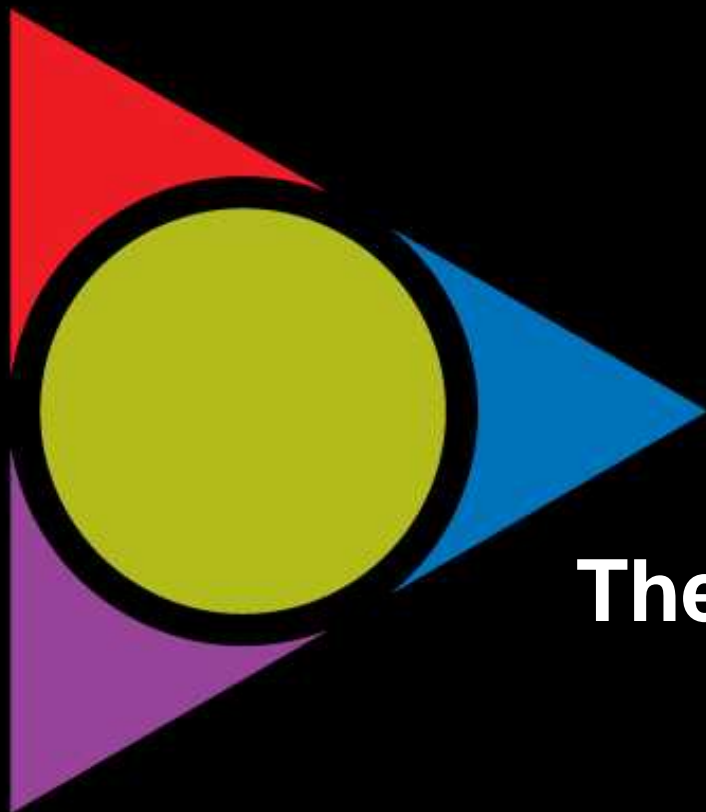


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The Chemistry of Biodiesel Oxidation

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Presentation Overview

- **Chemical Properties and Environmental Factors affecting Biodiesel Stability**
- **Mechanistic Pathways of Biodiesel Degradation**
 - **Focus on Oxidation**
 - **FAME conversion to volatile compounds**
- **Diversity of Chemicals Produced**
- **Summary**

