



Experimental study of the autoignition of $C_8H_{16}O_2$ ethyl and methyl esters in a motored engine

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ABSTRACT

Autoignition of two biodiesel surrogates, methyl heptanoate and ethyl hexanoate, was studied in a motored CFR engine at an equivalence ratio of 0.25 and an intake temperature of 155 °C. The engine compression ratio was gradually increased from the lowest point (4.43) to the point where significant high temperature heat release (HTHR) occurred. Within the test range of this work, both of the two esters exhibited evident cool flame behavior. At the same compression ratio, methyl heptanoate was observed to have both an earlier onset and a higher magnitude of low temperature heat release (LTHR) than ethyl hexanoate, indicating that methyl heptanoate is more reactive in the low temperature region than ethyl hexanoate. GC–MS analyses of the reaction intermediates from the oxidation of the two esters showed that the alkyl chain of fatty acid esters experiences the typical paraffin-like low temperature oxidation sequence. Based on the observations from GC–MS analyses, major low temperature oxidation pathways of ethyl hexanoate are proposed in this work. Also, it is observed that the abstraction of H-atoms on the α -carbon of the ester carbonyl group plays an important role in the oxidation of fatty acid esters. In addition, the identification of hexanoic acid among the reaction intermediates from low temperature oxidation of ethyl hexanoate together with the observation of more fuel carbon being converted to C_2H_4 during ethyl hexanoate oxidation than during methyl heptanoate oxidation provide evidence for the existence of the six-centered unimolecular elimination reaction during low temperature oxidation of ethyl esters.

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1. Introduction

Biodiesel is a renewable diesel fuel that is derived from vegetable oils or animal fats by transesterification with an alcohol. It is composed largely of long-chain fatty acid esters with the aliphatic chains of 16–18 carbon atoms. Since it can reduce dependence on fossil fuels and can also provide significant environmental benefits, biodiesel has become a promising alternative to petroleum-derived diesel fuels. The effects of biodiesel on engine performance and emissions have been extensively investigated by researchers in recent years [1–7]. However, despite the extensive engine combustion studies, there is still a lack of fundamental understanding of the combustion chemistry of fatty acid esters. In particular, few studies have been focused on the low temperature chemistry of fatty acid esters, which is of great importance for the application of biodiesel in modern engine designs that employ low temperature combustion strategies.

Due to the complexity of biodiesel compounds, researchers have been selecting small esters as surrogates for biodiesel to perform

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kinetics studies. Thus far, methyl butanoate ($C_5H_{10}O_2$) is the most commonly used model compound for biodiesel. The oxidation of methyl butanoate has been studied in jet-stirred reactors [8,9], variable pressure flow reactors [8], shock tubes [10–12] and rapid compression machines [12,13]. Since methyl butanoate has the essential structure of biodiesel compounds, it has been used as a surrogate for biodiesel to study the soot suppression effect of biodiesel. However, for the purpose of studying the low temperature chemistry of biodiesel compounds, methyl butanoate may not be a good candidate due to its short alkyl chain. The lack of low temperature reactivity of methyl butanoate has been reported by Gail et al. [8] in their variable pressure flow reactor experiments (equivalence ratio = 0.35, 1, pressure = 1.266 MPa) and by Dooley et al. [12] in their rapid compression machine study, which further suggests that methyl butanoate is not a good model compound for biodiesel in terms of low temperature oxidation since long-chain fatty acid esters that comprise biodiesel are expected to exhibit pronounced cool flame behavior.

Therefore, it is necessary to select an ester that has a longer alkyl chain to represent biodiesel for low temperature oxidation study. Dagaut et al. [14] investigated the oxidation of rapeseed oil methyl esters (RME) in a jet-stirred reactor (temperature = 800–1400 K; equivalence ratio = 0.25–1.5) and used *n*-hexadecane as a surrogate

to model the oxidation of RME. Overall, there is a good agreement between the experimental and the modeling results in terms of the relative importance of olefins and the overall reactivity of RME. However, the early CO₂ production observed from the experiments is not reproduced from the high-temperature model. Szybist et al. [15] selected methyl decanoate as a surrogate for biodiesel and studied its premixed ignition behavior in a motored engine. Pronounced low temperature heat release (LTHR) was observed during methyl decanoate oxidation in their experiments, indicating methyl decanoate could potentially be a suitable model compound for biodiesel. Also, they observed the formation of CO₂ at the very early stage of methyl decanoate oxidation. Since CO₂ formation from CO oxidation is significantly inhibited while there are still appreciable amounts of hydrocarbon present [16], the authors attributed the observed early CO₂ production to the direct CO₂ removal from the ester functional group. Zhang et al. [17] further studied the autoignition behavior of four C₉ fatty acid esters with different degrees of unsaturation in a motored engine. It was observed that the presence of a double bond in the aliphatic chain of fatty acid esters significantly suppresses the extent of LTHR. Also, the magnitude of LTHR reduces as the double bond moves toward the center of the aliphatic chain. Recently, Herbinet et al. [18] developed a kinetic mechanism for methyl decanoate oxidation that includes detailed low temperature chemistry based on the previously established *n*-heptane [19], iso-octane [20] and methyl butanoate [21] oxidation mechanisms. With the alkyl chain of 10 carbon atoms, methyl decanoate has the advantage of better representing biodiesel in the low temperature region than methyl butanoate. However, detailed mechanism of methyl decanoate consists of 3036 species and 8555 reactions, which makes the direct incorporation of this mechanism into computational simulations of complex reaction systems (e.g., internal combustion engine systems, etc.) impossible without substantial reduction of the size of the mechanism. Furthermore, with this large size of mechanism, even zero-dimensional (0-D) simulations of methyl decanoate oxidation can be very time-consuming, as observed by Herbinet et al. [18] in their simulation of methyl decanoate oxidation using the 0-D, single-zone internal combustion engine model of CHEMKIN. Hence, it is of interest to find a model compound for biodiesel that not only exhibits evident low temperature oxidation behavior, but also has a chemical kinetic mechanism whose size is manageable for computational purposes.

