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

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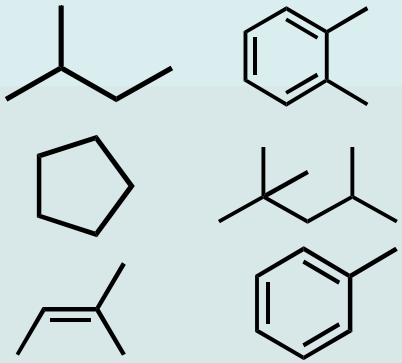
Each Class of Transportation Fuel Utilizes a Variety of Molecular Structures

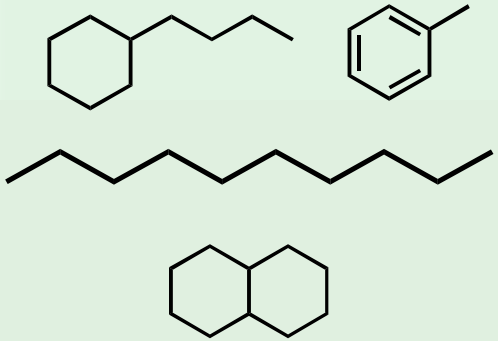
Gasoline

- Short branched chains (< C_8)
- Aromatics
- High octane number



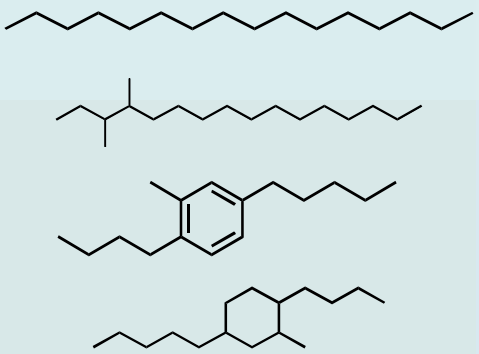
Jet Fuel

- Long straight chains (> C_9)
- Iso-alkanes
- Aromatics



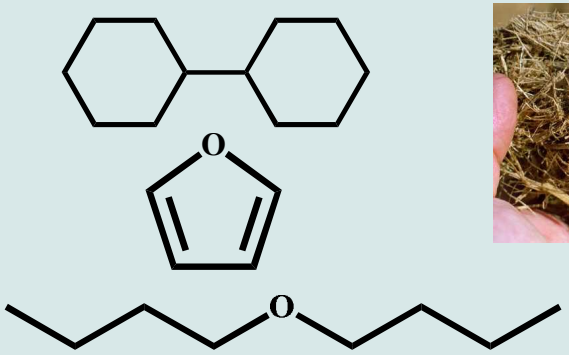
Diesel

- Long straight chains (> C_{12})
- Naphthalenes
- Aromatics

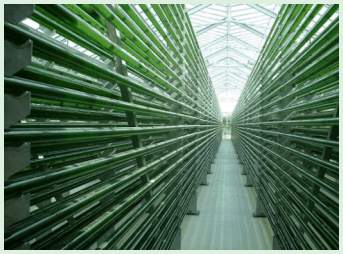


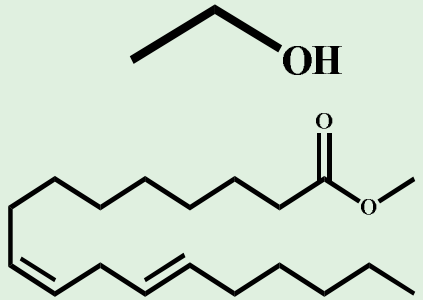
The Increased Market Entry of Biofuels will Introduce New Fuel Structures and Properties

