

Low Temperature Autoignition of $C_8H_{16}O_2$ Ethyl and Methyl Esters in a Motored Engine

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Need for Fundamental Understanding of Unconventional Fuels

2006 BRN Workshop on Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels identified a single over-arching grand challenge:

“the development of a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications.”

Second Generation and Optimal Biodiesel

- ❑ Howell (DEER 2007) pointed to optimizing the fatty acid ester distribution around mono-unsaturated esters
- ❑ Knothe (*Energy & Fuels*, 2008) recommended genetic modification of the fatty acid profile to fuel property issues simultaneously. Methyl palmitoleate and esters of decanoic acid are strong candidates for improving fuel properties besides methyl oleate
- ❑ Kinney and Clemente (*Fuel Processing Technology*, 2005) demonstrated that biotechnology can be used to shape the genetics of soybeans to optimize soybean oil for engine performance



Background

- ❑ Lack of fundamental understanding of the combustion chemistry of fatty acid esters
- ❑ Few studies have been focused on the low temperature chemistry of fatty acid esters, which is relevant to application of biodiesel in modern engine designs that employ low temperature combustion strategies
- ❑ Detailed chemical mechanism of long chain fatty acid esters (e.g. methyl decanoate) may pose considerable computational challenges for kinetic modeling studies in engine applications
- ❑ Need to find model compounds for biodiesel that not only exhibit evident low temperature oxidation behavior, but also have chemical kinetic mechanisms whose sizes are manageable for computational purposes.

- ❑ Kinetic mechanisms published for methyl butanoate (various authors) and methyl decanoate (Herbinet, Pitz, Westbrook, *Combust. Flame*, 2008)
- ❑ Comparisons of ignition characteristics of methyl decanoate with Fischer-Tropsch diesel and conventional diesel fuels (DEER 2006 and in Szybist, Boehman, Haworth, Koga, *Combust. Flame*, 2007)
- ❑ Examination of C9 fatty acid esters (Zhang, Yang and Boehman, *Combust. Flame*, 2009)

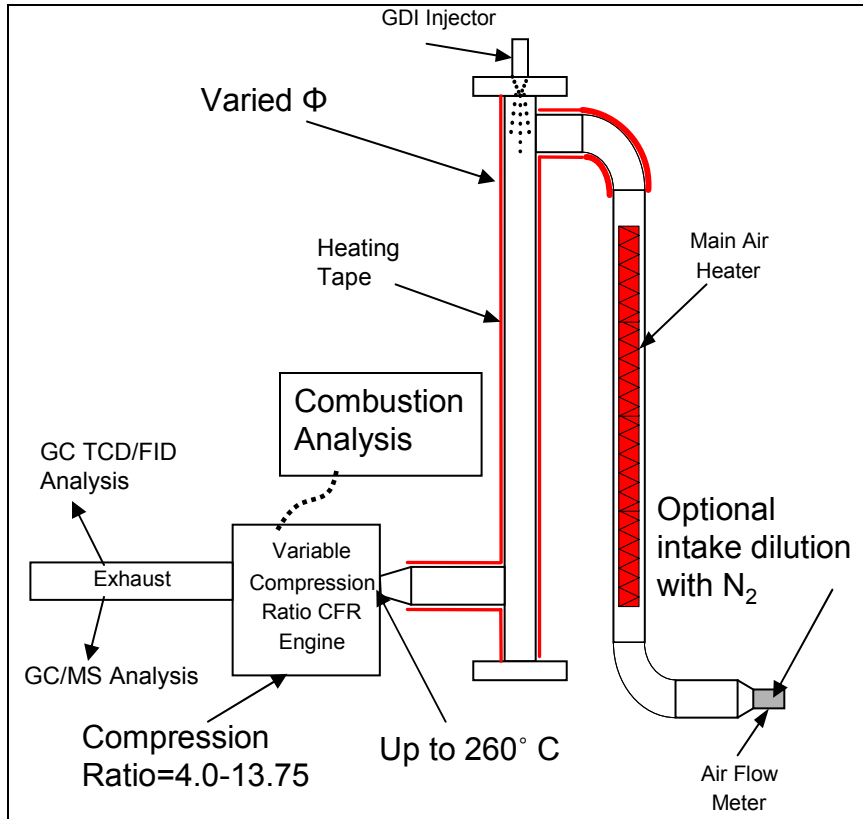
Objectives

- ❑ Investigate the premixed ignition behavior of fatty acid methyl and ethyl esters in a engine environment
- ❑ Examine the applicability of the two esters as surrogates for biodiesel in studies of low temperature oxidation
- ❑ Achieve a fundamental understanding of the major low temperature oxidation pathways of fatty acid ethyl esters

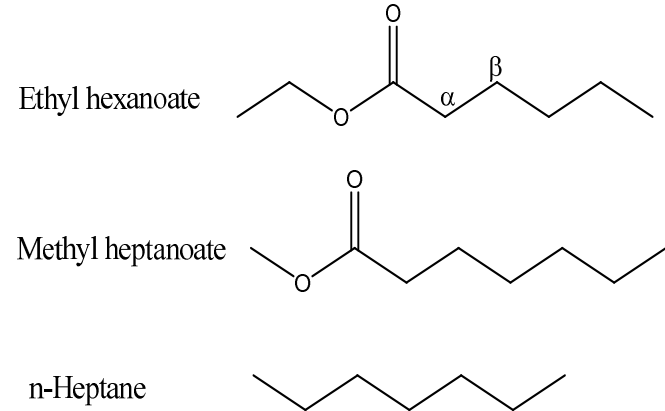
- ❑ An important step in the low temperature oxidation of paraffins is the isomerization of RO_2 into QOOH through internal H-atom shift by forming transition state ring-like structures. Six- and seven-membered rings have the most rapid reaction rate