Instability Concerns

Food - Cooking Oils - Whole oils / Triglycerides

-  “Going Rancid” - Production of undesirable odors or flavors

Fuel - Biodiesel - FAME

-  Increase in Acidity

-  Corrosion

-  Increase in Viscosity

-  Deposit formation

-  Fuel filter plugging

-  Injector Deposits

-  Fuel economy

-  Excessive smoke emission

Factors Affecting Biodiesel Stability

▶ Manufacturing Operation

- ▶ conditions and processes used

▶ Antioxidants

- ▶ natural or added

▶ Potential Impurities

- ▶ Acids, glycerin/glycerides, metals

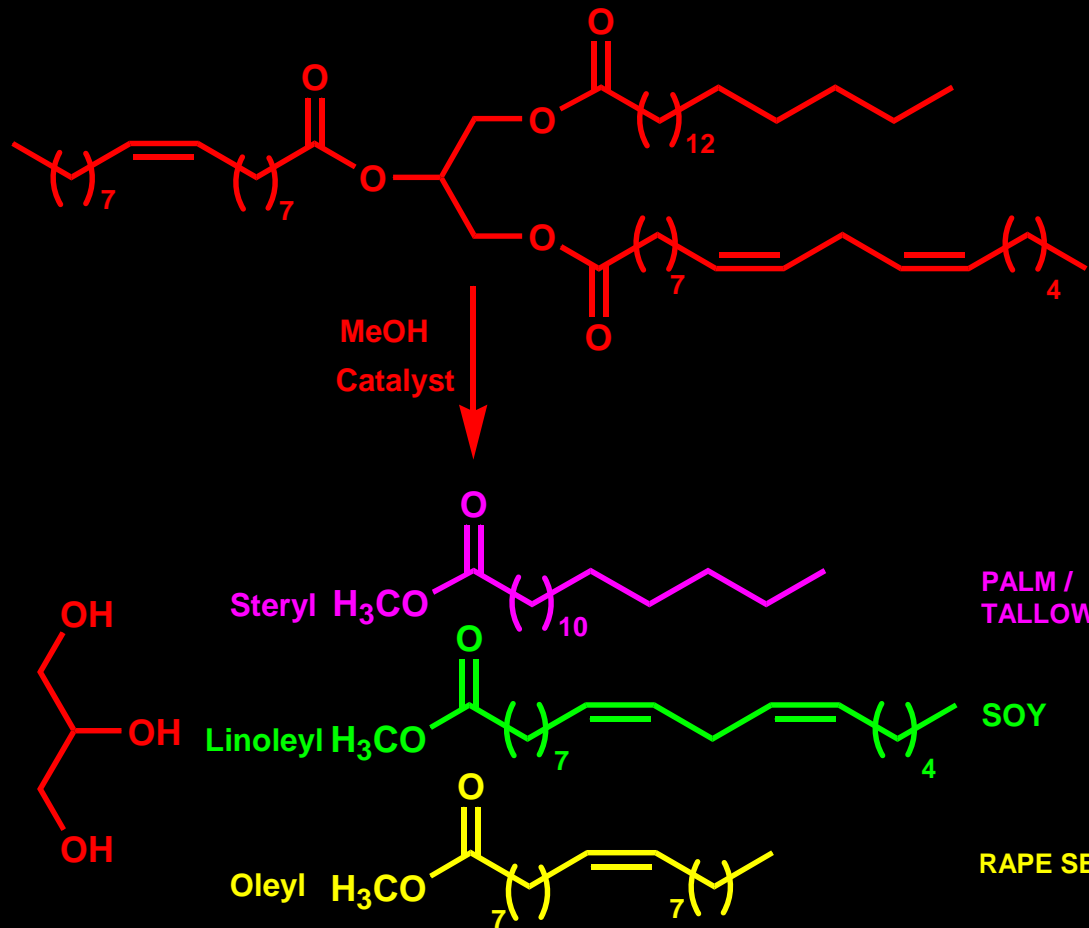
▶ Storage Conditions

- ▶ exposure to water, light or air

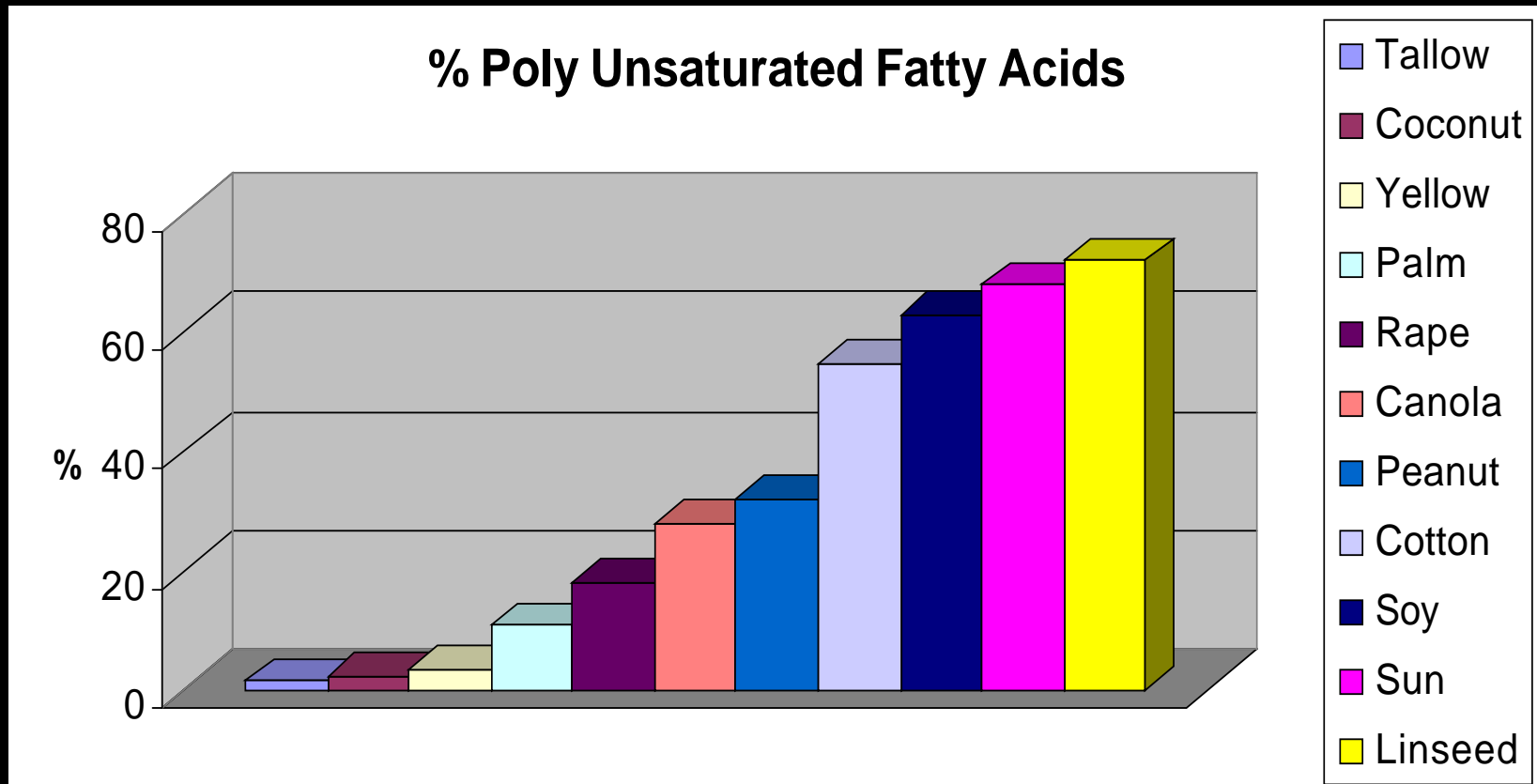
▶ Composition

Whole Oil to Biodiesel

WHOLE OIL / TRI GLYCERIDES



FAME Composition



Pathways to Biodiesel Instability

Thermal Instability

 Associated with Polymer forming reactions

Hydrolytic Instability



 Formation of acids via ester cleavage

Oxidative Instability

 Mixture of degradation products

Mechanisms of Biodiesel Degradation

Thermal Degradation

-  Bio Diesel relatively thermally stable – in absence of oxygen and water
-  Increasing Temperature increases the rate of other Degradation Pathways