Cellulosic/Lignocellulosic

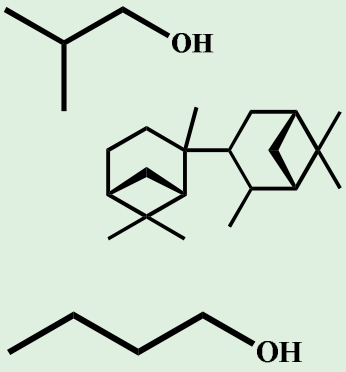


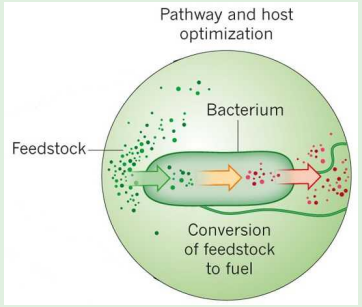
Algae Biodiesel and Ethanol



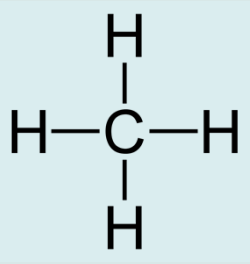


Microbial Synthesis





Anaerobic Digestion → Biogas

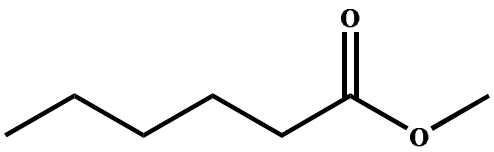


Research Question:
How does the position of a C=C bond affect combustion properties of a biodiesel-like fuel?