Experimental Setup

Engine Setup



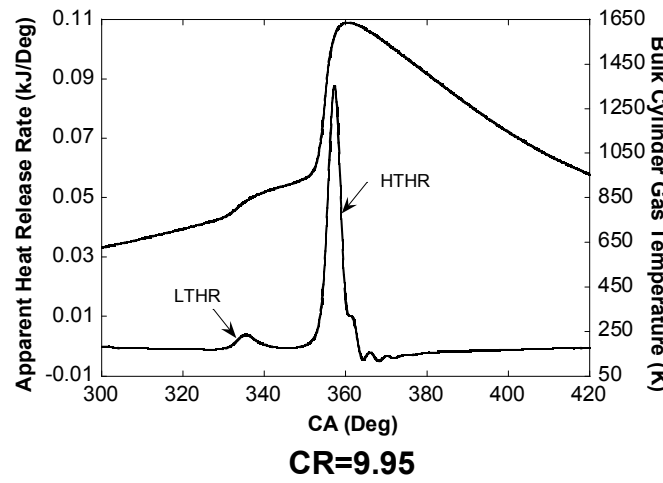
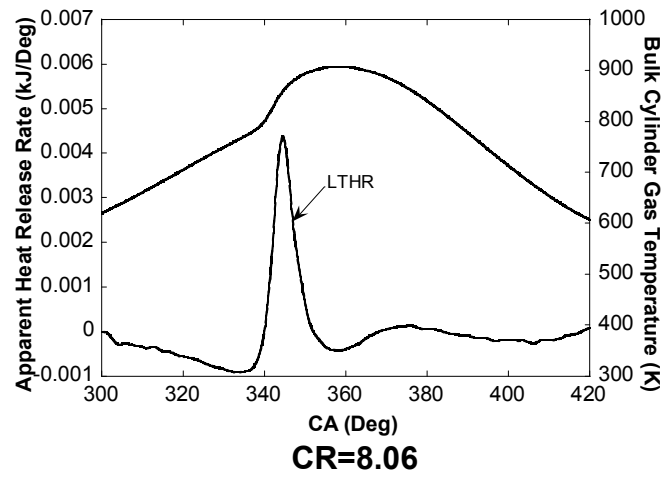
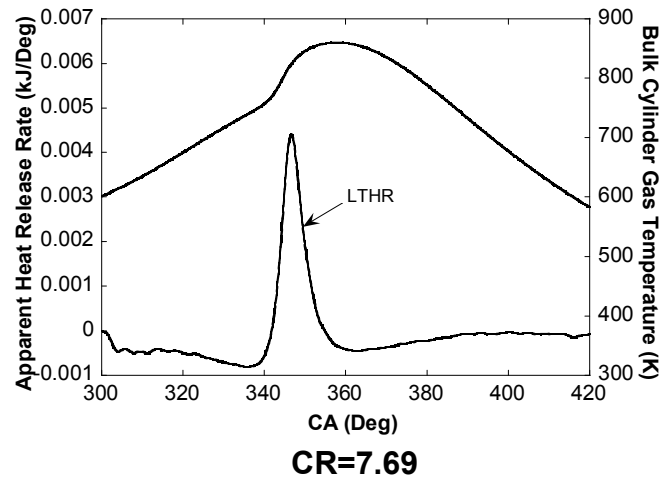
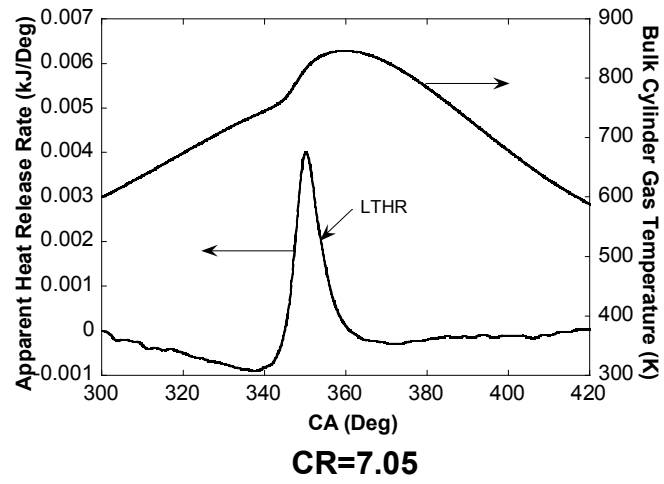
Test Fuels



