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Experimental and chemical kinetic modeling investigation of methyl butanoate as a component of biodiesel surrogate

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ABSTRACT

Biodiesel is a potential alternative to fossil diesel. In combustion simulations, in order to circumvent the difficulty in integrating reaction schemes for biodiesels, which are typically of a large size and not well understood, a surrogate approach to simplify the representation of its long chain methyl ester components is adopted. In this work, a compact reaction scheme for methyl butanoate, which is a potentially important candidate for biodiesel surrogates, is derived from a detailed reference mechanism (Dooley et al., 2008). An existing well-validated model for *n*-dodecane (Narayanaswamy et al., 2014) oxidation, which is a suitable base to model biodiesel surrogates, is augmented with the oxidation pathways of methyl butanoate. The resulting combined mechanism is comprehensively assessed for methyl butanoate kinetic description. Several rate constants pertaining to methyl butanoate kinetics are updated in the resulting chemical mechanism based on recent rate recommendations from the literature in a consistent manner. The revised kinetic model has been validated comprehensively against a wide range of experimental data and found to be satisfactory. In addition, auto-ignition delay times of methyl butanoate have been measured in a rapid compression machine (RCM). The ignition delay time measurements cover a wide range of experimental conditions: temperatures of 850–1100 K and pressures of 10–40 bar. The impact of varying equivalence ratios on ignition delay times has also been investigated for $\phi = 0.5$–1.5 and ignition delay times are reported for the rich mixtures for the first time as a part of this work. No two-stage ignition or negative temperature coefficient (NTC) behavior has been observed for methyl butanoate in the experimental investigation. The effect of addition of low-temperature chemistry pathways to the methyl butanoate chemical kinetic mechanism has also been explored.

1. Introduction

Increase in the use of renewable alternative fuels will decrease our dependence on fossil fuels and help reduce greenhouse gas emissions. Biodiesel is one such potential alternative to partially or completely replace fossil diesel [1]. It consists of long chain saturated as well as unsaturated methyl esters ranging from C_{14}–C_{24} [2]. These constituents are present in varied compositions based on the source of biodiesel. A detailed kinetic mechanism developed for these constituents runs into several thousands of species and reactions [3]. To circumvent the difficulty in utilizing such a large kinetic scheme in engine simulations, several studies have investigated the use of various surrogates for biodiesel [4–9], which have been recently summarized in Ref. [10].

In developing a reaction mechanism for a surrogate fuel, it is crucial to capture the component kinetics accurately in order to make meaningful assessment about suitability of the surrogate to represent the real fuel. Thus, although methyl decanoate has been used in recent studies [7–9] as a surrogate component owing to its ability to reproduce the reactivity, negative temperature coefficient (NTC) behavior, and early CO_2 rise, characteristic to the long chain methyl esters in biodiesels, methyl butanoate (MB), which is the most comprehensively investigated methyl ester in terms of kinetic studies [11], is selected here to represent the ester content in biodiesels. Methyl butanoate has not been found to exhibit any NTC behavior in the conditions where longer esters did show NTC behavior and it lacks the reactivity characteristic of long chain ester molecules. Nonetheless, methyl butanoate, in combination with *n*-alkanes is found to predict combustion and

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emission characteristics of biodiesel [19], which can therefore be considered as a promising candidates for biodiesel surrogates.

Fisher et al. [12] developed the earliest model for methyl butanoate oxidation and validated it against pressure measurements in a constant volume chamber. Their model exhibited a weak NTC and was in qualitative agreement with the available experimental data at that time. Several detailed mechanisms have been developed [11,13–15] thereafter, along with a wide variety of experimental studies for auto-ignition and pyrolysis of methyl butanoate [11,15,29,56–58] and its flames [13,37,46,47]. These kinetic descriptions are mainly derived from the relatively well understood alkane kinetics by accounting for ester specific effects.

Dooley et al. [11] developed a comprehensive reaction mechanism for methyl butanoate and validated it against a wide range of experiments. This model did not include any low-temperature chemistry pathways. Gail et al. [13,16] performed an experimental and kinetic modeling study of methyl butanoate and methyl crotonate. They investigated the effects of unsaturation and identified reaction pathways responsible for differences between saturated and unsaturated methyl ester. Hakka et al. [15] generated a detailed kinetic mechanism for methyl butanoate using the mechanism generation software EXGAS [17]. Gail et al. [13] and Hakka et al. [15] models included the pathways for low-temperature oxidation of methyl butanoate although NTC behavior has not been observed in any of the existing auto-ignition experiments.

Complementing the kinetic modeling efforts, several researchers have examined methyl butanoate kinetics using theoretical techniques [18–24]. Huynh et al. [25] developed a sub-mechanism for methyl butanoate based on a detailed ab-initio study. This sub-mechanism was verified against shock tube pyrolysis experiments. Some researchers [20,21,26] also investigated the important reactions for auto-ignition such as H-atom abstraction from methyl butanoate by different radicals using different levels of theories. Low-temperature chemistry pathways important for methyl butanoate oxidation have also been explored recently [22,23] using quantum chemical calculations. Although no NTC behavior is observed, these studies suggest that the inclusion of low-temperature oxidation pathways might be important for predicting auto-ignition at low temperatures.

