

# Autoignition of Methyl Butanoate as a Biodiesel Surrogate

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## 1 Introduction

Biodiesel is increasingly employed as an alternative fuel or fuel additive. In order to better understand its combustion properties and assess the associated emission benefits, fundamental research is needed. Because of the difficulties in modelling the long chain methyl esters that make up biodiesel, the chemical kinetic modelling of methyl ester oxidation is best approached by considering shorter chain methyl esters as surrogate fuels, such as methyl butanoate. This approach is analogous to the central role of hydrogen and methane chemistry in the kinetic modelling of larger hydrocarbons. A model has been proposed for methyl butanoate [1] and through experimental [2, 3, 4, 5] and theoretical [6] investigations, modifications have been suggested to enhance its applicability to a wider range of combustion conditions. Since the ignition properties of a fuel are central to its choice for specific combustion engine applications, one of the combustion characteristics employed in chemical kinetic mechanism validation is the ignition delay of homogeneous gas-phase mixtures, often measured behind reflected shock waves. Relatively few shock tube ignition studies [3, 4] of biodiesel surrogate ignition are available for performing the necessary validation, as compared to traditional hydrocarbon fuels. The ignition data by Metcalfe et al. [3] were performed at pressures of 1 atm and 4 atm at rich, stoichiometric and lean compositions in an argon bath. Low temperature data at higher pressures have been reported [5, 4]. Herein we report experimental data at average pressures of 1 atm, 4 atm and 10 atm. Post reflected shock temperatures range from 1060 K to 1700 K. The effect of argon dilution is also investigated. These experimental data provide further insight into the oxidation of methyl esters with regards to the effect of pressure, argon dilution and equivalence ratio on ignition.

## 2 Experimental technique

Experiments are carried out in a 5 cm inner diameter stainless steel shock tube. The driver and driven sections are 3 m and 4.2 m, respectively. Mixtures are prepared in a 90 L tank and allowed to mix for at least 24 hours. The mixing tank and the shock tube can be evacuated with a vacuum pump rated to  $2 \times 10^{-3}$  mbar. For the purpose of preparing mixtures, a 100 torr Barocel pressure transducer and a 1000 torr MKS Baratron pressure transducer are employed to accurately determine the partial pressures of the fuel, oxygen and argon. The liquid fuel is injected into the evacuated mixing tank by means of a gas-tight syringe. The liquid fuel volume is chosen so that the resulting gaseous fuel pressure does not exceed 50% of the vapour pressure at room temperature. The shock tube is helium driven, with the driven and driver sections separated by polycarbonate diaphragms. The incident shock velocity is determined by means of shock arrival times measured by four fast-response pressure transducers (models PCB 113A24 and PCB 113A26) mounted 50 cm apart. The ignition delay is obtained from light emission

Mixture	$\phi$	% MB	%O <sub>2</sub>	%Ar	Ar/O <sub>2</sub> ratio
Mixture A	1.0	1.0	6.5	92.5	14.23
Mixture B	1.5	1.5	6.4	92.1	14.39
Mixture C	0.5	0.5	6.5	93.0	14.31
Mixture D	1.0	3.1	20.3	76.6	3.77

Table 1: List of gas mixtures employed in this study

and pressure at the endwall. Light emission is observed using a Thorlab photodiode equipped with a bandpass optical filter centered at 430 nm with a 10 nm bandwidth. Data acquisition is by means of a 12-Bit 60 MHz digitizer (National Instruments PCI 5105). In the present work sampling was carried out at 10 MS/s. The methyl butanoate was 99% purity and the gases employed in this studies were oxygen (99.995%) and argon (99.995%), with helium (99.995%) used as a driver gas. The shock tube facility has been characterised and found to perform well by comparing *n*-heptane and iso-octane ignition data with those found in literature. The ignition delay is obtained by the intersection of the line of maximum slope of the CH signal with the average photodiode signal prior to ignition onset. Figure 1 shows that the rise in CH emission and pressure occur at the same time, so that either signal can be used to determine the ignition delay. Table 1 lists the mixtures used in this study.

### 3 Results and discussion

The chemical kinetic software package CANTERA [7] was employed to simulate the constant volume ignition delays for the chosen conditions. The chemical kinetic mechanism used is the Fisher et al. [1] mechanism as modified by Dooley et al. [4]. The ignition delays were corrected for pressure variations from shot-to-shot using the approximate relation  $\tau \propto p^{-0.75}$ . The high temperature ignition of methyl butanoate follows an Arrhenius type process, if the ignition delay is considered as the reciprocal of the global rate constant. Figure 2 shows the effect of pressure on the ignition behaviour as the temperature varies. It is observed that whereas there is fairly good agreement at 1 atm with simulation and results obtained by Dooley et al. [4], high temperature ignition delays at 4 and 10 atm are shorter than predicted

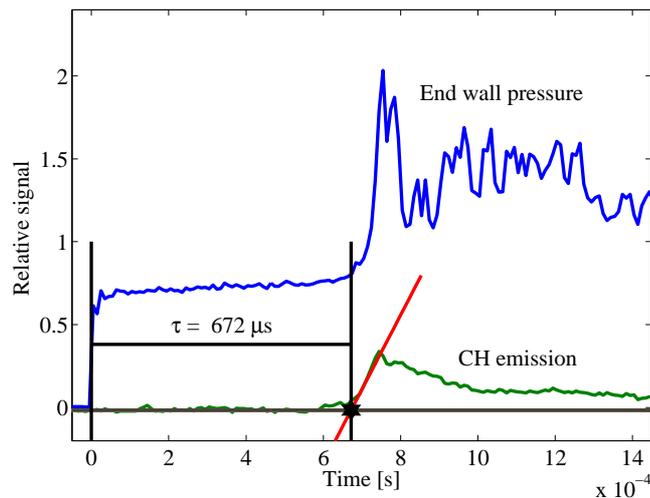


Figure 1: End wall pressure measurement and chemiluminescence of the CH radical (430 nm) with corresponding ignition delay.