Test Conditions

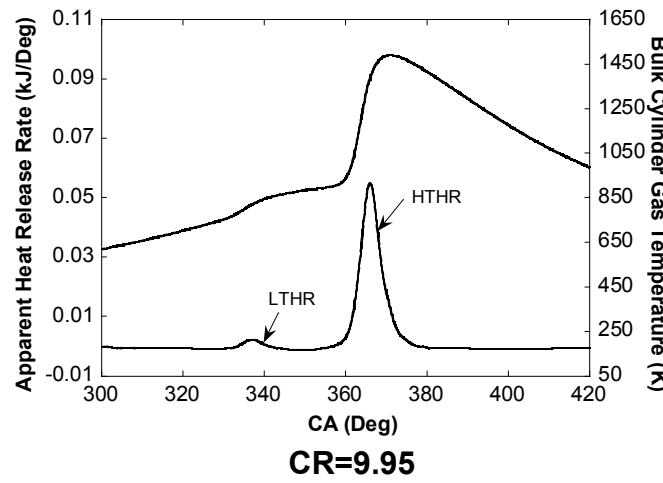
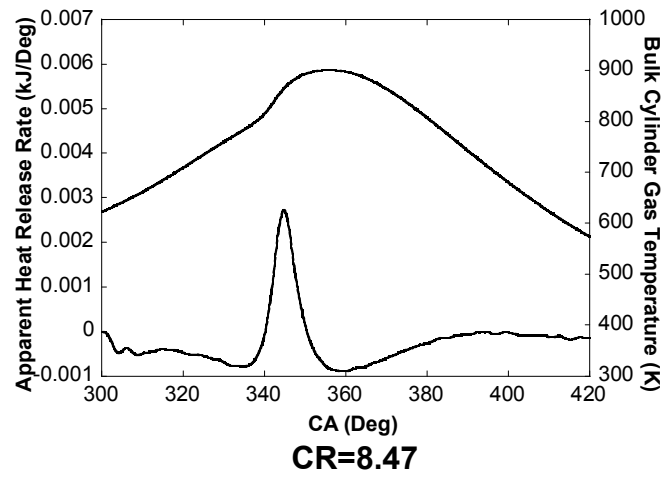
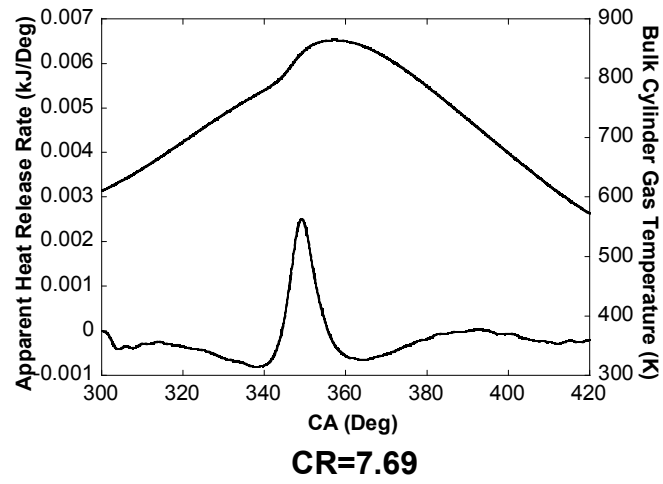
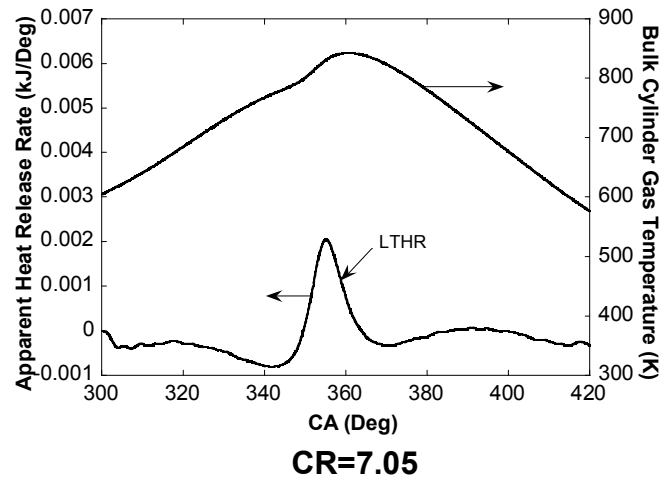
- P_{in} : 1 atm T_{in} : 155 °C
- Equivalence Ratio : 0.25

Ignition Progression of Methyl Heptanoate



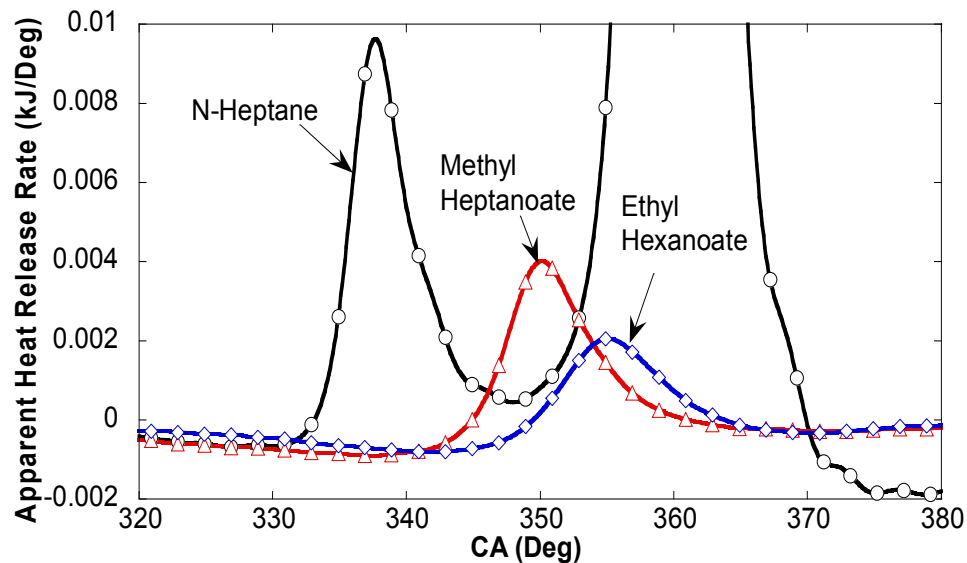
□ As CR increases, methyl heptanoate experiences the transition from single stage LTHR to two-stage ignition

Ignition Progression of Ethyl Hexanoate

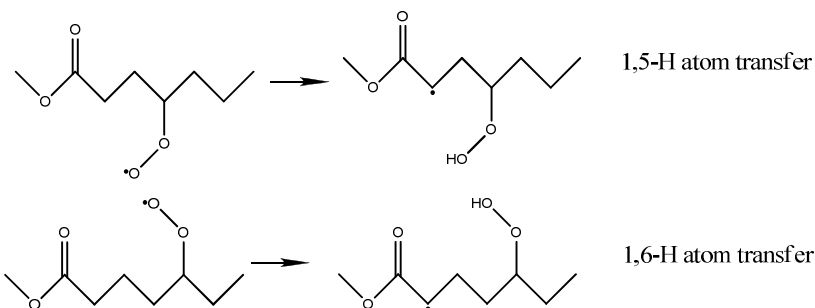


Both of the two esters exhibit evident low temperature heat release

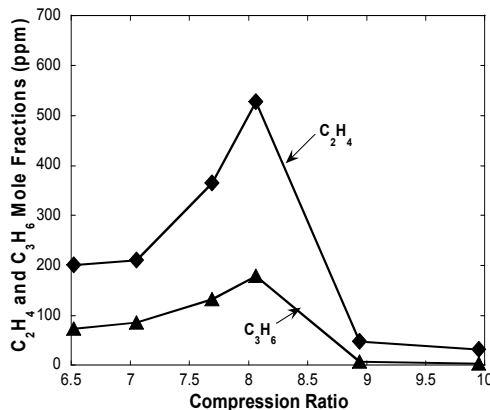
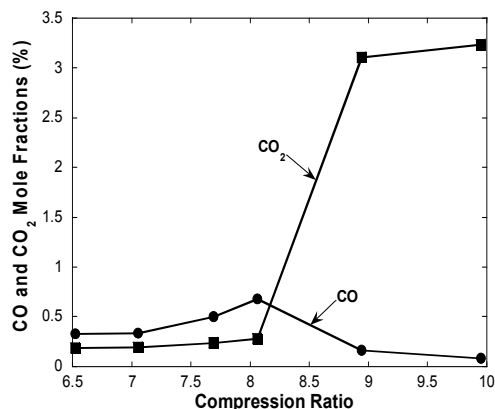
Ignition Behavior of Test Fuels at CR=7.05



