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Biofuel Combustion Chemistry: Influence of C=C Bond Position on Chain-Termination in Methyl Ester Oxidation

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Abstract

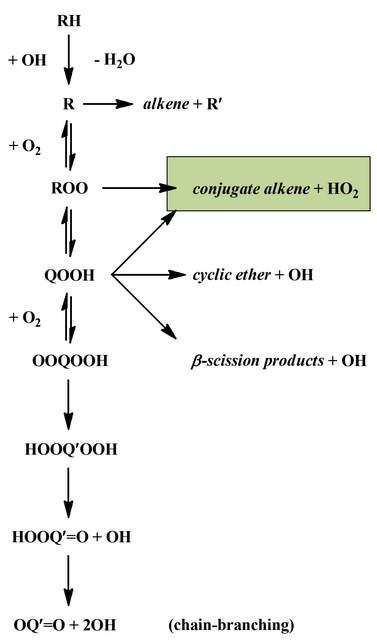
In the coming years, our fuel supply will diversify as biofuels grow more economical. The **molecular structure of biofuels vary widely**. To utilize these fuels efficiently and design biofuel-compatible advanced engines, we must **understand how biofuels behave under low temperature combustion** (500-1000K). During low temperature combustion (LTC), thousands of intermediate reactions take place. These reactions heavily influence autoignition at higher temperatures.

Hydrocarbon + O_2 → Intermediates → CO_2 + H_2O

This study investigates **how the position of a double bond in a biodiesel-like compounds affect the intermediate reactions under LTC**. Using pulsed laser photolysis, we measured the concentration of HO_2, a key intermediate product.

We found that when the **double bond is closer to the ester group, the HO2 produced decreases.** Notably, the HO_2 production of the **compounds tested did not display significant temperature dependence.**

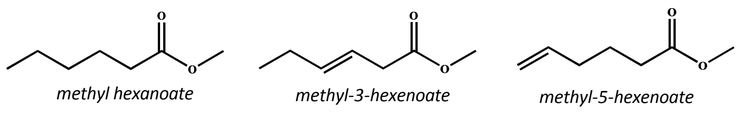
Introduction



LTC occurs via pathways of chain initiation, propagation, branching, and termination. The balance between these pathways controls heat release and sets the stage for autoignition.

- **RH:** fuel molecule
- **HO_2:** unreactive, chain terminating
- **OH:** highly reactive, supports chain branching
- **QOOH:** highly reactive and unstable, supports chain branching

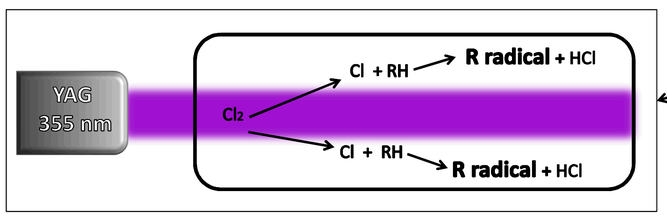
Biodiesel **chain length, number of double bonds, and position of double bonds influences fuel combustion properties** and pollutant formation.

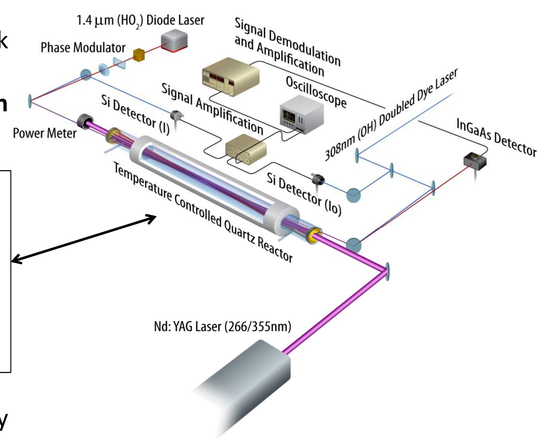


This experiment focuses on how the position of a double bond in the three compounds above affects HO_2 formation between 600 and 750 K. We selected these compounds because they **mimic the methyl ester portion of a biodiesel molecule.**

