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The high-temperature autoignition of biodiesels and biodiesel components

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ABSTRACT

Ignition delay time measurements are reported for two reference fatty-acid methyl ester biodiesel fuels, derived from methanol-based transesterification of soybean oil and animal fats, and four primary constituents of all methyl ester biodiesels: methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate. Experiments were carried out behind reflected shock waves for gaseous fuel/air mixtures at temperatures ranging from 900 to 1350 K and at pressures around 10 and 20 atm. Ignition delay times were determined by monitoring pressure and ultraviolet chemiluminescence from electronically-excited OH radicals. The results show similarity in ignition delay times for all methyl ester fuels considered, irrespective of the variations in organic structure, at the high-temperature conditions studied and also similarity in high-temperature ignition delay times for methyl esters and *n*-alkanes. Comparisons with recent kinetic model efforts are encouraging, showing deviations of at most a factor of two and in many cases significantly less.

1. Introduction

Biodiesel fuels offer reductions in important pollutant emissions (carbon monoxide, unburned hydrocarbons, and particulates) when used as alternatives to petroleum-based fuels in diesel engines and offer a potential pathway to reduced green house gas emissions from the light- and heavy-duty transportation sectors [1]. In order to develop high-efficiency, clean, and robust engines operating on biodiesel, an understanding of biodiesel combustion characteristics is desired, including the fundamental chemical kinetic behaviors of biodiesels. Among macroscopic chemical kinetic properties, the ignition delay time, the time delay prior to ignition for a fuel/oxidizer mixture at specified conditions, has drawn special attention since it describes a process of fundamental importance to diesel engines, autoignition. Autoignition initiates combustion in diesel and other compression-ignition engines; hence, its prediction is important for the design of these engines with optimized performance and minimized pollutant emissions.

There are a variety of experimental methods available to study autoignition, including shock tubes, rapid compression machines, and flow reactors. While each method has its advantages and drawbacks, shock tubes have been widely used for the following reasons. First, the shock tube provides nearly stationary, spatially uniform, and homogeneous conditions behind the reflected shock wave, which are amenable to simplified zero-dimensional modeling. Second, conditions similar to practical combustion systems can be obtained in shock tubes including elevated pressures, a wide range of temperatures, and fuel/oxidizer mixtures. Third, the shock tube provides a relatively simple experimental platform offering highly reproducible experimental conditions for which quantitative measurements of chemical kinetic behaviors can be realized. Here we present a study of biodiesel autoignition using the shock tube technique.

1.1. Biodiesel composition

Biodiesels are mixtures of long-chain mono-alkyl esters formed via the transesterification of fatty acids. Methanol is typically used in the transesterification process yielding fatty-acid methyl esters, which when derived from most feedstocks have carbon chains between 14 and 20 carbon atoms with zero to three double bonds found in the carbon chain. See Fig. 1 for the organic structures of several methyl esters found in large quantities in biodiesels and Table 1 for a compositional characterization of methyl ester biodiesels synthesized from different feedstocks [2]. The methyl ester components are described using a standard nomenclature for their organic structure, CXX:Y, where XX represents the length of the carbon chain attached to the methyl ester functionality and Y is the number of double bonds within the carbon chain.

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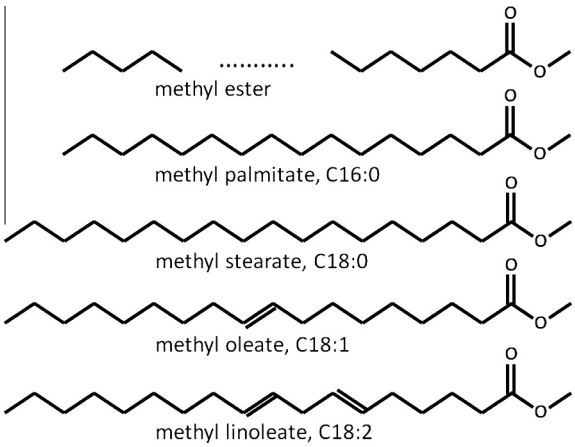

Fig. 1. Organic structure of methyl esters.

Table 1
Typical composition of biodiesels [2].

Oil feedstock	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3
Rapeseed	–	4	–	1	64	22	8
Sunflower	–	6	–	3	17	74	–
Safflower	–	9	–	2	12	78	–
Soybean	–	11	–	5	23	52	8
Lard	1–2	28–30	–	12–18	40–50	7–13	–
Tallow	3–6	24–32	–	20–25	37–43	2–3	–
Yellow grease	2	23	4	13	44	7	1
Brown grease	2	23	3	13	42	12	1

As shown in Table 1, biodiesels synthesized via methanol-based transesterification of vegetable oils (rapeseed, sunflower, safflower, and soybean), animal fats (tallow and lard), and waste grease (yellow and brown grease) contain four predominate methyl esters (structures given in Fig. 1): methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), and methyl linoleate (C18:2).