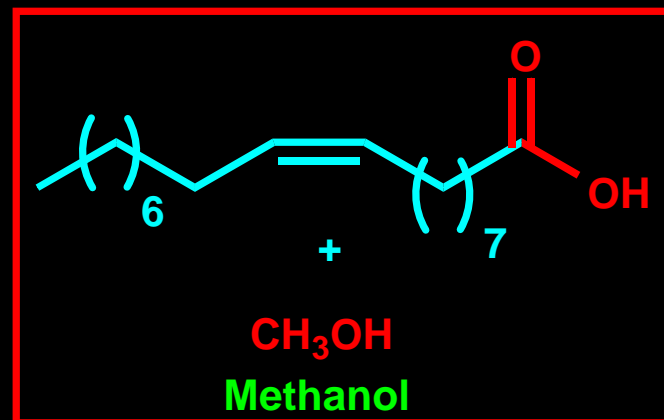
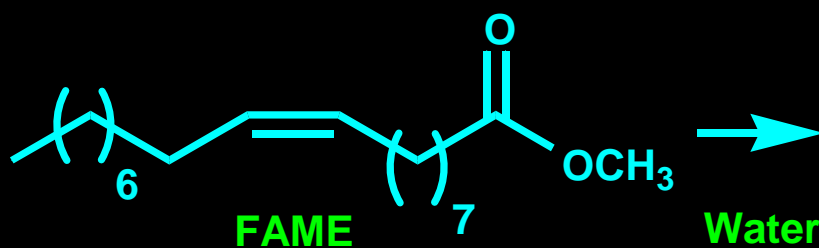
Mechanisms of Biodiesel Degradation

Hydrolytic Degradation

- Breakdown of the Biodiesel by the reaction with water
- Catalyzed by acids, bases and enzymes



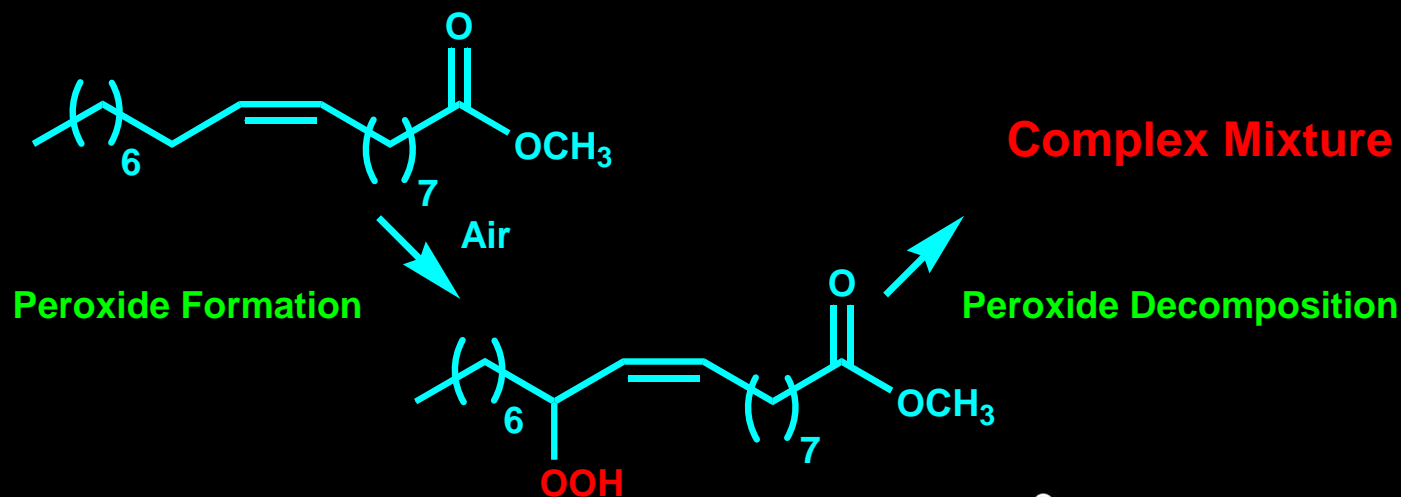
Ester Hydrolysis



Mechanisms of Biodiesel Degradation

Oxidative Degradation

- Main mode of Biodiesel Instability
- Two Step Process
 - Peroxide Formation
 - Peroxide Decomposition



