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Premixed ignition behavior of C₉ fatty acid esters: A motored engine study

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ABSTRACT

An experimental study on the premixed ignition behavior of C₉ fatty acid esters has been conducted in a motored CFR engine. For each test fuel, the engine compression ratio was gradually increased from the lowest point (4.43) to the point where significant high temperature heat release (HTHR) was observed. The engine exhaust was sampled and analyzed through GC-FID/TCD and GC-MS. Combustion analysis showed that the four C₉ fatty acid esters tested in this study exhibited evidently different ignition behavior. The magnitude of low temperature heat release (LTHR) follows the order, ethyl nonanoate > methyl nonanoate ≫ methyl 2-nonenoate > methyl 3-nonenoate. The lower oxidation reactivity for the unsaturated fatty acid esters in the low temperature regime can be explained by the reduced amount of six- or seven-membered transition state rings formed during the oxidation of the unsaturated esters due to the presence of a double bond in the aliphatic chain of the esters. The inhibition effect of the double bond on the low temperature oxidation reactivity of fatty acid esters becomes more pronounced as the double bond moves toward the central position of the aliphatic chain. GC-MS analysis of exhaust condensate collected under the engine conditions where only LTHR occurred showed that the alkyl chain of the saturated fatty acid esters participated in typical paraffin-like low temperature oxidation sequences. In contrast, for unsaturated fatty acid esters, the autoignition can undergo olefin ignition pathways. For all test compounds, the ester functional group remains largely intact during the early stage of oxidation.

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1. Introduction

Despite the extensive studies on the combustion and emissions characteristics of biodiesel in diesel engines [1–8], the ignition chemistry of biodiesel is still not well-understood. Since large fuel molecules, such as biodiesel compounds, pose considerable challenges to kinetic modeling, researchers have been selecting smaller methyl esters as surrogates for biodiesel to perform experimental and kinetic modeling studies [9–14].

Fisher et al. [9] developed a detailed kinetic model for methyl butanoate (C₅H₁₀O₂), which was considered “large enough to allow fast RO₂ isomerization reactions important in the low-temperature chemistry that controls the autoignition under the conditions found in diesel engines.” Gail et al. [10] slightly revised the model developed by Fisher et al. and examined it over a wide range of combustion conditions. In their variable pressure flow reactor experiments (equivalence ratio = 0.35, 1, pressure = 1.266 MPa), no evident negative temperature coefficient (NTC) behavior was observed, suggesting that methyl butanoate is not an ideal surrogate for biodiesel in terms of autoignition characteristics since long-chain fatty acid esters that comprise biodiesel are expected

to exhibit pronounced low temperature oxidation behavior. Szybist et al. [11] performed an ignition study for methyl decanoate (C₁₁H₂₂O₂) in a motored engine. They observed evident low temperature heat release (LTHR) during the oxidation of methyl decanoate, which indicates that the long alkyl chain of the methyl ester experiences the classic paraffin-like low temperature oxidation process [15]. They also reported that CO₂ was produced at the very early stage of oxidation. It was then speculated by the authors that the early CO₂ production during the low temperature oxidation of methyl decanoate is due to the direct CO₂ formation from the ester group, as CO₂ formation from CO oxidation is significantly inhibited when there are still sufficient amounts of hydrocarbons present [16]. The phenomenon of early CO₂ formation during oxidation of fatty acid methyl esters was also observed by Dagaut et al. [17] in jet-stirred reactor experiments for the oxidation of rapeseed oil methyl esters (RME). They also suggested that the early CO₂ production mainly comes from the pyrolysis of the ester functional group. Buchholz et al. [18] studied the molecular structure effects of dibutyl maleate (an oxygenate that contains two ester functional groups per fuel molecule) on soot emissions in a direct injection (DI) diesel engine by using carbon-14 isotope tracing. Their experimental results showed that the carbon atoms in the ester carbonyl groups of dibutyl maleate (DBM) did not contribute to soot formation. Instead, those carbon atoms were found to reside

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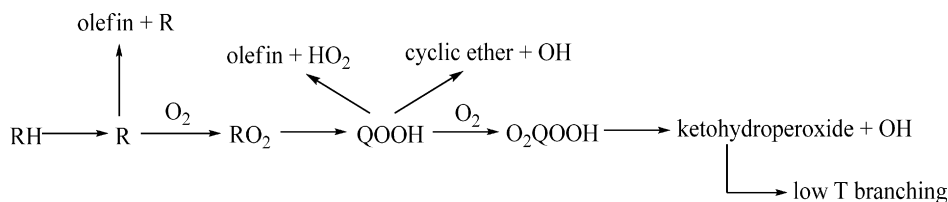


Fig. 1. Primary oxidation reaction pathways for methyl decanoate suggested by Herbinet et al. [20].