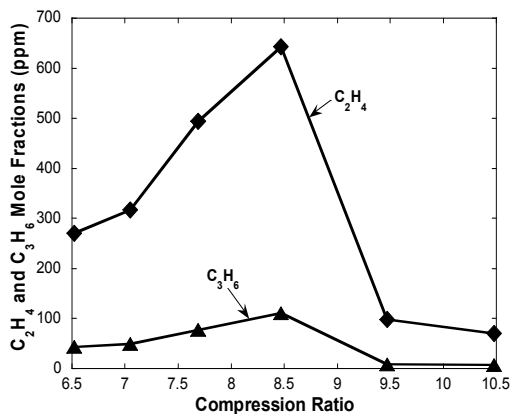
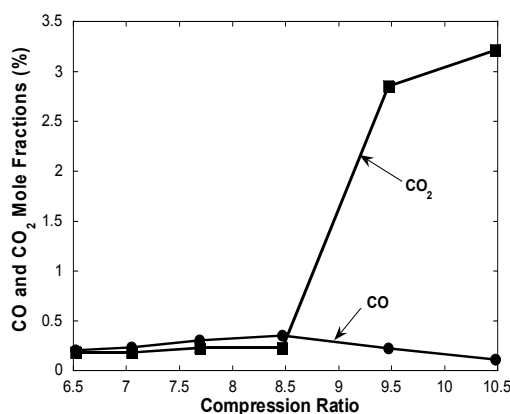
- ❑ The presence of ester functionality suppresses low temperature reactivity
- ❑ Methyl heptanoate is more reactive than ethyl hexanoate in the low temperature regime due to the higher possible number of 1,5-H and 1,6-H atom transfers available for the isomerization of peroxy alkyl ester radicals during methyl heptanoate oxidation than during ethyl hexanoate oxidation



Methyl Heptanoate



Ethyl Hexanoate

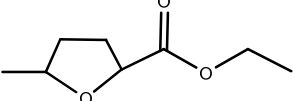
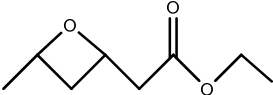
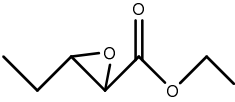
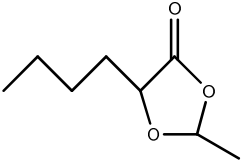


□ In the early stage of oxidation, CO is mainly formed through the decomposition of aldehydes; small olefins are produced through C-C bond β-scission reactions

□ The higher concentration of CO for methyl heptanoate in the early stage of oxidation further confirms the higher low-temperature reactivity of methyl heptanoate

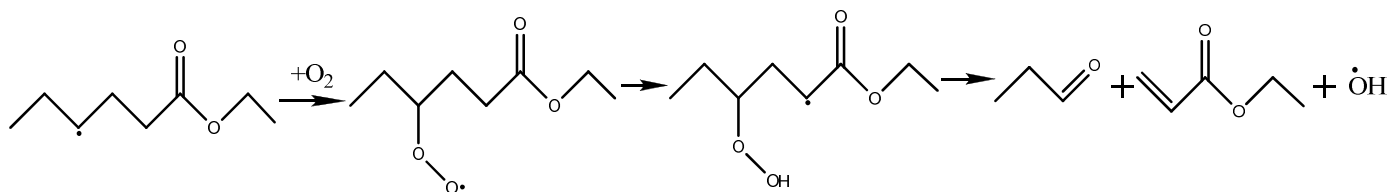
□ More fuel carbon is observed to be converted to ethylene during ethyl hexanoate oxidation than during methyl heptanoate oxidation despite that ethyl hexanoate is less reactive than methyl heptanoate in the low temperature regime

Condensed Species Collected from the Oxidation of Ethyl Hexanoate at CR= 7.69

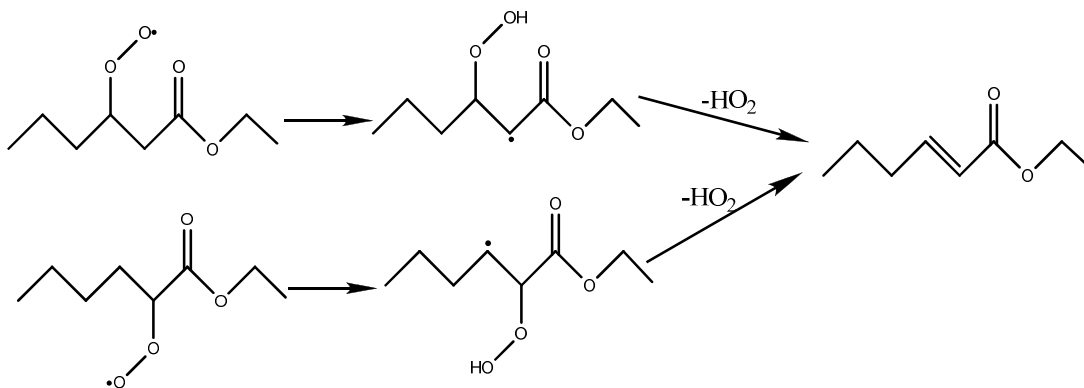
<i>Methyl Esters</i>	<i>Aldehydes</i>
Ethyl 2-Propenoate	Acetaldehyde
Ethyl 3-Butenoate	Acrolein
Ethyl 4-Pentenoate	Propanal
Ethyl 3-Hexenoate	Butanal
Ethyl Hexanoate	2-Butenal
Ethyl 2-Hexenoate	Pentanal
Ethyl 2,5-Epoxyhexanoate	
	