Two Stage Oxidation



Stage I



Peroxides - distinct step in the oxidation



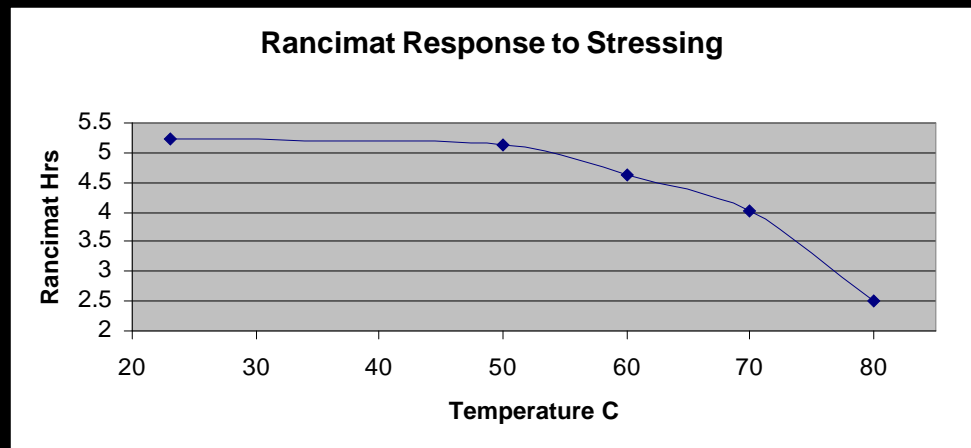
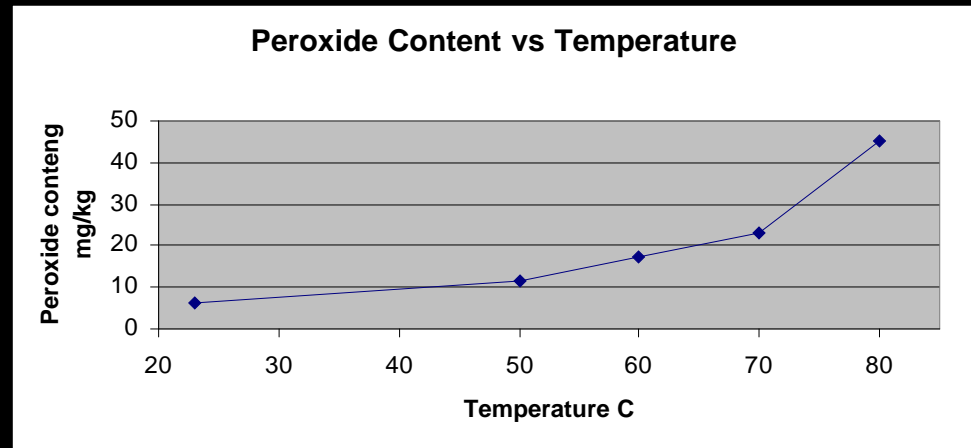
Stage II



Rancimat measure decomposition products



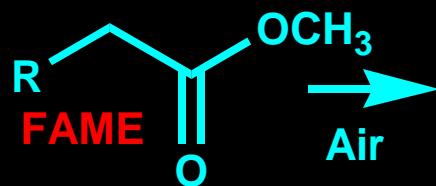
Increased peroxide content directly impacts Induction period