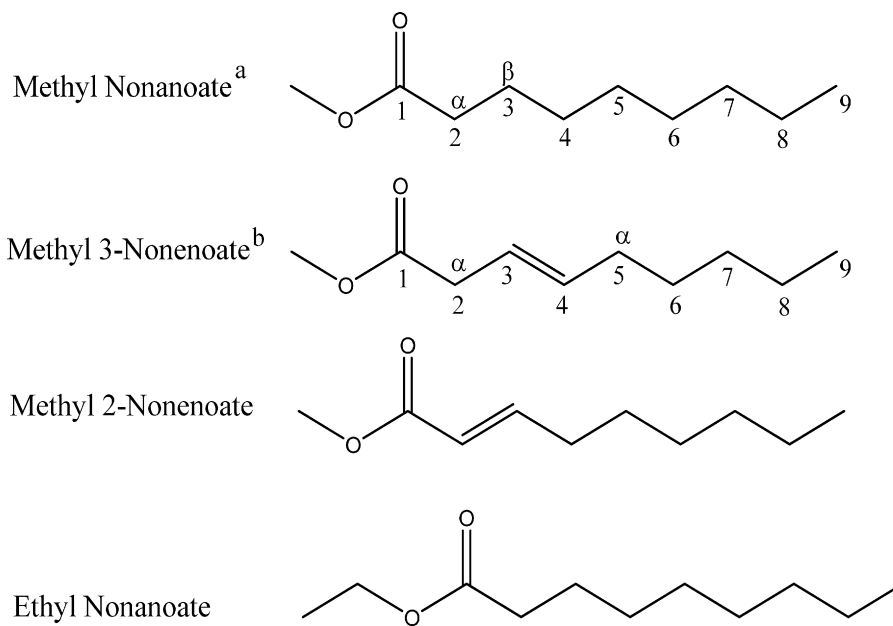


Fig. 2. Molecular structures of the C_9 fatty acid esters tested in this study. ^aThe carbon atom of the carbonyl group is carbon no. 1. Carbon no. 2 corresponds to the α -carbon of the carbonyl group. ^bThe α -carbons of the ethylenic bond correspond to the carbon no. 2 and carbon no. 5 for methyl 3-nonenoate.

entirely in the exhaust CO_2 , indicating that the $\text{C}=\text{O}$ bond in the ester functional group of DBM does not break during combustion.

More recently, Dayma et al. [19] studied the oxidation of methyl hexanoate in jet-stirred reactor (JSR) experiments at 10 atm and a constant residence time of 1 s under both fuel-lean and fuel-rich conditions within the temperature range of 500–1000 K. Furthermore, a kinetic model for methyl hexanoate oxidation was developed by the authors, which gives good agreement with the experimental results from the JSR. Reaction path analysis indicates 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. 2) over the temperature and pressure range that was studied.

To provide a kinetic model for a methyl ester that can more accurately represent practical biodiesel molecules, Herbinet et al. [20] developed a detailed kinetic mechanism for methyl decanoate oxidation based on the previous *n*-heptane [15], iso-octane [21] and methyl butanoate [9] oxidation mechanisms. In their mechanism, the primary oxidation reaction pathways for methyl decanoate are shown in Fig. 1.

At high temperature, the main reaction pathway proceeds through β -scission of the alkyl-ester radicals, producing olefins and smaller alkyl-ester radicals. The low temperature oxidation sequence is initiated by the addition of O_2 to the alkyl-ester radicals. Subsequently, the peroxy alkyl-ester radicals (RO_2) experience isomerization to form hydroperoxy alkyl-ester radicals (QOOH). The hydroperoxy alkyl-ester radicals can then decompose into either unsaturated esters and hydroperoxy radicals or cyclic ether methyl esters and hydroxyl radicals. Alternatively, the hydroperoxy alkyl-ester radicals can undergo another attack by O_2 , yielding ketohydroperoxides and hydroxyl radicals via isomerization. The

decomposition of ketohydroperoxides leads to the formation of carbonyl radicals and additional hydroxyl radicals. As the decomposition of one molecule of stable ketohydroperoxide yields at least two radical species, low temperature chain branching is initiated at this stage.

Since biodiesel is mainly composed of fatty acid esters with different degrees of unsaturation, it is important to understand the impact of the presence of double bonds on the oxidation behavior of fatty acid esters. Gaíl et al. [22] recently studied the oxidation of methyl 2-butenoate ($\text{C}_5\text{H}_8\text{O}_2$) and methyl butanoate ($\text{C}_5\text{H}_{10}\text{O}_2$) in a jet-stirred reactor (JSR) and under counterflow flame conditions. In the JSR experiments (equivalence ratio = 0.375, 0.75, 1.0, pressure = 1 atm and residence time = 0.7 s), the two esters were observed to exhibit similar reactivity and most of the stable products from the oxidation of the two esters were the same. Osmont et al. [23] studied the thermochemistry of C–C and C–H bond breakings in fatty acid methyl esters by applying density functional theory quantum calculations. According to their calculations, for monounsaturated fatty acid methyl esters, the abstraction of H atoms on the α -carbon of the ethylenic bond (refer to Fig. 2) is preferred among the C–H bond scissions and the breakage of the C–C bonds β to the ethylenic bond is favored among the C–C bond breakings.

The objectives of the current study are to understand the ignition chemistry of fatty acid esters with different degrees of unsaturation and to compare the ignition behavior between fatty acid esters produced from different alcohols under practical engine conditions. Also, it is of interest to get a better understanding of the primary reaction paths responsible for the early CO_2 production during low temperature oxidation of fatty acid esters.

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