



Ensuring Oxidative Stability Quality in Biodiesel—The Impact of Metals and Accelerated Aging

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The Problem of Oxidation

Biodiesel



Catalysts

Free Radicals



O_2

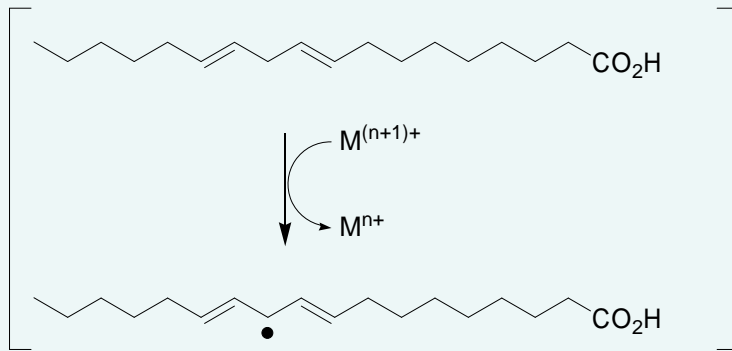
Peroxides



Decomposition Products

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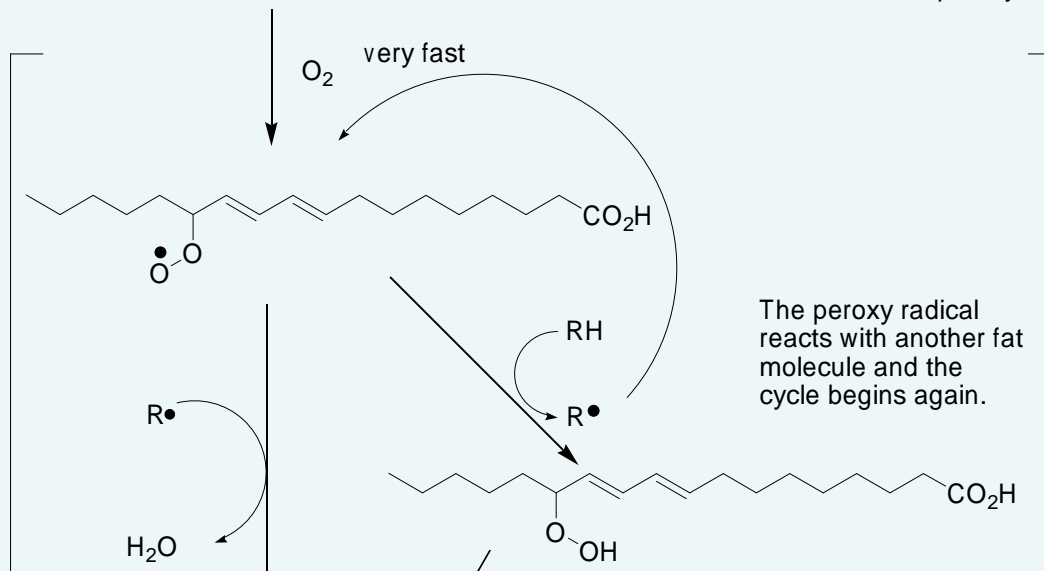
Initiation



The abstraction of the hydrogen is a metal catalyzed reaction. It may also be catalyzed by a photosensitizer in the presence of UV light.

The resultant fat radical reacts rapidly with oxygen to form the peroxy radical.

Propagation



The peroxy radical reacts with another fat molecule and the cycle begins again.