Ethyl 3,5-Epoxyhexanoate	
	
Ethyl 2,3-Epoxyhexanoate	
	
2-methyl-5-butyl-1,3-dioxolan-4-one	
	
	<i>Acids</i>
	Formic Acid
	Acetic Acid
	Acrylic Acid
	Hexanoic Acid
	<i>Ketone</i>
	2-Butanone
	<i>Cyclic Ether</i>
	Ethylene Oxide
	<i>Alkenes</i>
	Propene
	1-Butene
	1,3-Butadiene
	1-Pentene
	2-Pentene

Reaction Pathways Analysis

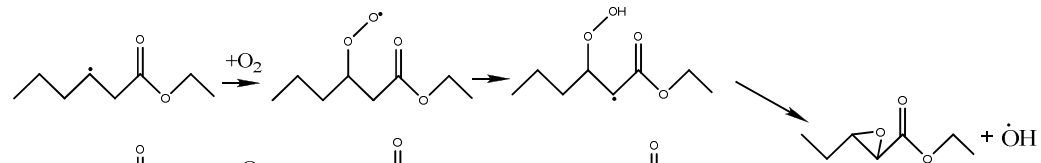
- Type Ia. C-C bond scission to form aldehydes, unsaturated esters with a terminal double bond and hydroxyl radicals



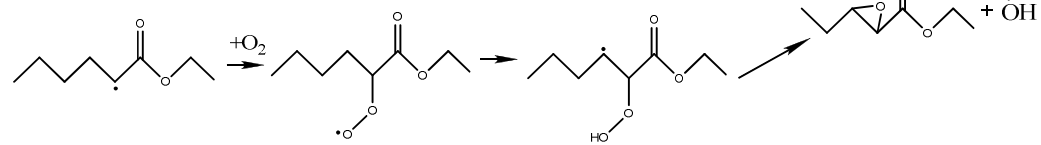
- Type Ib. C-O bond scission to form unsaturated esters and hydroperoxy radicals



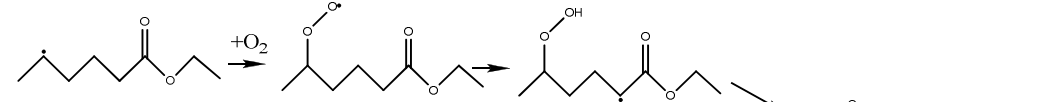
□ Type Ic. O-O bond scission to form epoxy esters and hydroxyl radicals



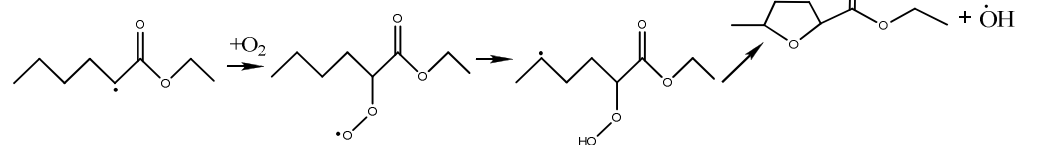
1,4-H atom transfer



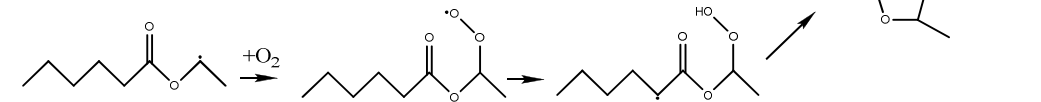
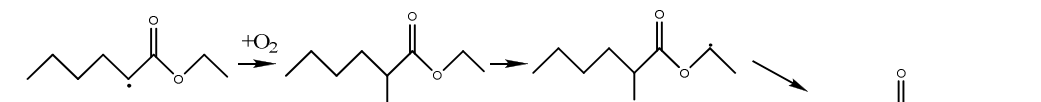
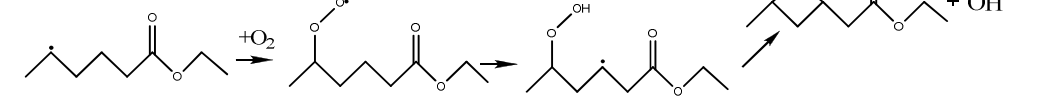
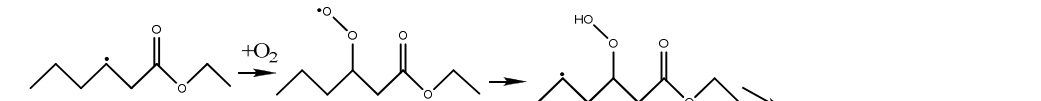
1,6-H atom transfer