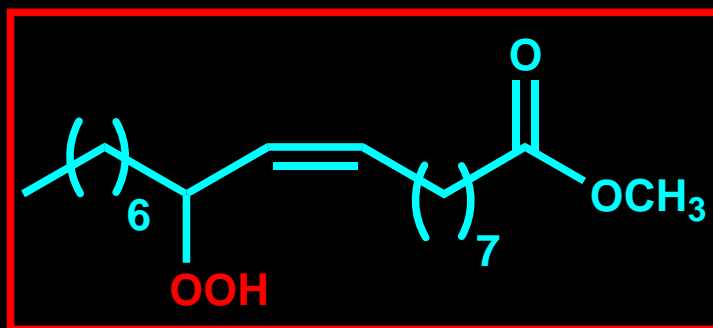
Mechanisms of Biodiesel Degradation

► Peroxide Formation

Peroxide Formation



Air



Peroxide Decomposition

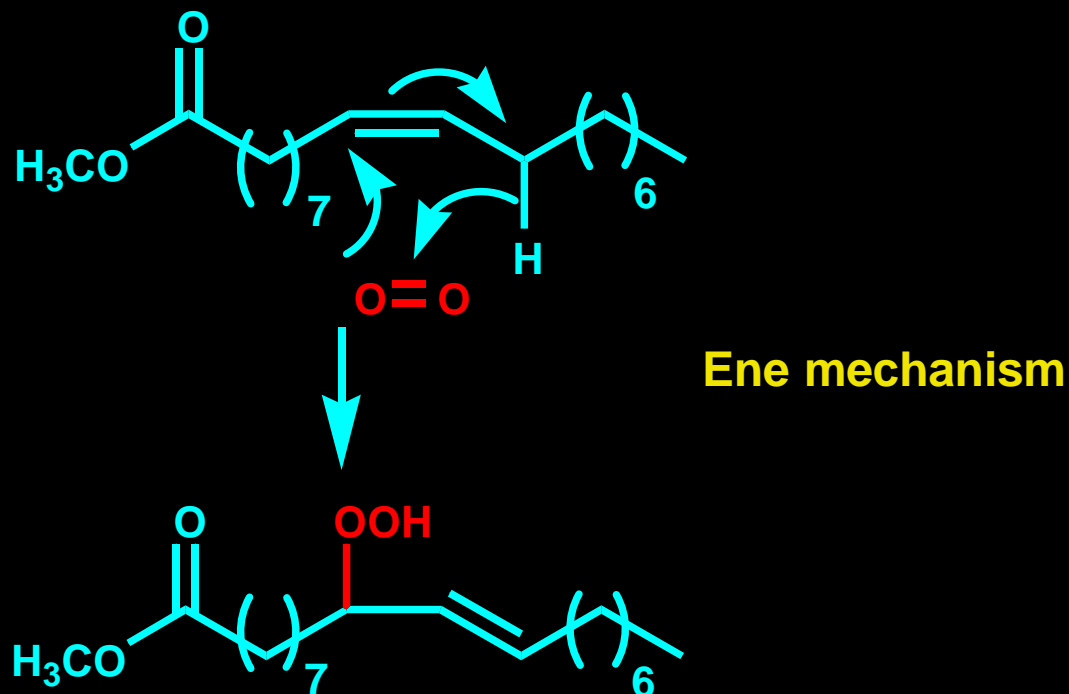
Complex Mixture

Volatile Organics

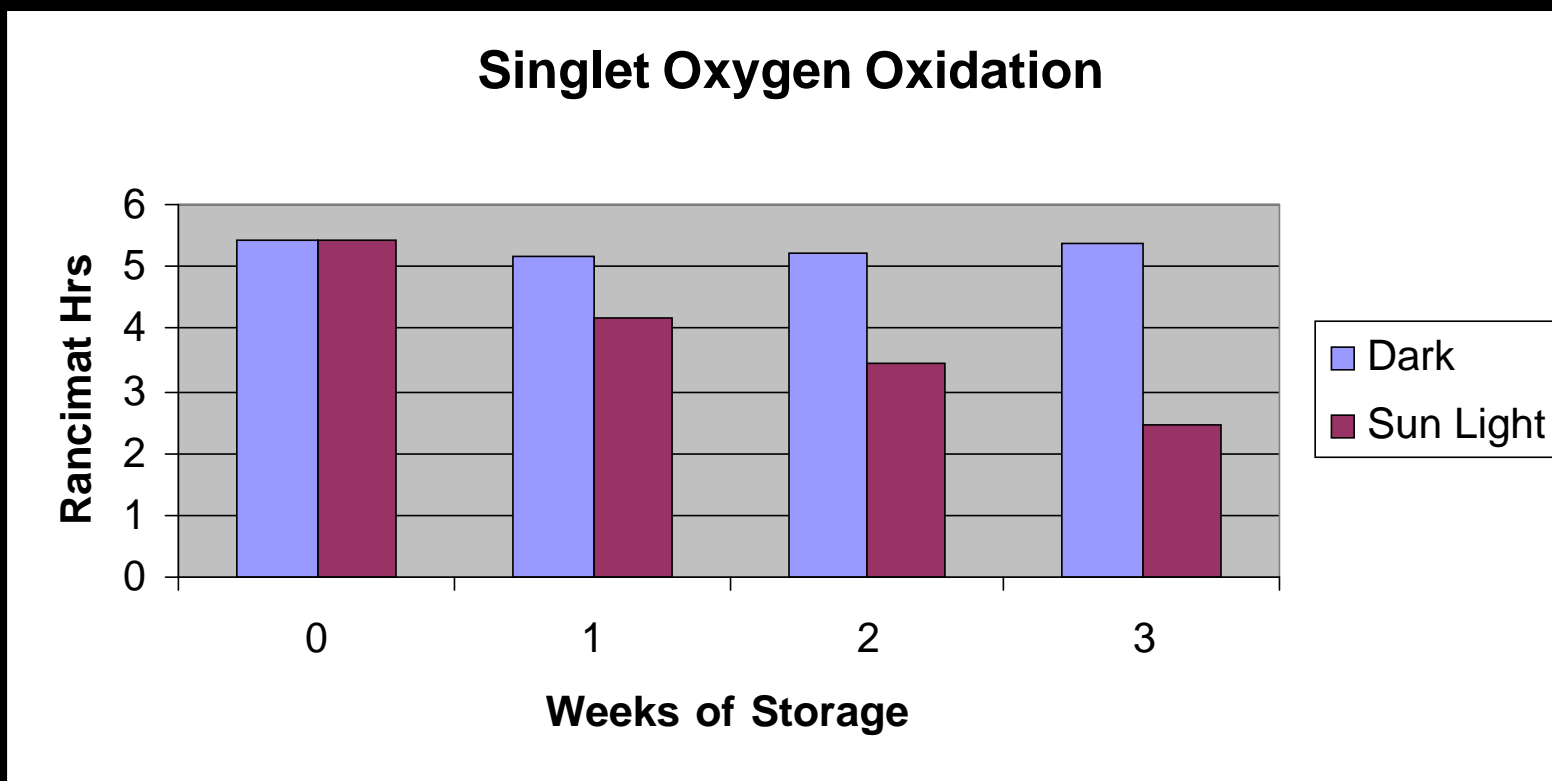
Stage I - Peroxide Formation

▶ Singlet Oxygen

- ▶ Formed via a photochemical process



Stage I - Peroxide Formation




Stage I - Peroxide Formation

Triplet Oxygen

 Free radical oxidation

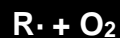
 Common Initiation

 Two pathways
for propagation

INITIATION



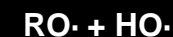
PROPAGATION [A] (OO·)