The number of double bonds in the methyl ester carbon chain, or degree of saturation, influences the ignition quality of neat methyl esters or multi-component methyl ester biodiesel in diesel engines, with more highly saturated methyl esters being more reactive than less saturated methyl esters. The degree of variation in reactivity has been demonstrated through the variation in the cetane number (CN). For example, fully saturated methyl stearate has a CN = 76, while methyl oleate (one double bond) and methyl linoleate (two double bonds) have CN = 57 and 37, respectively [3]. Cetane numbers ranging from 44 to 70 have been reported for multi-component biodiesels derived from vegetable oils and animal fats [4].

1.2. Previous chemical kinetic studies

As shown in Table 1, the compounds found in biodiesels are large in carbon number (C14+), complicating kinetic modeling due to the numerous species and reaction pathways needed to describe their oxidation. The large size of biodiesel compounds also complicates gas-phase experiments, necessary to elucidate the chemical kinetic behaviors unique to biodiesels, due to their low vapor pressures. Therefore, most kinetic investigations performed to date have focused on smaller surrogate compounds containing the chemical functionalities found in biodiesel but without the long carbon chain. For example, methyl butanoate (C4:0) has been the subject of a number of studies (e.g., [5,6]) and a number of recent studies have investigated intermediate-sized methyl ester biodiesel surrogates, including methyl decanoate (C10:0) (e.g., [7,8]).

Fewer studies have focused on the larger compounds found in biodiesel; however, Dagaut et al. [9] performed jet-stirred reactor oxidation studies on rapeseed biodiesel, Marchese et al. [10] studied the ignition of methyl oleate and commercial soy biodiesel fuel droplets, and Bax et al. [11] have studied methyl oleate oxidation in a jet-stirred reactor. Relevant to the present study, Campbell et al. [12] performed the first shock tube autoignition study of biodiesel compounds, measuring ignition delay times using an aerosol shock tube technique for methyl oleate and methyl linoleate at dilute conditions (4% O_2), pressures of 3.5 and 7.0 atm, and temperatures from 1100 to 1400 K. In a following study Campbell et al. [13] made measurements of ignition delay times for methyl decanoate, laurate, myristate, and palmitate and a methyl oleate/FAME blend at similar high-temperature (1026–1388 K) argon–dilute conditions.

Detailed kinetic models have been developed by several groups for large biodiesel components. Detailed kinetic models containing low- and high-temperature oxidation chemistry for methyl palmitate, stearate, oleate, linoleate, and linolenate (C18:3) have been reported by Westbrook et al. [14,15] and for methyl palmitate and stearate by Herbinet et al. [16]. Saggese et al. [17] have reported kinetic models developed using a reaction and species lumping approach for saturated and unsaturated large biodiesel compounds, including methyl palmitate, stearate, oleate, linoleate, and linolenate. When used in combination, models from these authors can describe biodiesels comprised of mixtures of methyl esters (e.g., Table 1). Golovitchev and Yang [18] have reported a highly reduced kinetic model for rapeseed methyl ester biodiesel and diesel engine simulations performed with their model. See the reviews of Coniglio et al. [19] and Violi et al. [20] for details regarding kinetic modeling for biodiesel compounds.

To the authors' knowledge, there have been no previous fundamental studies of autoignition for multi-component biodiesel fuels, other than those that have been performed in engines, and the only one previous autoignition study for the predominate biodiesel components given in Fig. 1 and Table 1, that of Campbell et al. [12,13] who investigated methyl oleate and methyl linoleate autoignition at dilute conditions. Here we report shock tube ignition delay time measurements carried out at elevated-pressures and lean to stoichiometric fuel/air conditions for the four biodiesel components shown in Fig. 1, methyl palmitate, stearate, oleate, and linoleate, as well as for two reference multi-component methyl ester biodiesels, derived from soybean oil and animal fats.

2. Experimental method

Shock tube ignition delay time measurements were performed in the Rensselaer heated high-pressure shock tube (5.7 cm inner diameter, 2.59 m long driver, 4.11 m long driven) [21]. There are five points relating to the shock tube experiments described here: shock tube heating, fuel/air mixture preparation, determination of post-shock conditions, measurement of ignition delay times, and the fuels studied and experimental conditions considered.

2.1. Shock tube heating

The shock tube and mixing vessel, where gas-phase fuel/oxidizer mixtures were prepared prior to experiments, were uniformly heated to temperatures of 200 °C with an electronically controlled external electrical resistance heating system to ensure full vaporization of the biodiesels and components used in this study. The driven section temperature profiles were measured regularly by translating a thermocouple along the inner wall of the driven section to ensure uniformity prior to performing experiments. The heating system provides uniformity within ±3–4 °C at