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Ignition behavior of pure and blended methyl octanoate, *n*-nonane, and methylcyclohexane

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Abstract

Excited-state species profiles and ignition delay times were obtained under dilute conditions (99% Ar) using a heated shock tube for methyl octanoate ($C_9H_{18}O_2$), *n*-nonane (*n*-C_9H_{20}), and methylcyclohexane (MCH) over a broad range of temperature and equivalence ratio ($\phi = 0.5$, 1.0, 2.0) at pressures near 1 and 10 atm. Measurements were then extended to include two ternary blends of the fuels using 5% and 20% (vol.) of the methyl ester under stoichiometric conditions. Using three independently validated chemical kinetics mechanisms, a model was compiled to assess the influence of methyl ester concentration on ignition delay times of the ternary blends. Under near-atmospheric pressure, ignition delay times were of the following order for the pure fuels: methyl octanoate < *n*-nonane < methylcyclohexane. Experimental results indicate that the ignition behavior of the higher-order methyl ester approaches that of the higher-order linear alkane with increased pressure regardless of equivalence ratio. Methyl octanoate also displayed significantly lower pressure dependence relative to the linear alkane and the cycloalkane species. Both of these results are supported by model calculations. Blending of methyl octanoate with *n*-nonane and methylcyclohexane impacted ignition delay time results more strongly at 1.5 atm, yet had only a small effect near 10 atm for temperatures above 1400 K. The study provides the first shock-tube data for a ternary blend of a linear alkane, a cycloalkane, and a methyl ester. Ignition delay time measurements for the C_9:0 methyl ester were also measured for the first time.
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Keywords: Methyl octanoate; *n*-Nonane; Methylcyclohexane; Biofuel blend; Shock tube

1. Introduction

Largely due to the high volumetric percentage (40–60%) of higher-order normal alkanes in transportation fuels relative to more-complex fuel molecules, a significant amount of experimental combustion data are available for this hydrocarbon class which has led to the development of several chemical kinetics models [1–7]. Cycloalkanes are also abundant in diesel and aviation fuels, ranging from 30% to 50%, and species such as cyclohexane, methyl-, and ethyl-cyclohexane have been the focus of several experimental and modeling studies [8–22]. Within this class, methylcyclohexane (MCH) has been paid significant attention as a representative in surrogate fuel modeling. Methyl esters ($R{-}C({=}O){-}OCH_3$) are of interest as a biofuel supplement to petroleum-based transportation fuels, yet the chemical interplay of this species with linear and cyclic alkanes has yet to be studied in detail with respect to blending effects.

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The understanding of biofuel combustion by studying blending effects in detail is essential because practical utilization of biofuels will almost always be as a blend with petroleum distillate fuels. Although alternative and petroleum-based fuels have been studied individually, fundamental chemistry of biofuel blends cannot be captured simply through combination of the pure-fuel combustion behaviors. Therefore, measurements of blended biofuel oxidation are needed. Furthermore, a chemical kinetics model capable of describing blending effects on combustion behavior is necessary for engine designers to include biofuels in the development of next-generation, fuel-flexible engines.

Methyl ester species from biological sources have relatively high molecular weights. Çanakçi and Van Gerpen [23] analyzed the composition of methyl ester species within various organic compounds and found that methyl pentadecanoate ($C_{16}H_{32}O_2$) and methyl heptadecanoate ($C_{18}H_{36}O_2$) occupy the largest mass-percentage of saturated methyl esters. While higher-molecular-weight, saturated methyl esters comprise biological oils, experiments and modeling using smaller methyl ester species are less difficult to perform and require considerably lower computational demands while compromising only the size of the alkyl chain attached to the ester group.

Experimental data on higher-molecular-weight saturated methyl esters approaching those found in biological sources have recently been reported from jet-stirred reactor [24–26], diffusion-flame [27–29], and RCM experiments [30]. Higher-order saturated methyl esters ranging from C_7 to C_{10} have been the subject of recent experiments, and several chemical kinetics models for these species have been developed [31–34]. Battin-Leclerc performed a thorough analysis on elementary reactions involving ethers, esters, and other species utilized in biofuel surrogates [35] and, more recently, has composed a seminal review concerning chemical kinetics modeling of biofuel combustion [36]. Biet et al. reported computational findings using automatic mechanism generation (EXGAS) in which saturated methyl esters above methyl octanoate (C_9:0) show strong similarity with respect to both low- and intermediate-temperature reactivity and ignition behavior above 1000 K [32]. Therefore, using this assessment, methyl octanoate can be used as a representative for the higher-order methyl ester species common to biological oils, tallow, and other biofuel sources, while placing a ceiling on the number of species and reactions requisite for a detailed mechanism.

Shock-tube studies on methyl esters have been performed on lower-molecular weight esters [37–39], yet experimental data on species with carbon number greater than 9 are relatively scarce. Garner and Brezinsky [40,41] were the first to report methyl octanoate measurements in a shock tube, performing speciation measurements from pyrolysis and oxidation experiments at elevated pressures with an emphasis on NO_x formation mechanisms. Characterization of yields from shock-tube and jet-stirred reactor experiments led to the development of a chemical kinetics mechanism. Ignition delay times from methyl decanoate combustion in air near 15 atm have recently been reported [42].

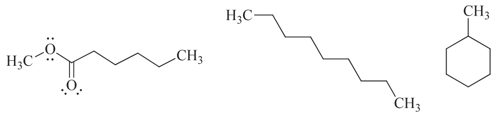

Fig. 1. Molecular structures of methyl octanoate (MO), *n*-nonane, and methylcyclohexane (MCH).

To date, shock-tube experiments have involved only single-component studies of the species of interest in the current work. The present study therefore focuses on blending effects of conventional hydrocarbons (*n*-alkane, cycloalkane) with a methyl ester, measured for the first time under shock-tube conditions. Methyl octanoate ($C_9H_{18}O_2$, MO), *n*-nonane (n-C_9H_{20}), and methylcyclohexane ($(C_6H_{11})-CH_3$, MCH) were employed to represent methyl ester, *n*-alkane, and cycloalkane classes, respectively (Fig. 1).

Discussed in the sections below are the experimental and modeling approaches undertaken. Results of ignition delay times are then discussed, with correlations and pressure dependencies presented for constituent species. The chosen ternary blends use concentrations of 5% and 20% (vol.) of the methyl ester, which are within the limits of addition to diesel fuel as discussed by Alptekin and Çanakçi [43], where concentrations up to 20% were found not to compromise properties such as density and viscosity. A discussion on the impact of methyl ester concentration on ignition then ensues, and results of a first-generation chemical kinetics model compiled to analyze blending effects are presented.

2. Experimental approach

Two shock tube facilities were employed for the experiments, and all of the tests were performed under highly dilute conditions (99% Ar) to minimize unsteady thermodynamic conditions during chemical reaction. The heated shock tube described by Rotavera and Petersen [44] was employed for all measurements excluding those involving MCH for which the high-pressure shock tube facility described by de Vries et al. [45] was utilized. Both facilities make use of inner diameters large enough, 10.9 cm and 15.0 cm, respectively, such that boundary layer effects are minimized within the timeframe of the experiment. Additionally, overlapping results are