Dayma et al. [22] developed a kinetic oxidation mechanism for methyl hexanoate and studied its oxidation in a jet-stirred reactor at a pressure of 10 atm and a constant residence time of 1 s with the temperature range of 500–1000 K and the equivalence ratio range of 0.5–1.5. Within the test conditions in their study, the kinetic modeling results give overall good agreement with the experimental results. Reaction path analysis showed that the oxidation behavior of methyl hexanoate is mainly controlled by the weakness of the C–H bond on carbon No. 2 (refer to Fig. 1). The quantum calculations on the thermochemistry of C–C and C–H bond breakage in fatty acid methyl esters performed by Osmont et al. [23] further show that

the abstraction of H-atoms on the α -carbon of the carbonyl group is favored among the C–H bond scissions. Recently, Hadjali et al. [24] examined the low temperature autoignition behavior of a series of C₄–C₈ fatty acid esters in a rapid compression machine within the pressure range of 4–20 bar and post-compression temperature range of 600–850 K. Among the esters tested, methyl hexanoate was selected for detailed investigation of its low temperature oxidation schemes. Based on the GC–MS analyses of the reaction intermediates from methyl hexanoate oxidation, it was observed that the alkyl chain of methyl hexanoate experiences the low temperature oxidation sequence that is typical of paraffins.

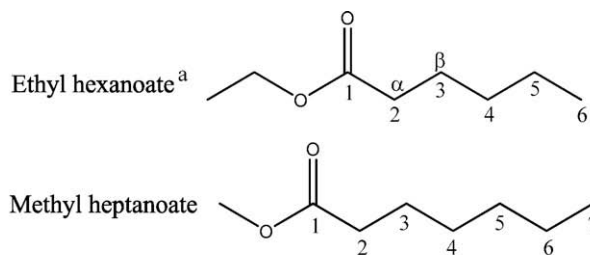
In addition to the studies on the oxidation of methyl esters, the oxidation of ethyl esters have also drawn the interest of researchers. Ethyl propanoate (EP) has been used as a surrogate for ethyl esters for kinetics study [10,25,26]. Schwartz et al. [25] studied the effect of doping 5000 ppm of ethyl propanoate in a methane/air co-flowing non-premixed flame on the change of the intermediate hydrocarbon species concentrations. Based on the experimental results, they found that six-centered unimolecular dissociation is the primary step for ethyl propanoate decomposition ($EP \leftrightarrow C_2H_5COOH + C_2H_4$). Metcalfe et al. [10,26] further developed a detailed chemical kinetic mechanism for ethyl propanoate oxidation and examined it in a shock tube experiment (temperature: 1100–1670 K; pressure: 1 and 4 atm; equivalence ratio: 0.25, 0.5, 1.0, 1.5) [10] and a jet-stirred reactor experiment (temperature: 750–1100 K; pressure: 10 atm; equivalence ratio: 0.3, 0.6, 1.0, 2.0). Overall, good agreement between the simulation results and the experimental results has been observed. It is also noted by the authors that the production of propanoic acid and ethylene through six-centered unimolecular dissociation of ethyl propanoate is an important step in the oxidation of ethyl propanoate.

The overall goal of this work is to investigate the autoignition behavior of ethyl hexanoate and methyl heptanoate under a fuel-lean condition in an engine environment and to examine the applicability of the two esters as surrogates for biodiesel in studies of low temperature oxidation. Particularly, it is of interest to explore the major reaction pathways of ethyl hexanoate in the low temperature region. In addition, this work also aims to examine the impact of ester functionality on fuel ignition behavior.

2. Experimental

2.1. Test fuels

In the present study, two C₈H₁₆O₂ esters, methyl heptanoate and ethyl hexanoate, were selected as the surrogates for biodiesel in the motored engine experiments. The molecular structures of these two alkyl esters are shown in Fig. 1. Also, *n*-heptane was used as the selected *n*-alkane for the purpose of comparing its ignition behavior with that of the alkyl esters under the same test conditions.



^a The carbon atom of the carbonyl group is carbon no. 1. Carbon no. 2 corresponds to the α -carbon of the carbonyl group.

Fig. 1. Molecular structures of methyl heptanoate and ethyl hexanoate.

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