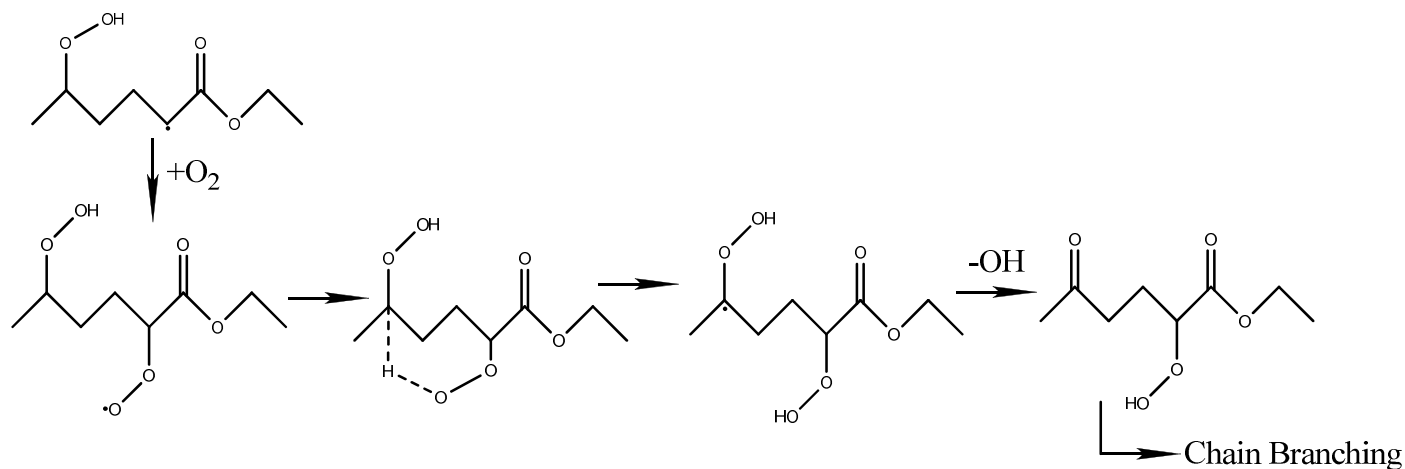
1,5-H atom transfer



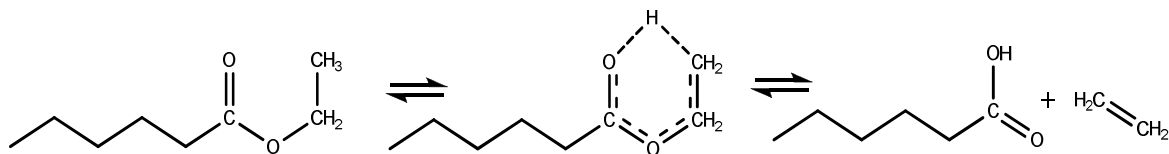
1,6-H atom transfer



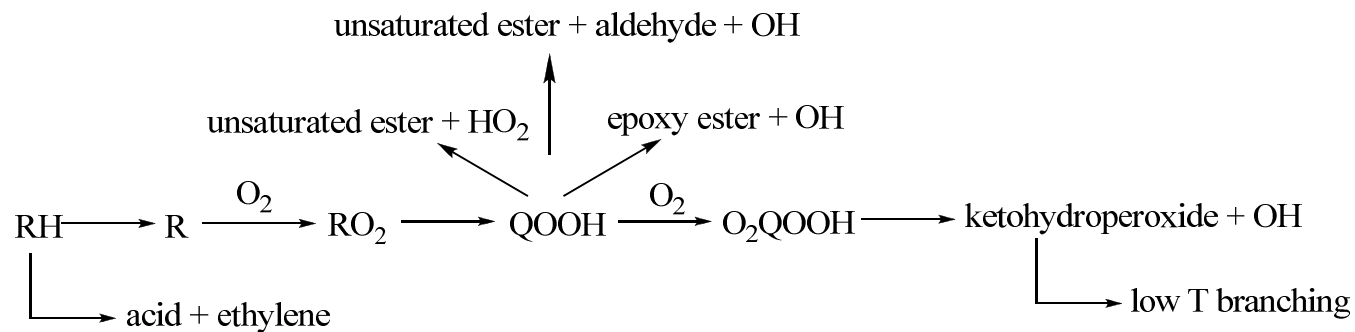
□ Type II. reaction pathways leading to low temperature chain branching



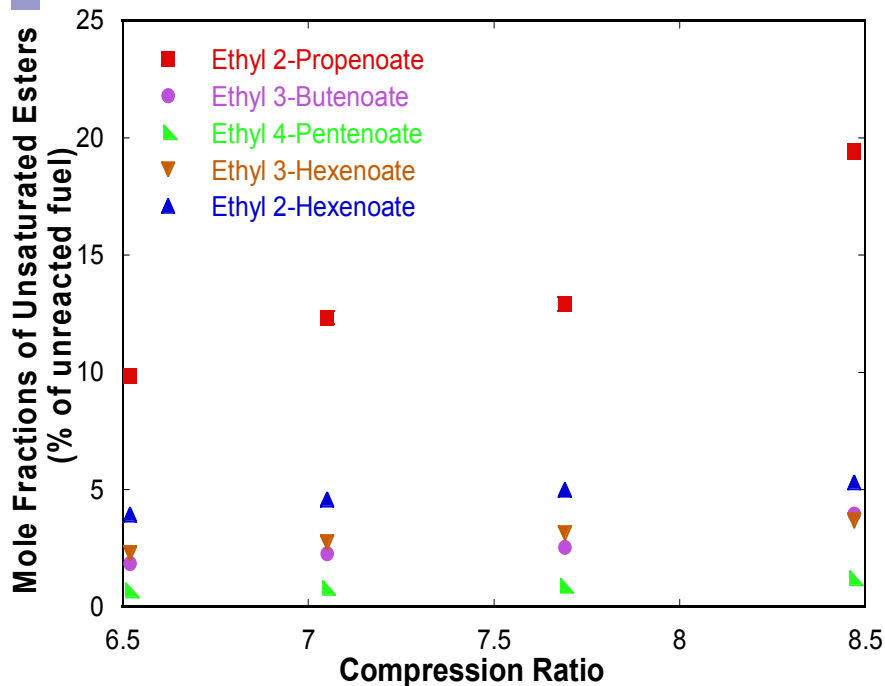
□ The observation of more fuel carbon being converted to C_2H_4 during ethyl hexanoate oxidation together with the identification of hexanoic acid among the reaction intermediates from the oxidation of ethyl hexanoate provide the evidence for the existence of the six-centered unimolecular elimination reaction during low temperature oxidation of ethyl esters



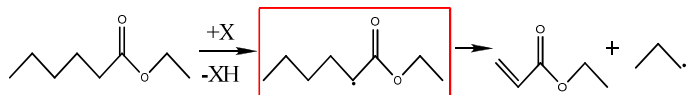
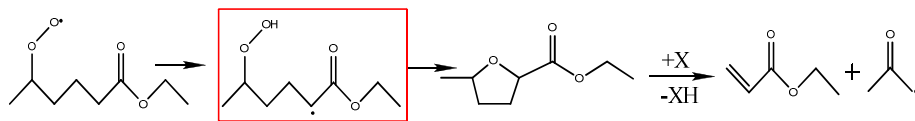
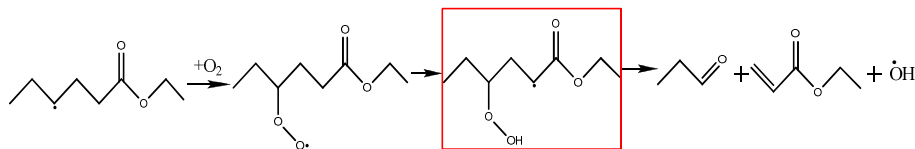
- Based on the above analysis, major low temperature oxidation pathways of fatty acid ethyl esters can be summarized as follows



