



A kinetic model for methyl decanoate combustion

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ABSTRACT

A detailed kinetic model for the oxidation of the biodiesel surrogate, methyl decanoate, has been developed and tested against a broad range of experimental data. The methyl decanoate model consists of both low and high temperature oxidation chemistry. It has been constructed strictly through the extension of the chemical kinetic and thermochemical parameters used to describe the oxidation of the better-understood small methyl ester, methyl butanoate. The constructed model is tested in an *a priori* manner by the computation of all of the appropriate experimental data available for methyl decanoate oxidation.

The results show a generally improved performance of the present model relative to that of literature models which have generally been constructed based on similarity to alkane oxidation reaction kinetics. Chemical path flux analyses of all available methyl decanoate models are analyzed and the results reveal that the fuel oxidation pathways exhibit completely different chemical mechanisms depending on the modeling prescriptions of the kinetic and thermochemical parameters. In particular, there is a wide degree of variability in the fate prescribed to the methyl ester functionality. In addition, experimental analysis of diffusion flame extinctions for methyl butanoate and methyl decanoate reveals that the high temperature reactivity of methyl butanoate is similar to that of methyl decanoate by introducing a concept of transport-weighted enthalpy. Consequently, the present modeling work and experimental analysis suggest that further studies of small methyl ester systems, such as methyl butanoate are required in order to improve the model fidelity of large biodiesel like methyl esters.

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1. Introduction

Recent climate change and energy security concerns have been driving significant interests in bio-fuels such as biodiesels and alcohols that provide means to replace petroleum use and reduce net CO₂ emissions associated with transportation. Biodiesel is derived from the transesterification of triglyceride lipid with methanol (or ethanol), and is composed of a mixture of long alkyl chain methyl (or ethyl) esters. The specific molecular components and their distribution depend on the lipid source, but are limited to a small set of alkyl and alkenyl esters of 17–23 carbon atoms with zero to three unsaturations [1]. Understanding the combustion properties of these molecular structures and their interactions in blends with petroleum derived diesel fuel has been of considerable interest for the last decade. However, biodiesel compounds are difficult to study in the gas phase (fundamental fuel vapor/oxidizer experiments such as shock tube, flow reactor, jet stirred reactor, flame configurations) because of their large molecular weight and hence low vapor pressures. Thus, investigations of the kinetics of smaller molecular species that might behave combustion kinetically similar to actual biodiesel constituents have been prevalent.

Such model fuels are referred to as surrogates. A surrogate fuel is either a single molecule, or a simple mixture of several molecules [2–5] that would mimic the chemical and/or the physical properties of the fuel of interest. As a result, the oxidation kinetics of a number of different esters has been studied [6–20].

Methyl butanoate, MB (C₅H₁₀O₂) was one of the first to be proposed to emulate biodiesel reaction kinetics. Fisher et al. [6] constructed the first detailed kinetic model by assuming similarity to the oxidation kinetics of n-alkanes. This model was later tested against experimental measurements of jet-stirred reactor (JSR), variable pressure flow reactor (VPFR), and counter-flow diffusion flame speciation profiles [7]. Recently, recognizing the uniqueness of the reactivity of the methyl ester moiety, Dooley et al. [8] further developed this MB model structure. Their model was tested comprehensively against the previous experimental data [7] and the ignition delays of MB/O₂/Diluent mixtures in both a shock tube (ST) and a rapid compression machine (RCM) over the temperature range 640–1760 K. The RCM experiments at high pressure (40 atm) confirmed JSR and flow reactor measurements that showed methyl butanoate exhibits no low temperature oxidation behavior, and thus cannot be considered as an appropriate biodiesel surrogate at low temperatures.

Consequently, more recent studies recommended larger methyl esters than MB as biodiesel surrogates to emulate the negative

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temperature coefficient (NTC) behavior of actual biodiesel. HadjAli et al. [12] studied experimentally the ignition of C_4 to C_8 methyl esters in a RCM, and then studied in more detail the behavior of methyl hexanoate ($C_7H_{14}O_2$). Dayma et al. [13] also studied this particular ester in a JSR at 10 atm and confirmed the presence of NTC behavior. Based on the kinetic model of Fisher et al., Dayma et al. developed a kinetic model of methyl hexanoate and tested it against their experimental data. More recently, experimental and modeling studies have been extended to the larger methyl esters, methyl heptanoate ($C_8H_{16}O_2$) [14], methyl octanoate ($C_9H_{18}O_2$) [15] and methyl decanoate, MD ($C_{11}H_{22}O_2$) [16–23]. Most of these kinetic models for larger methyl esters have been developed based on an assumed similarity to the oxidation kinetics of n-alkanes, for which there exists a larger reaction kinetic data base. Thus in methyl ester kinetic model development to date, there has been quite a limited focus on the specific role of the methyl ester functional group. As a result, these models occasionally over-predict the reactivity of methyl ester oxidation, in the example of MD, exhibiting shorter ignition delays (Fig. 1) and higher extinction limits of diffusion flames [9].