PROPAGATION [B] (OOH)



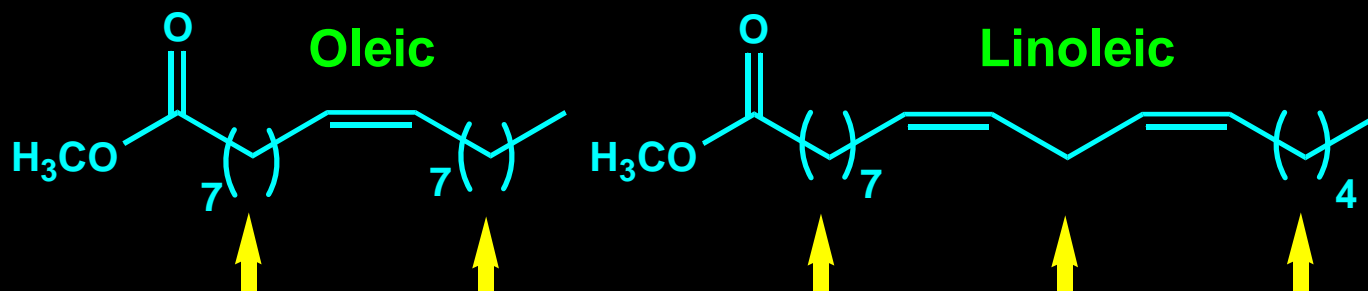
TERMINATION



Initiation Rate Factors

Hydrogen abstraction

Allylic hydrogen most easily removed



Main Component

Rape (18:1)

Soy (18:2)

Linseed (18:3)