Detection of the Reaction Intermediate, HO_2

- Fuel and Cl_2 vapors flow through a temperature controlled reactor
- High-energy laser light collides with the vapors to break Cl_2 into Cl atoms
- These reactive Cl atoms trigger **fuel radical formation and chain branching cascades**

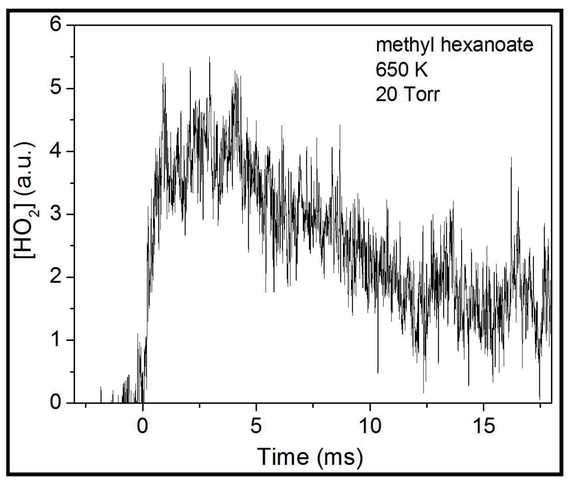




- **HO_2 signal is recorded as a voltage** and normalized by number of chlorine atoms

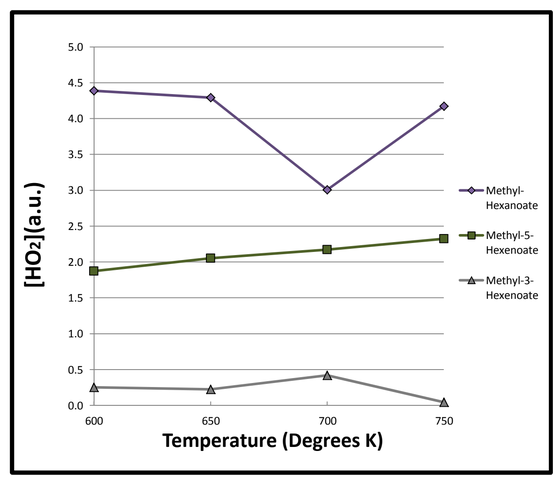
Average and Peak HO2 Signals

Average HO_2 Production vs. Time



- At 0 ms, the laser pulses and triggers reaction cascade
- HO_2 production peaks, then gradually declines

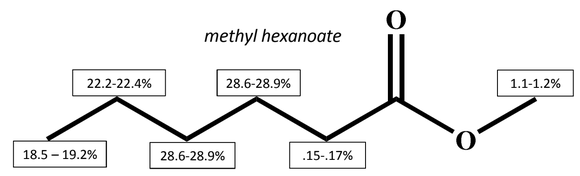
Peak HO_2 Production, 600-750 K

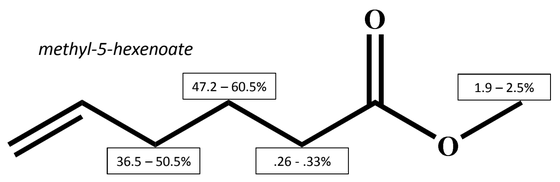


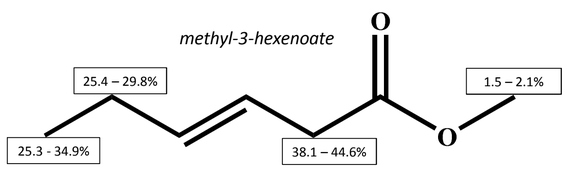
- Peak HO_2 trend: **methyl-hex > methyl-5 > methyl-3**
- Methyl-3's HO_2 production ≈ 0

Structure-Activity Relationships

- Structure-activity relationships use rate constants and bonding characteristics to **estimate the distributions of which radical sites occur at specific sites**
- SAR data indicates that radicals form rapidly at sites near double bonds







Conclusion

- Methyl-hexanoate produced the highest peak HO_2, while methyl-3-hexenoate produced the lowest peak HO_2
- **We note a correlation between close proximity of the C=C bond to the ester group and lowered HO_2 formation**
- In the future, we aim to validate these results with computational modeling and use this knowledge to improve numerical models for simulating engine combustion

Acknowledgements

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