Auto-ignition of methyl butanoate has already been investigated experimentally using shock tubes and rapid compression machines (RCM). Dooley et al. [11] measured ignition delays of methyl butanoate in a shock tube ($P = 1{,}4$ bar, $T = 1250$–1760 K and $\phi = 0.25$–1.5) and RCM ($P = 10$–40 bar, $T = 640$–949 K and $\phi = 0.33$–1.00). Hakka et al. [15] also studied auto-ignition of methyl butanoate in shock tube at higher pressure ($P = 8$ bar, $T=$ 1250–2000 K and $\phi = 0.25$–2). Additional measurements of ignition delays have also been obtained in RCM facilities [27–29]. Of these, Kumar and Sung [29] have recently explored a wide range of conditions ($P = 15$–75 bar, $T = 833$–1112 K and $\phi = 0.25$–1.00). Notably, auto-ignition of rich MB mixtures has not been investigated yet at intermediate temperature ($850\ \mathrm{K} < T < 1100\ \mathrm{K}$) under engine relevant conditions.

The primary goal of this work is to: (a) present additional auto-ignition data for methyl butanoate at conditions not investigated earlier along with (b) a compact reaction scheme for methyl butanoate oxidation, yet thoroughly examined for its kinetic description and validated against an array of experimental configurations. This work is organized as follows. Firstly, ignition delay time measurements for MB in a rapid compression machine covering a wide range of operating conditions ($P = 10$–40 bar, $T = 850$–1100 K and $\phi = 0.5$–1.5) are presented in Section 2. It is to be highlighted that ignition delays for rich MB mixtures are reported for the first time in the intermediate temperature (850–1100 K) regime, thereby providing valuable data for kinetic model validation at these conditions. Thereafter, the development of the kinetic scheme is described in Section 3. The oxidation pathways of methyl butanoate are derived from a detailed mechanism [11] and incorporated into a well-characterized model for n-dodecane oxidation [30], considering the potential of this long chain alkane as a component of a possible biodiesel surrogate [19,63,64]. The kinetic description of methyl butanoate oxidation in the resulting mechanism is revised and updated based on rate parameter recommendations for methyl butanoate oxidation from recent theoretical studies, which have not been utilized yet for model development. The proposed model is then comprehensively validated against available methyl butanoate experimental data as well as the new data-sets obtained in the present work (Section 4). The revised model is found to Result in improved model predictions for methyl butanoate.

The existing set of experiments, including the ones presented in this work, do not show NTC or two-stage ignition. Nonetheless, the addition of low-temperature chemistry pathways has also been explored here for completeness. Since the validity of the low-temperature model cannot be ascertained with the available experimental data, this discussion is presented separately in Section 5. This investigation points toward potential experimental studies required to assess the low-temperature chemistry of methyl butanoate in future.

2. Experimental methodology

The rapid compression machine used in this study is located at Physikalisch-Technische Bundesanstalt (PTB), which is similar to that used by Mittal and Sung [31]. It consists of a single piston design, where a pneumatically driven and hydraulically controlled creviced piston compresses the mixture inside the reaction chamber to a desired end of compression pressure (P_C) and temperature (T_C). The reaction chamber has a maximum working pressure of 200 bar and an operating temperature range of 600–1100 K. The rapid compression machine has been designed to obtain a wide range of compression ratios with adjustable stroke length and clearance. A compression ratio of 25.6:1 has been used in this study.

The test mixtures were prepared manometrically in a stainless-steel tank at the room temperature by using a 5000-mbar barometer (MKS Baratoron) to an accuracy of ±1 mbar to measure the partial pressures of the gases. The steel tank is cleaned with the bath gases to remove impurities prior to filling of the constituent gases. Methyl butanoate (99%, Sigma Aldrich) is used as a fuel for autoignition. Different combinations of argon (99.999%) and nitrogen (99.999%) are used as bath gases in RCM experiments to obtain the appropriate value of ϕ and different end of compression temperatures T_C. A small mass of methyl butanoate is introduced into the evacuated mixing tank via a septum by means of a syringe, such that its partial pressure is well below its vapour pressure. Oxidizer (99.999% purity O_2) and diluent gases are added manometrically according to the mixture composition. These gaseous mixtures are allowed to mix in the steel tank for at least 12 hours before transferring to the reaction chamber to ensure homogeneity. Table 1 lists the mixture compositions used in the experiments. Along with the use of different diluent gases, preheating is also used to obtain desired T_C. Uniform heating of reaction chamber, mixing cylinder and gas filling assembly has been ensured for this purpose by using a combination of heating tapes and temperature monitoring using Pt-Rh thermocouples. This entire arrangement was insulated to avert the formation of any cold spots.

Owing to the difficulty of directly measuring the temperature inside the reaction chamber, $\mathrm{T_C}$ is determined assuming an adiabatic core using GasEq [32] as,

$$\int_{T_0}^{T_C} \frac{\gamma}{\gamma - 1}\frac{dT}{T} = \ln\left(\frac{P_C}{P_0}\right), \tag{1}$$