Relative Abundance of Unsaturated Ethyl Esters



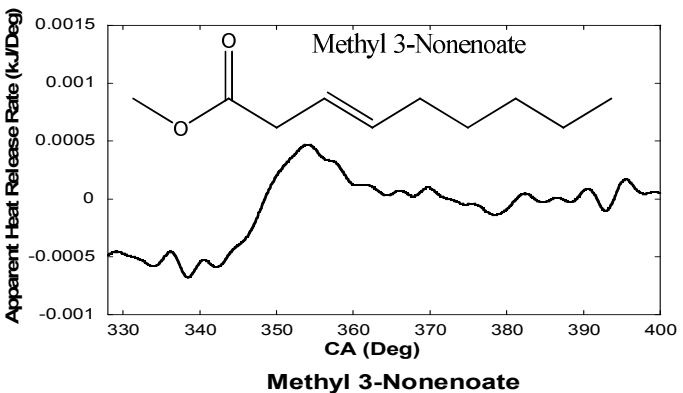
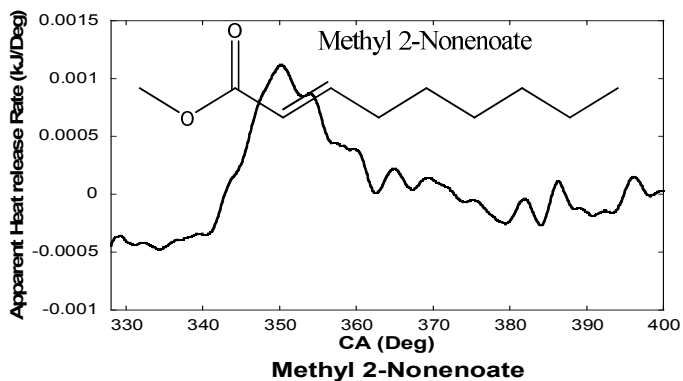
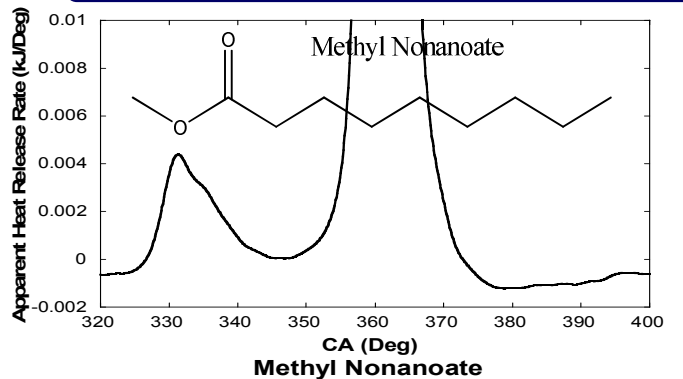
- The appreciably higher abundance of ethyl 2-propenoate than the rest of the unsaturated esters suggests the abstraction of H-atoms on the α -carbon of the ester carbonyl group plays an important role in the oxidation of ethyl hexanoate
- The preferred H-atom abstraction on the α -carbon of the ester carbonyl group among the C-H bond breakings is primarily due to the electron-withdrawing nature of the oxygen atom in the ester carbonyl group
- Ethyl 2-propenoate can be formed mainly through the reaction pathways shown on the left





Ignition Studies of Unsaturated C9 Fatty Acid Methyl Esters

CR=6.08, $T_{in} = 250\text{ }^{\circ}\text{C}$, Equivalence Ratio=0.25

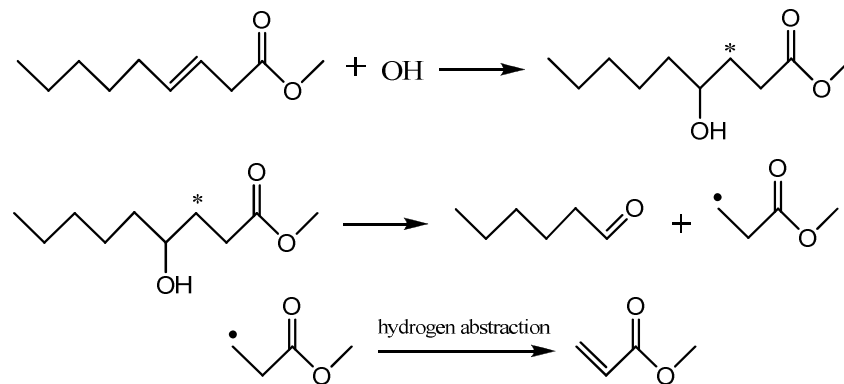


- ❑ Low temperature reactivity follows the order: Methyl Nonanoate > Methyl 2-Nonenoate > Methyl 3-Nonenoate
- ❑ The presence of a double bond in the aliphatic chain of fatty acid esters inhibits low temperature reactivity; the inhibition effects becomes more pronounced as the double bond moves toward the center of the aliphatic chain
- ❑ Unsaturated fatty esters are less reactive in the low temperature region due to the fact that the presence of double bonds inhibits the formation of six- and seven-membered transition state rings for internal H-atom transfers that are important in low temperature oxidation