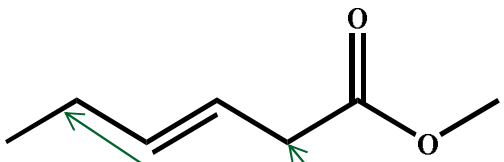
Saturated

Un-Saturated

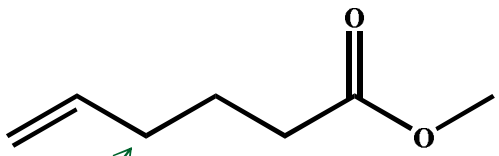
Methyl hexanoate



Methyl-3-hexenoate



Methyl-5-hexenoate

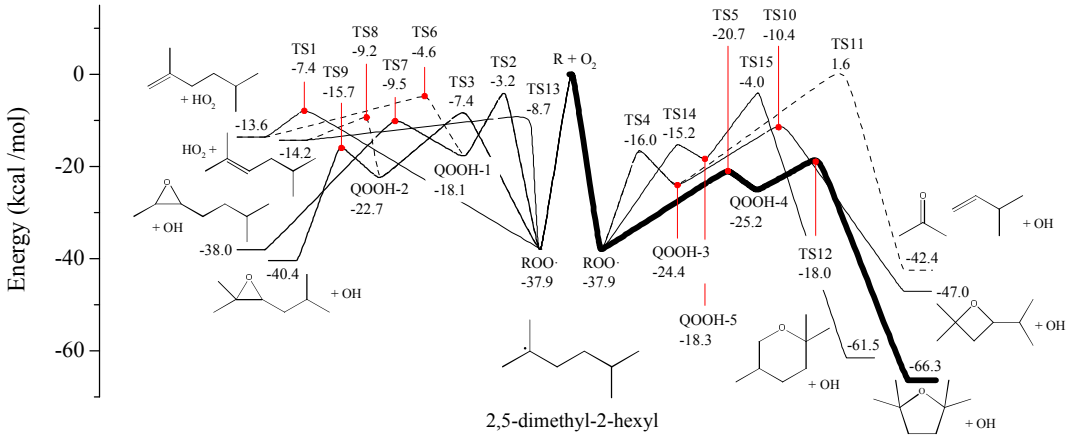


Weakly bonded allylic sites, readily form radicals

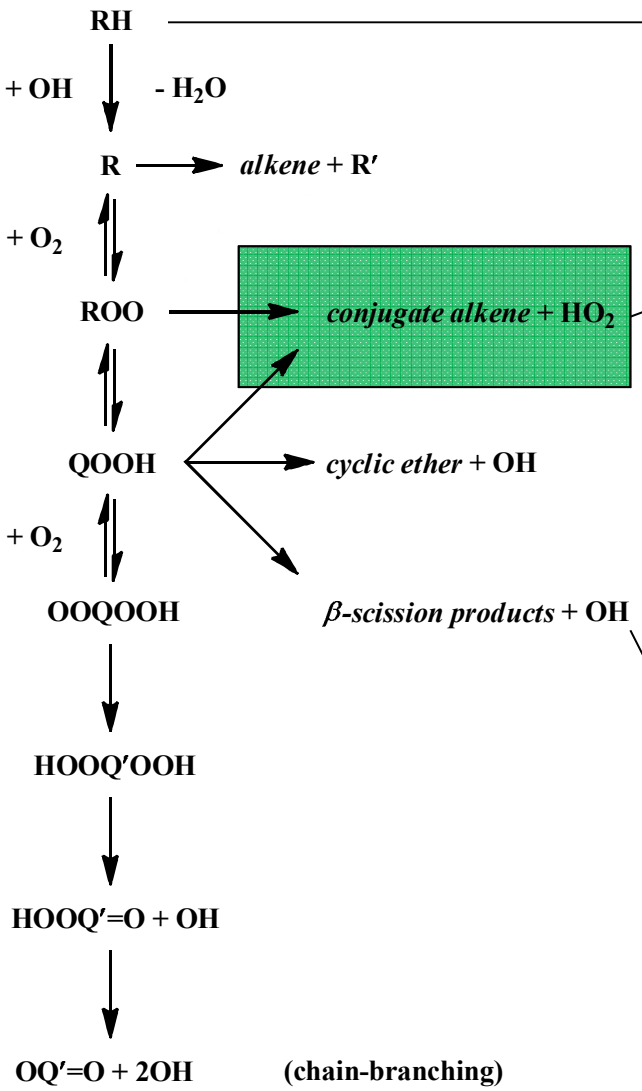
Low Temperature Combustion (500 – 1000 K)

- Chemistry complex and strongly influenced by fuel structure
- Important for designing efficient engines with lower emissions

