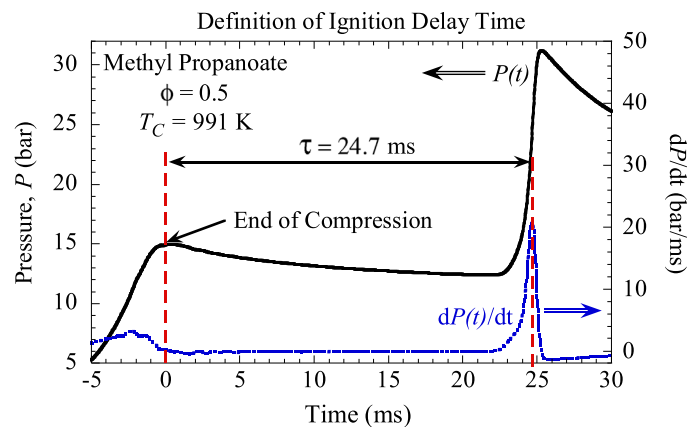


Fig. 1. Definition of ignition delay time.

reported in this work. Additionally, a comparison with both methyl ethanoate and methyl butanoate experiments under stoichiometric conditions using the same oxidizer composition is reported for a compressed pressure of  $P_C = 30$  bar. The primary data recorded in these experiments is the pressure-time trace for the compression and the subsequent autoignition. The dynamic pressure is recorded by means of a Kistler 6125B piezoelectric pressure transducer with a 5010B charge amplifier. Additional details related to the experimental procedure can be found in our previous RCM studies on *n*-decane [15], oxygenated fuels [16,17], and binary blends [18].

The elevated pressure and temperature conditions at the end of compression set into motion chemical reactions in the premixed fuel/oxidizer mixture which ultimately leads to an autoignition event that is characteristic of the fuel type. Based on the pressure rise during the autoignition process, the ignition delay time is defined to be the time interval between the end of compression and the subsequent maximum rate of pressure rise. An experimental pressure trace exhibiting the autoignition event is shown in Fig. 1. The definition of ignition delay time based on the maximum rate of pressure rise is also illustrated in the figure. As can be seen in Fig. 1, the end of compression provides the reference time ( $t = 0$ ) with respect to which the ignition delay time ( $\tau$ ) is reported.

### 2.2. Experimental uncertainty

For each test condition, the experiments are repeated at least four times to ensure that the results are repeatable. A representative experimental pressure trace is then selected for reporting the ignition delay time. The typical experimental repeatability observed in the current methyl propanoate experiments is shown in Fig. 2(a). The traces are for a compressed pressure of 15 bar, and two different equivalence ratios corresponding to  $\phi = 0.5$  and 1.0. Figure 2(a) shows that the fuel lean mixture exhibits a greater scatter in the ignition delay times when compared to the stoichiometric condition. The standard deviation representative of this scatter in ignition delay time is reported as the y-error bar in the Arrhenius plots of ignition delay time as a function of inverse temperature. These standard deviations in ignition delay times for all methyl propanoate experiments are provided in Table 1. The uncertainty in the compressed temperature is estimated based on the work of Weber et al. [19] for the RCM used in this study. Weber et al. [19] showed that the relative uncertainty in the estimated temperature at the end of compression does not exceed 0.7% of the mean calculated temperature. We therefore assume that the same holds true for the current study and assign a  $\pm 0.7\%$  uncertainty in the estimation of  $T_C$ . This is shown as the x-error bar in the Arrhenius plot of Fig. 2(b).

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