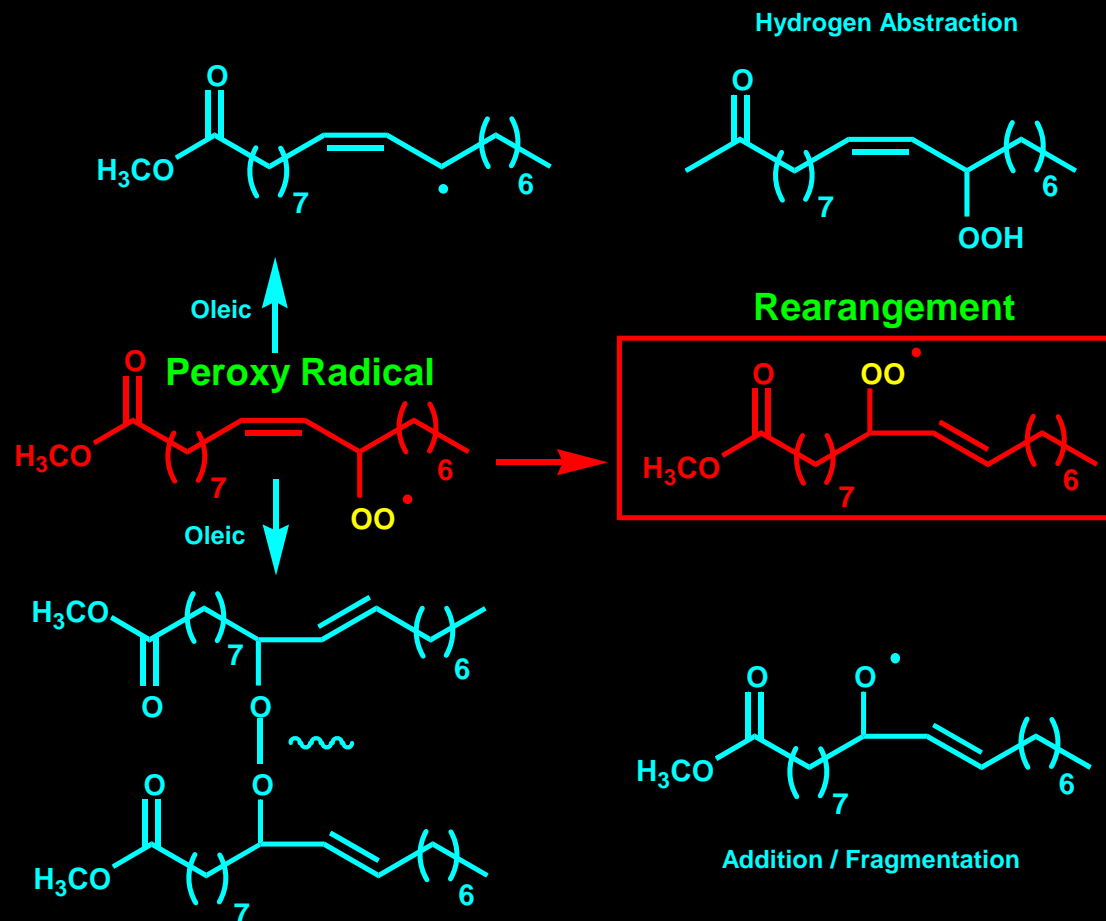
Oxygen Uptake Rates

1

41

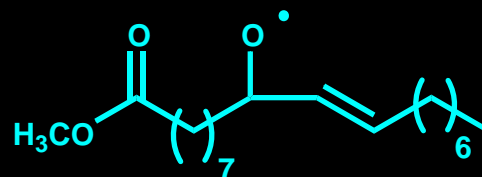
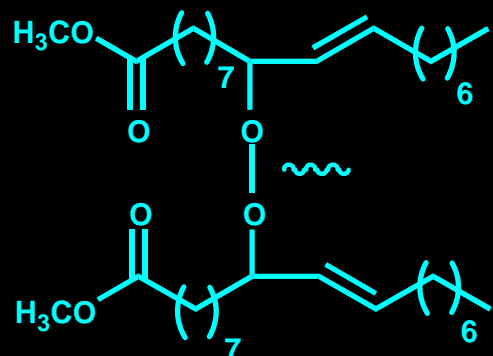
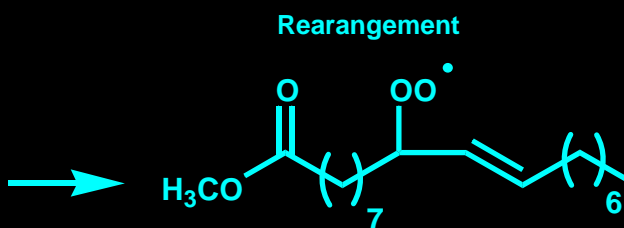
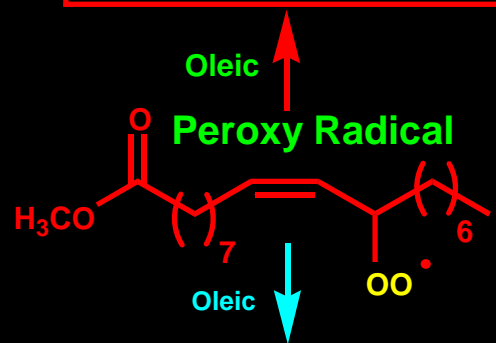
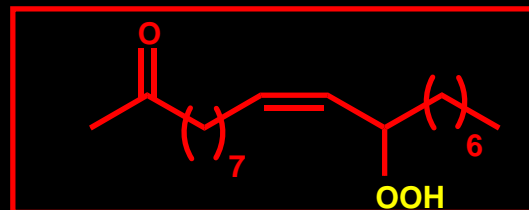
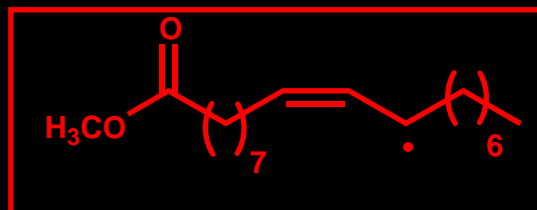
98