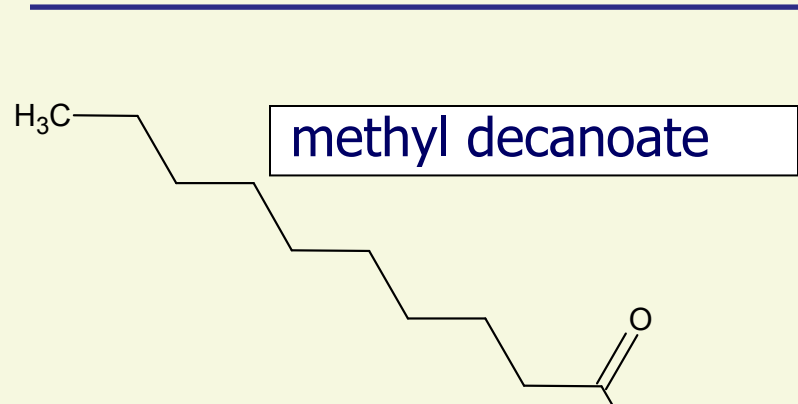
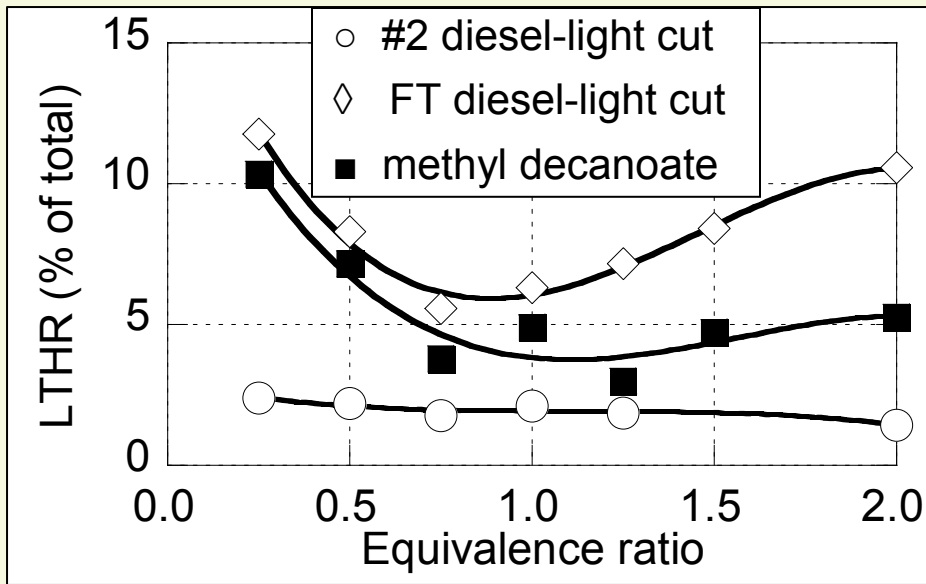
Selected Condensed Species Collected from the Oxidation of Methyl 3-Nonenoate at CR=5.54

<i>Species</i>	<i>Relative Peak Area</i>
Methyl 2-Propenoate	0.16
Butanal	0.3
Pentanal	0.2
Hexanal	1

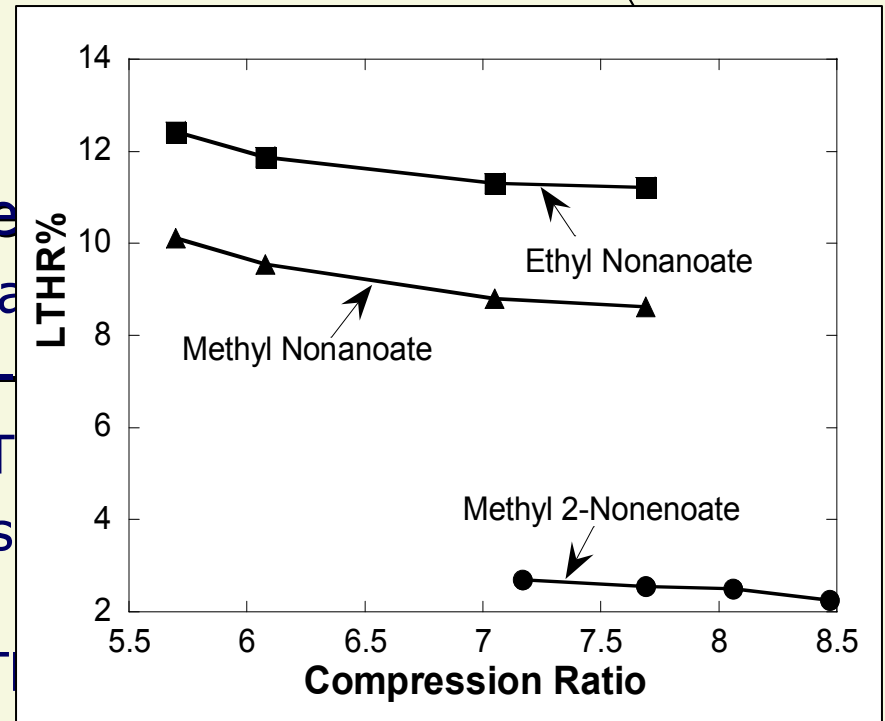
- The presence and high abundance of hexanal and methyl 2-propenoate implies methyl 3-nonoate experiences the following olefin-like reaction sequence



LTHR magnitude is dependent on CN and equivalence ratio



- LTHR magnitude trends with derivative
 - FT diesel-light cut > methyl decanoate
- Methyl decanoate LTHR likely over-
 - Aliphatic chain is responsible for LTHR
 - Over 50% of soy-based biodiesel is unsaturations
 - Unsaturated species exhibit less LTHR



Conclusions

- ❑ The alkyl chain of fatty acid esters experience the typical paraffin-like low temperature oxidation sequence; the alkyl chain length of fatty acid esters has a crucial impact on the ignition behavior of fatty acid esters
- ❑ The six-centered unimolecular elimination reaction occurs during the early stage oxidation of fatty acid ethyl esters
- ❑ The abstraction of H-atoms on the α -carbon of ester carbonyl group plays an important role in the oxidation of fatty acid esters
- ❑ The presence of a double bond in the aliphatic chain of fatty acid esters suppresses the low temperature reactivity of fatty acid esters; the inhibition effect becomes more pronounced as the double bond moves toward the center of the aliphatic chain of fatty acid esters
- ❑ For unsaturated esters, the autoignition can undergo olefin ignition pathways



Acknowledgements

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