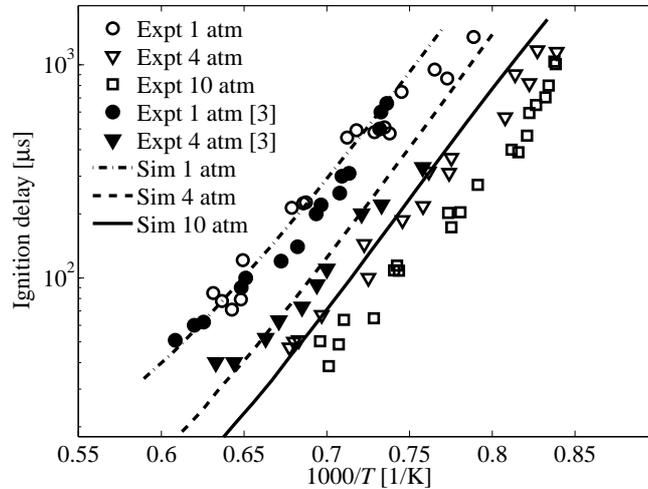


Figure 2: Effect of pressure on the ignition of stoichiometric MB/O<sub>2</sub>/Ar mixtures.

by the mechanism. Deviations at higher pressures were also observed in previous Rapid Compression Machine (RCM) studies by [4, 5]. Walton et al. [5] further modified the Metcalfe et al. mechanism [3] to obtain agreement with data from both shock tube studies and their RCM. However, this later version of the mechanism was not immediately available to be tested against the present data. In Fig. 3, ignition at lean, stoichiometric and rich conditions at 10 atm are compared. Unlike the trend observed at 4 atm by Dooley et al. [4] where rich mixture at  $\phi = 1.5$  had slightly higher but very similar ignition delays to  $\phi = 1.0$  while the lean mixtures displayed shorter delays, in this work at 10 atm shorter ignition delays with increasing equivalence ratio are observed. The performance of a chemical kinetic mechanism may differ at different degrees of oxygen-argon dilution. Figure 4 shows that a lower argon-oxygen ratio leads to shorter ignition delays. The simulations also show this trend, though without good agreement with the experiments.

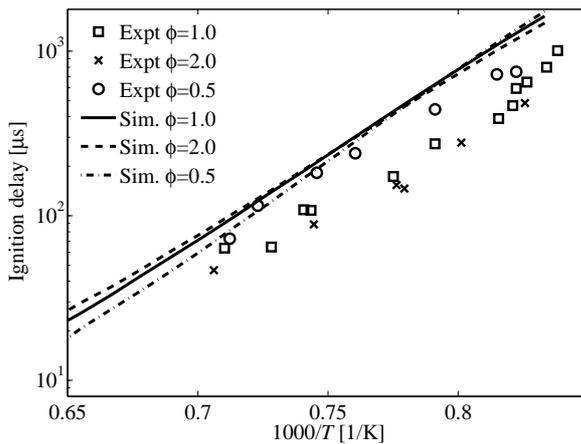


Figure 3: Effect of equivalence ratio on ignition delay at a pressure of 10 atm and Ar/O<sub>2</sub> dilution level of 14.23.

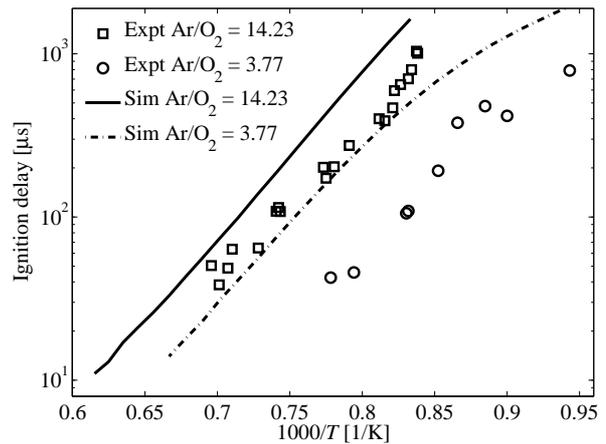


Figure 4: Effect of argon dilution level on ignition delays for stoichiometric mixtures at a pressure of 10 atm.

## 4 Conclusion

Shock tube ignition data for methyl butanoate, oxygen and argon mixtures at pressures up to 10 atm have been obtained. The effect of pressure on ignition delay has been investigated by studying ignition at 1, 4 and 10 atm. Compared to the simulations, there is fairly good agreement at 1 atm, suggesting that the results are in good agreement with previously published data [4]. However both simulations and previous experiments show longer ignition delays than those obtained in this work at 4 atm. The present experiments indicate that ignition delays are not very sensitive to equivalence ratio at 10 atm, although rich mixtures tend to have shorter ignition delays than lean or stoichiometric. The kinetic mechanism also predicts a weak dependence of ignition delay on equivalence ratio at higher pressures, with lean mixtures exhibiting the shortest delays at high temperatures. Reduced dilution with argon results in much shorter ignition delays than predicted by the mechanism. These deviations may be due to pressure dependent unimolecular decomposition reactions competing with hydrogen abstraction reactions from the fuel. A detailed assessment of the relative contributions of the two pathways as well as reactions with oxygen could further improve understanding of methyl ester oxidation mechanism, through further theoretical and modelling studies.

## 5 Acknowledgements

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