Propagation - Peroxy Radical

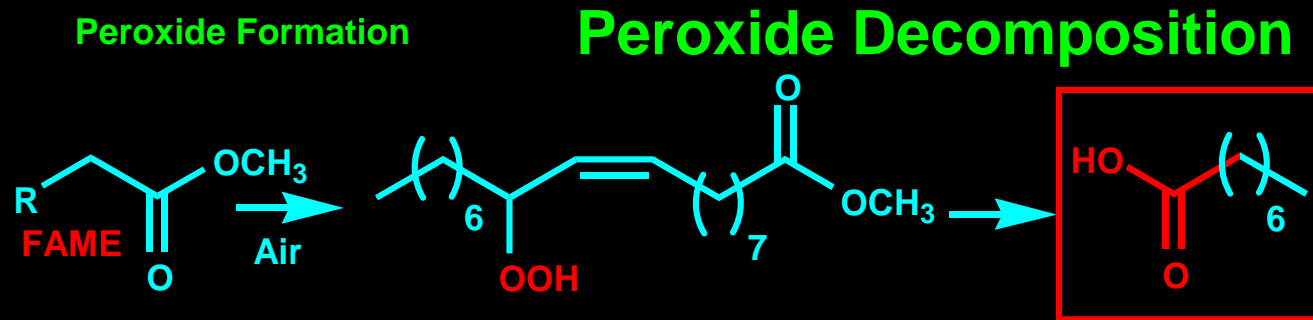


Propagation - Peroxy Radical

Hydrogen Abstraction

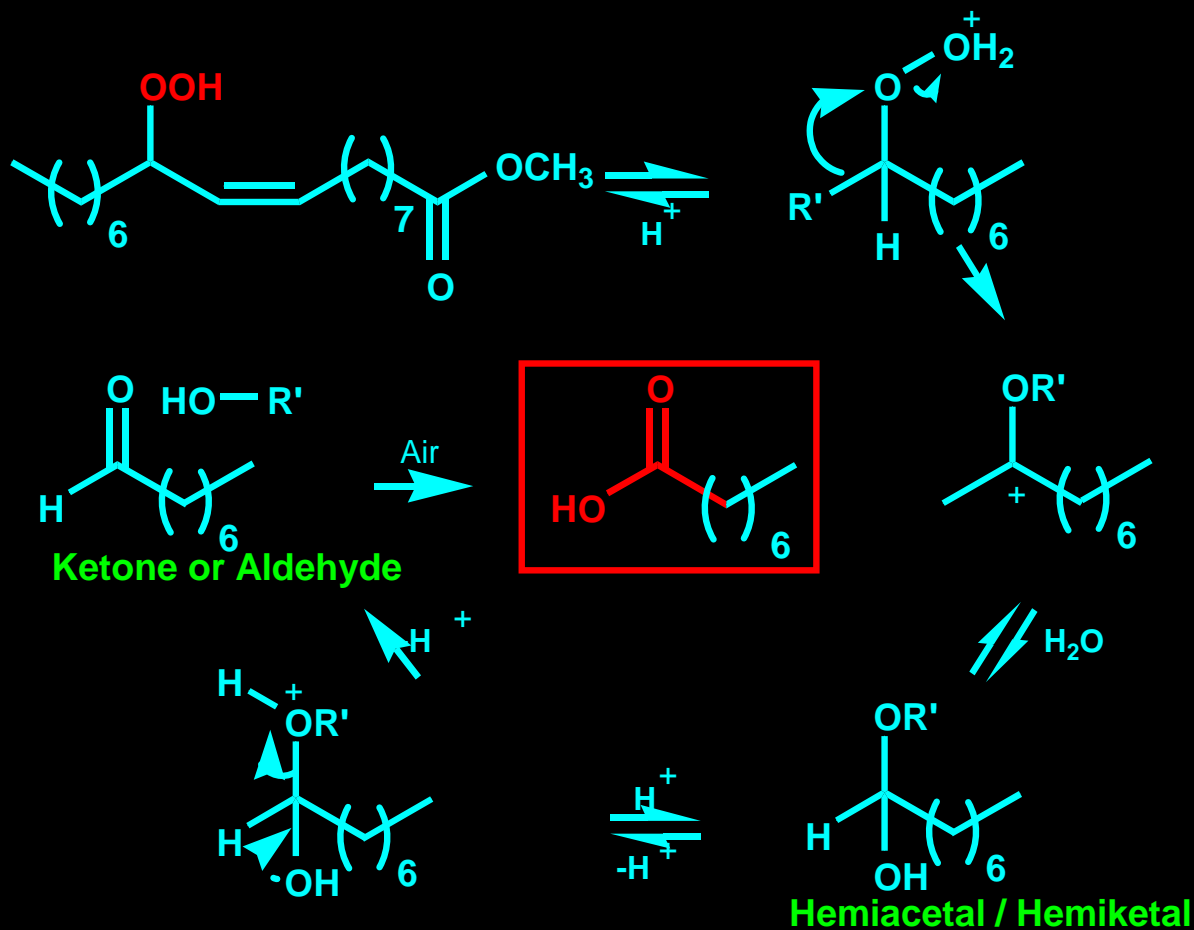


Peroxide Decomposition



- **Peroxide Formation**
 - Two alternative routes
 - Reasonable well defined
- **Peroxide Decomposition**
 - Many reacting species involved
 - Alternative pathways
 - Less well defined

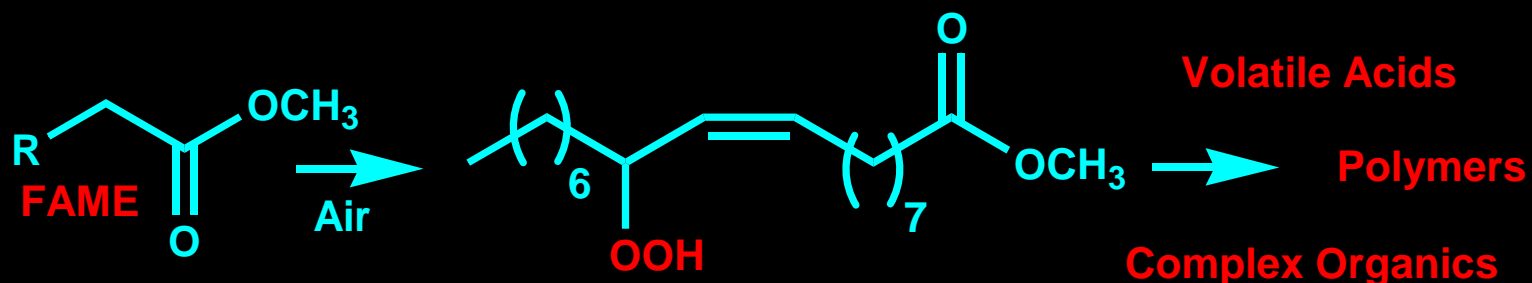
Hydroperoxide Rearrangement



Peroxide Decomposition

Peroxide Formation

Peroxide Decomposition



Many different decomposition pathways

- Free radical
- Metal mediated
- Acid induced degradation

Many different decomposition products

- Volatile polar compounds
- Monomeric compounds
- Dimers – trimers - polymers

Summary

- Oxidation main mechanism of Biodiesel degradation
- Oxidation occurs at or near sites of un-saturation
- Oxidation two distinctive stages
 - Stage I Peroxide formation
 - Stage II Peroxide decomposition
- Peroxide formation singlet or triplet oxygen
- Peroxide decomposition follows multiple reaction pathways to yield a diversity products
- The rate, amount and types of peroxides formed and the subsequent degradation products formed are dependant on a number of different factors
- **All chemical pathways must be considered when stabilizing Biodiesel**

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