Hydrocarbon + O_2 → **Intermediates** → **CO_2 + H_2O**



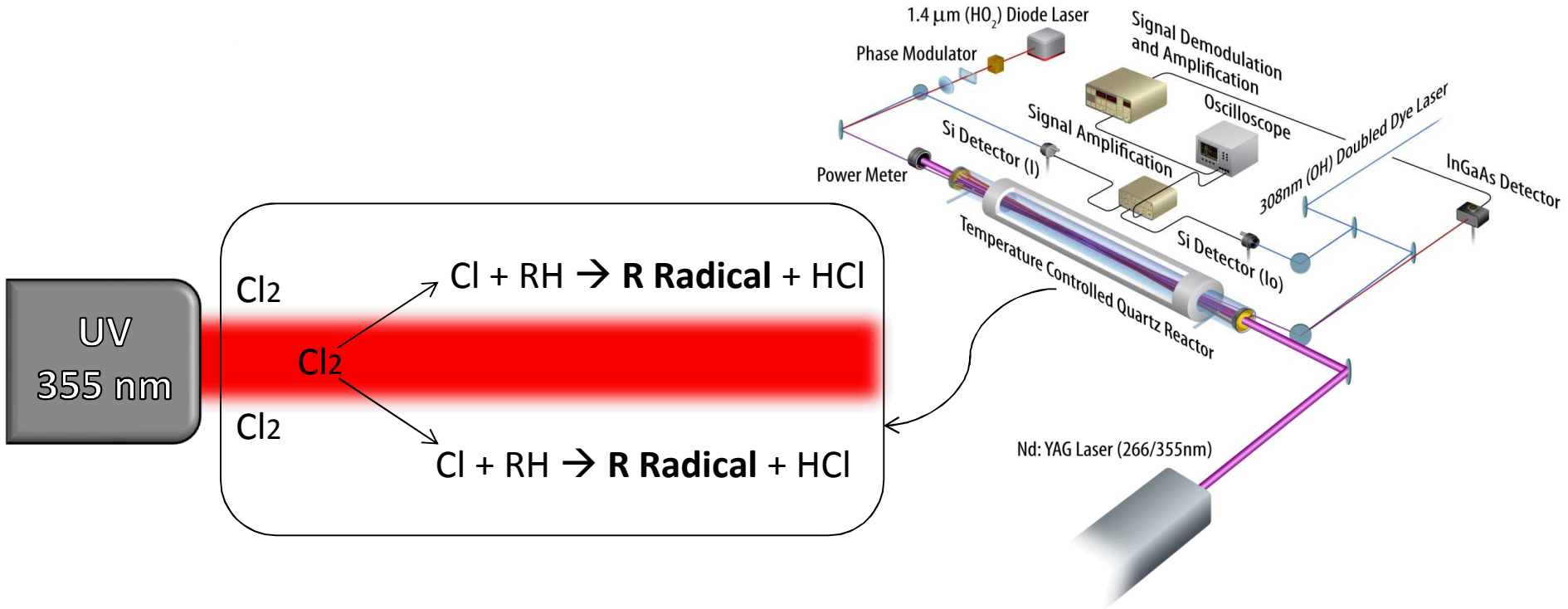
Chain Branching at Low Temperatures



- **"RH":** Fuel
- **HO2** : **Unreactive compound, chain terminating step**
- **QOOH** : Highly reactive and unstable species, supports chain branching
- **OH:** Highly reactive

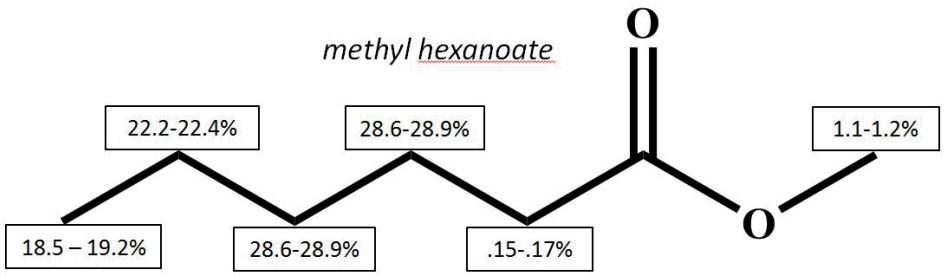
Measurement of HO2 Using Pulsed Laser Photolysis

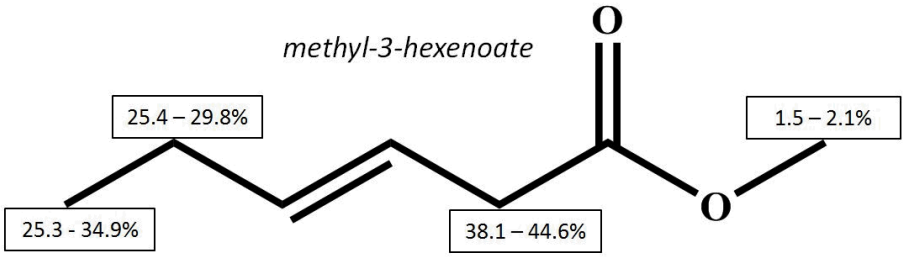
- Fuel and Cl_2 vapors flow through reactor