The previous models [16–18,21–23] of MD have been developed based on analogy to n-alkane chemistry with various modifications to rate constants relating to the reactions of the methyl ester functionality. This approach has resulted in a significant ambiguity in the description of the role of methyl ester moiety. Recent experimental studies of small methyl esters have shown clearly that fuel oxidation and CO_2 formation from methyl esters depend strongly on the particular molecular structure [24]. Therefore, an accurate kinetic model for biodiesel (or its surrogates) requires a specific knowledge of the kinetics of the methyl ester moiety. As described above, although MB does not display true low temperature reactivity, a comprehensive MB kinetic model has been developed and tested by Dooley et al. [8] resulting in relatively good agreement to a broad range of experimental data. It is logical to expect that any methyl ester specific kinetic processes are accentuated in smaller esters structures. While definite fundamental knowledge gaps certainly exist, the implication of the general reproduction of detailed experimental observations by the Dooley et al. model is that the important methyl ester specific kinetic processes have been adequately described.

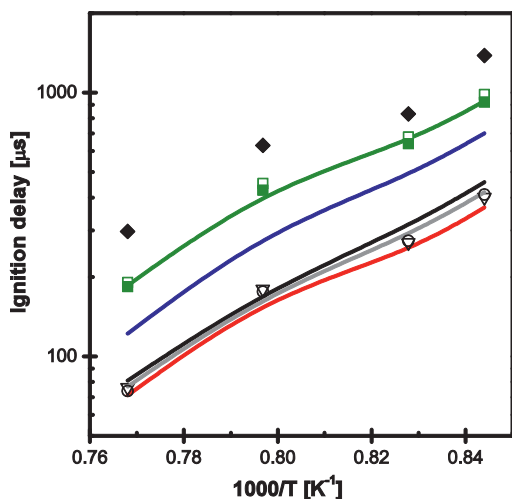


Fig. 1. Ignition delays [18] of methyl decanoate/oxygen/argon mixtures in an aerosol shock tube (◆): equivalence ratio, 0.09–0.17, fuel mole fraction, 1005–1823 ppm, and pressure, 7.57–8.03 atm. Computations with the models proposed in this study (detailed —, reduced 229 species □, reduced 529 species ■), the models of Herbinet et al. [21] (—), Herbinet et al. [22] (—), Seshadri et al. [16] (▽), Sarathy et al. [17] (—), Glaude et al. [18] (—) and Luo et al. [23] (○).

The objective of this study is to develop a kinetic model for MD, constructed by employing a similarity rule of the ester moiety from smaller methyl butanoate system to the larger MD system, and to evaluate the extent of chemical kinetic similarity between MB and MD at high temperatures. As a fundamental philosophy to model construction, we aim to utilize the rate constants and thermochemical parameter assemblies which have been derived for small methyl esters in the comprehensively tested MB kinetic model of Dooley et al. [8]. A similarity rule is applied for the estimation of rate constants and thermochemical parameters exactly as prescribed for MB to the similar MD chemistries, without any adjustment. Through this methodology, the MD kinetic model can be used to rationalize the appropriateness of the similarity rule with the hypothesis that alkyl chain length of greater than that of MB has little influence on the thermochemistry or kinetics of the ester moiety. In order to evaluate the extent of similarity in the high temperature oxidation of MB and MD a prior experimental analysis [9] is extended further. Finally, the present study evaluates and declares the fundamental knowledge gaps in methyl ester thermochemistry and reaction kinetics. The results recommend that further detailed studies on smaller methyl esters will be essential in order to construct a reliable kinetic model for bio-diesel type fuels.

2. Model construction

2.1. Methyl decanoate oxidation scheme

The kinetic model proposed here was designed from the original oxidation framework of methyl decanoate proposed by Herbinet et al. [21]. This scheme encompasses both low and high temperature kinetics of the fuel methyl ester, as well as the oxidation scheme of smaller methyl esters that may be produced from the degradation of the parent fuel. This chemical scheme was used only as a template. The rate constant parameters and thermochemical data were substituted consistently with the approach adopted in this study as described below. Necessarily, the oxidation kinetic of the smaller species (C_0 – C_5) was updated according to the recent work of Healy et al. [25].

2.2. Thermochemical data

A few recent studies deal with the estimation of the thermochemical properties of methyl (and ethyl) ester species. El-Nahas et al. [26] determined the Bond Dissociation Energies (BDEs) of MB and Ethyl Propanoate (EP) through *ab initio* computations (complete basis set method CBS-QB3). Osmont et al. [27,28] proposed a new computational approach to estimate the enthalpy of formation of a large set of hydrocarbons, including large methyl esters. Both groups derived the BDEs of the methyl (ethyl) ester moiety from their computational results. Sumathi and Green [29] worked on oxygenated fuels (alcohols, esters, ethers and carboxylic acids) and proposed new estimates for methyl ester group contributions, derived from *ab initio* computations (complete basis set method CBS-Q). The BDEs proposed by these three groups are presented in Table 1. Reasonable consistency, within 2–3 kcal mol⁻¹, is observed between the studies, but some important uncertainties and significant differences to equivalent alkane parameters are apparent. Especially, the C–H BDE of the methyl ester group falls in the range 98.95–100.5 kcal mol⁻¹, which is lower by 0.7–2.2 kcal mol⁻¹ than a primary C–H bond as in n-alkanes. The BDE of the C–H bond α to the carbonyl position has a value (92.0–94.2 kcal mol⁻¹) intermediate between that of a secondary C–H bond (\sim 98.5 kcal mol⁻¹) and a secondary allylic C–H bond (\sim 85.6 kcal mol⁻¹). A greater consensus of the thermochemical

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