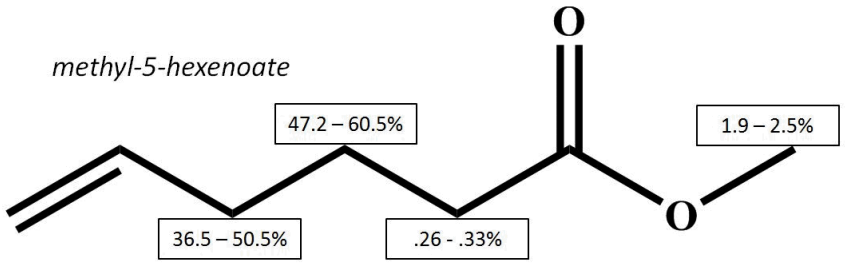


- **Fuel radical formation → Chain branching cascade**

Structure-Activity Relationships Estimate Initial Distribution of Radicals

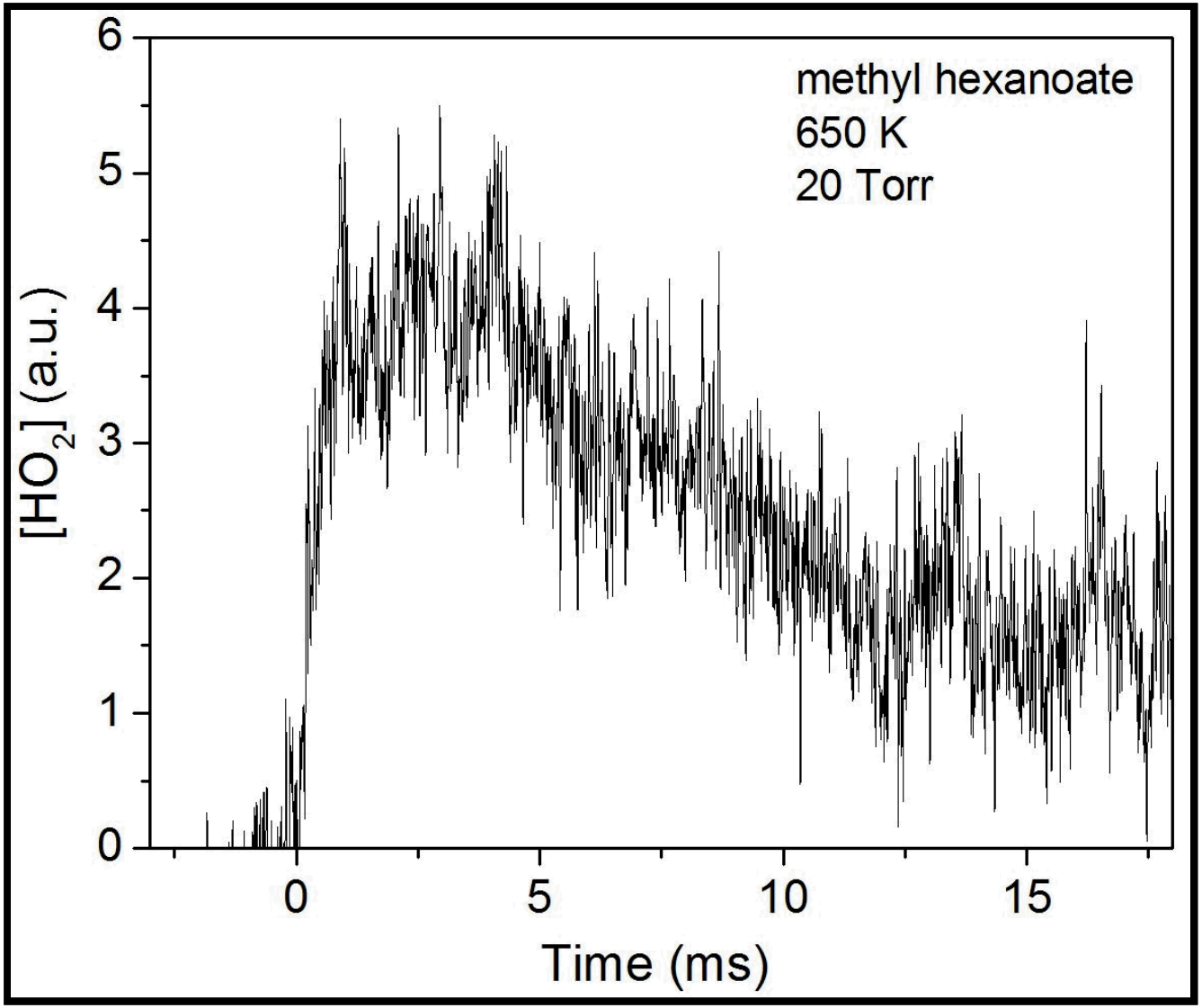




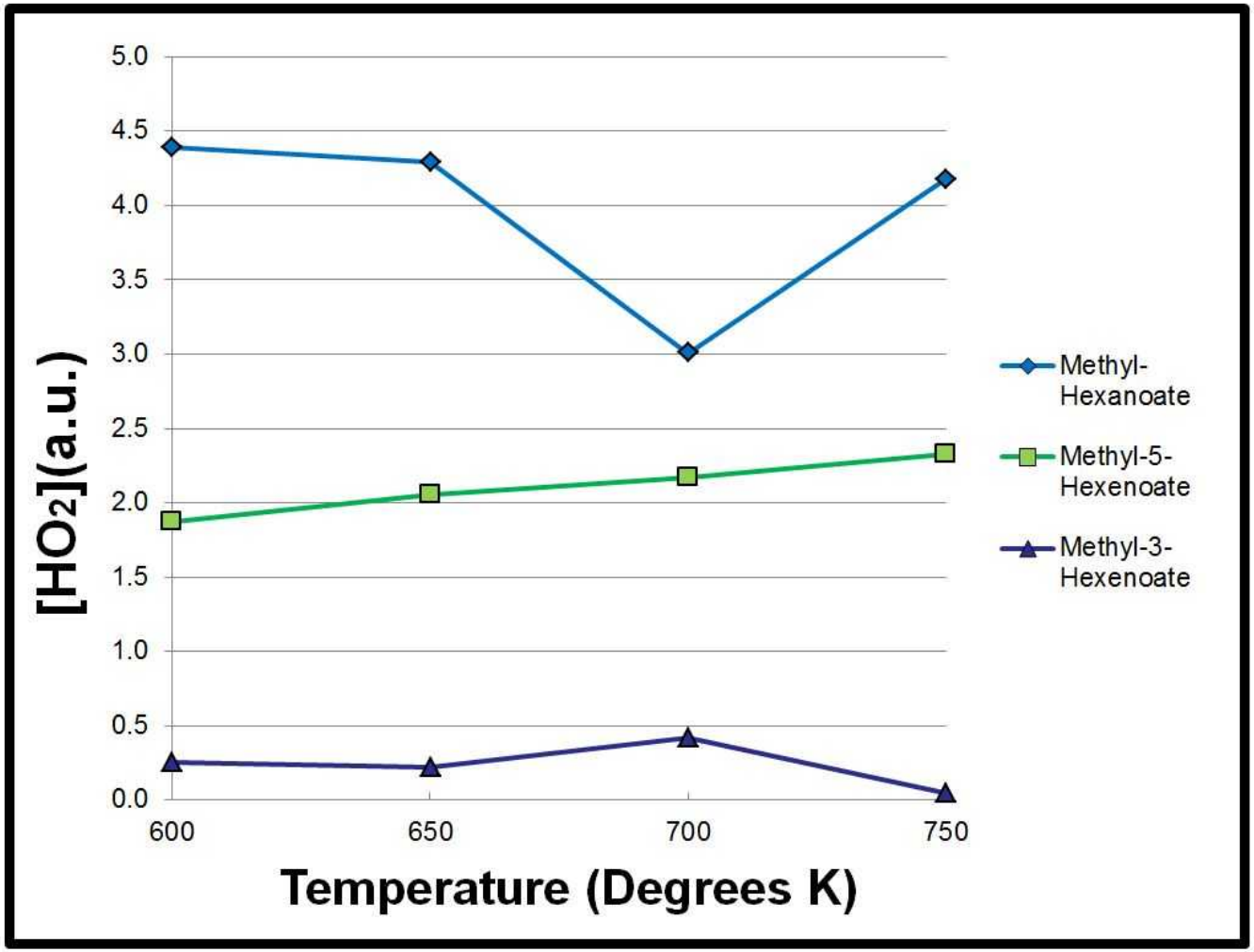


- Rate constants and substituent factors for each radical site are multiplied
- Distribution of radical formation is **higher near double bonds**

HO_2 Concentration vs. Time



Peak HO2 production was highest for methyl hexanoate, lowest for methyl-3-hexenoate



Experiment Implications:

- Results suggest that peak **HO2 production was independent of temperature**
- Compounds with **double bonds closer to ester produce less HO2**
- Important to consider when developing numerical models for engine simulations

Future Directions:

- Validate results with computational modeling
- Investigate combustion intermediate formation for other biofuel surrogates

I would like to extend a special thanks to:

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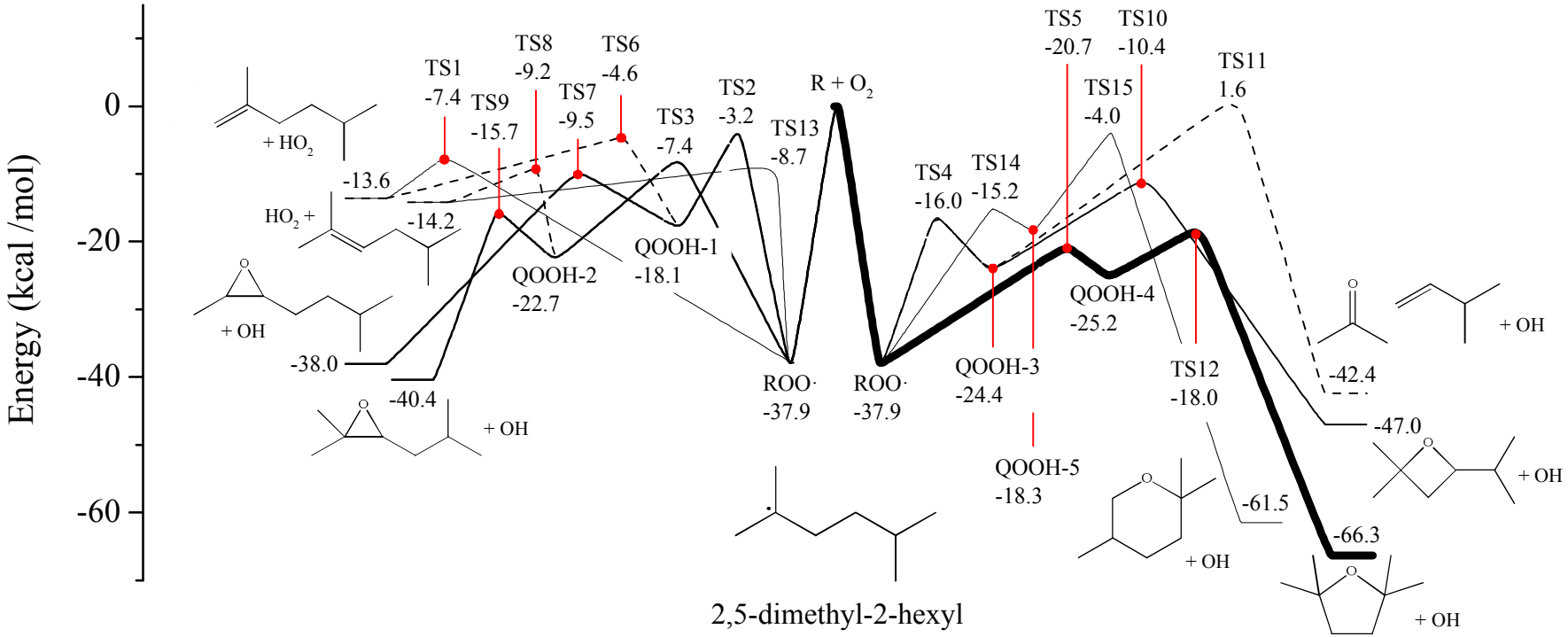
Questions?


Energy (kcal /mol)
0
-20
-40
-60
+ HO2
HO2 +
+ OH
+ OH
+ OH
+ OH
+ OH
TS1
-7.4
TS9
-15.7
TS8
-9.2
TS7
-9.5
TS6
-4.6
TS3
-7.4
TS2
-3.2
TS13
-8.7
R + O2
TS4
-16.0
TS14
-15.2
TS5
-20.7
TS15
-4.0
TS10
-10.4
TS11
1.6
TS12
-18.0
-13.6
-14.2
-38.0
-40.4
QOOH-1
-18.1
QOOH-2
-22.7
ROO·
-37.9
ROO·
-37.9
QOOH-3
-24.4
QOOH-4
-25.2
QOOH-5
-18.3
-42.4
-47.0
-61.5
-66.3
2,5-dimethyl-2-hexyl