Termination

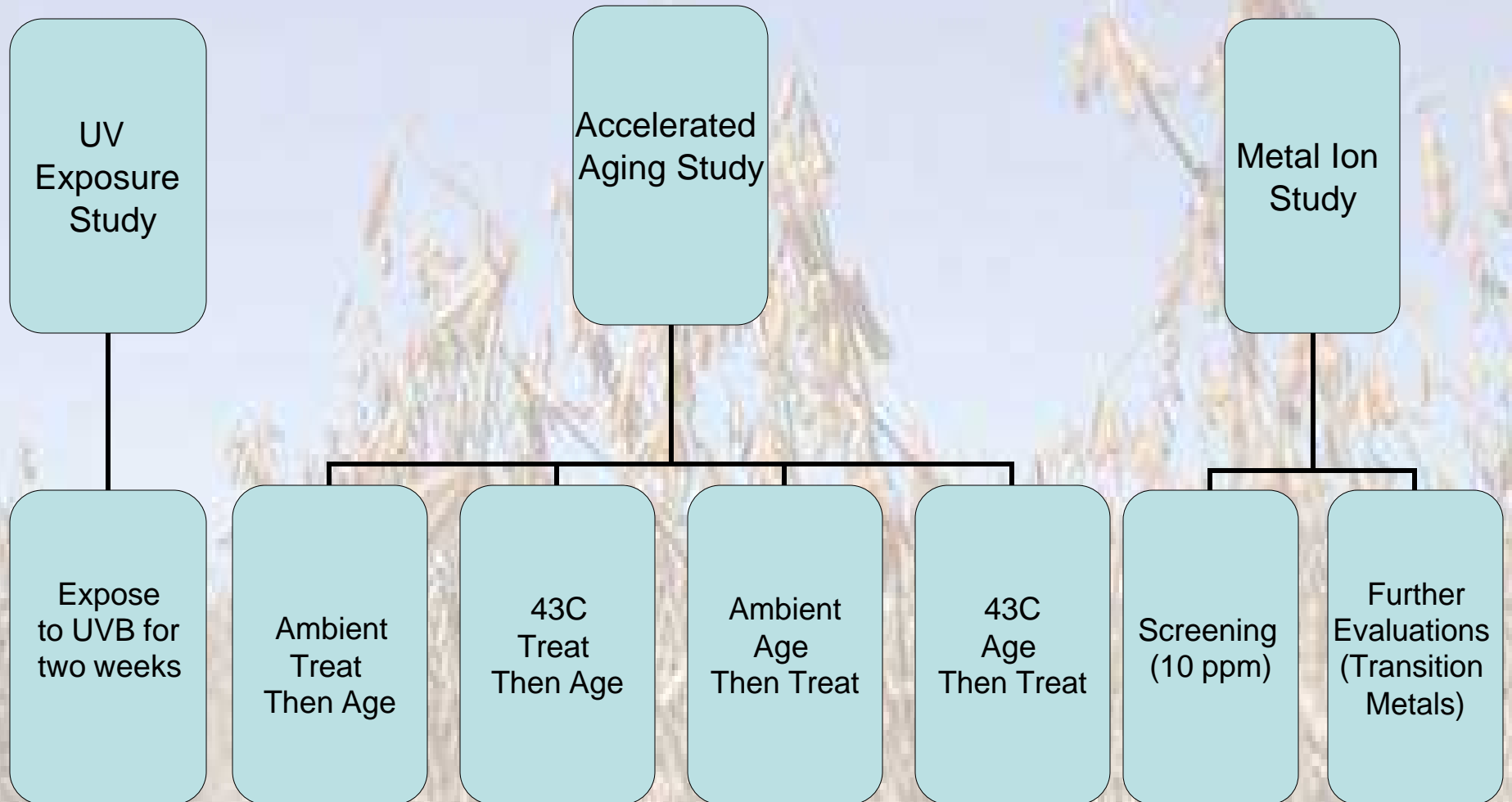
dimers, trimers, tetramers
Low MW breakdown products (aldehydes, acids, etc)

Reaction of the peroxy radical with a fat radical, or decomposition of the hydroperoxide results in the termination of the cycle. The product of the termination reactions are high molecular weight compounds or potentially corrosive compounds.

- Metal catalyzed initiation
- Peroxide formation and regeneration in propagation
- High molecular weight byproducts in termination

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The Experiments



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The Aging Experimental Design

- Obtain fresh biodiesel
- Treat with various antioxidants and timing
- Subject to various stresses
- Monitor oxidation via various analytical tools

The Stresses

- Time – Aged for 12 weeks
- Temperature – Ambient and 43° C
- Air – Periodic Air Sparging

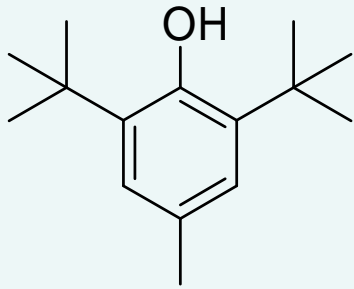
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The Analytical Tools

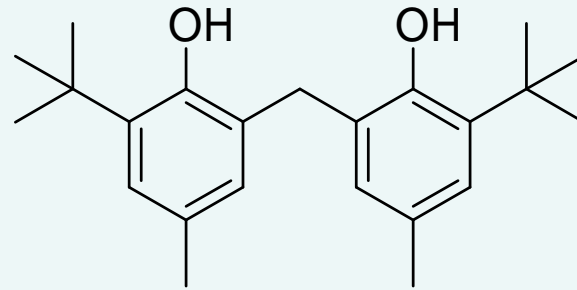
- Oil Stability Index (OSI)
- Peroxide Value (PV)
- Ultraviolet Absorbance (UV)
- Gel Permeation Chromatography (GPC)
- Yellowness Index (YI)

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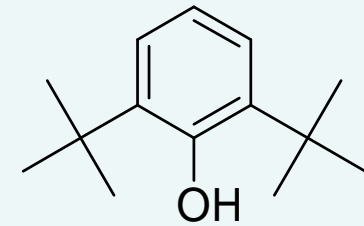
Antioxidants Evaluated



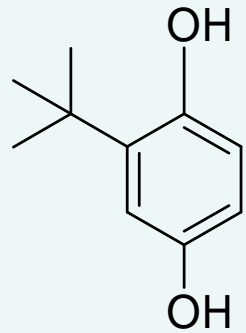
BHT



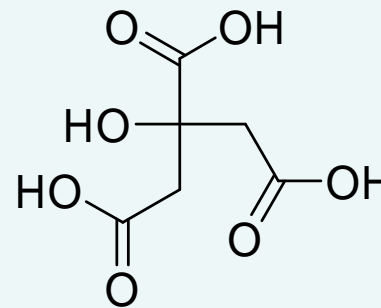
BKF



2,6-di-t-butylphenol



TBHQ



citric acid

Eastman BioExtend

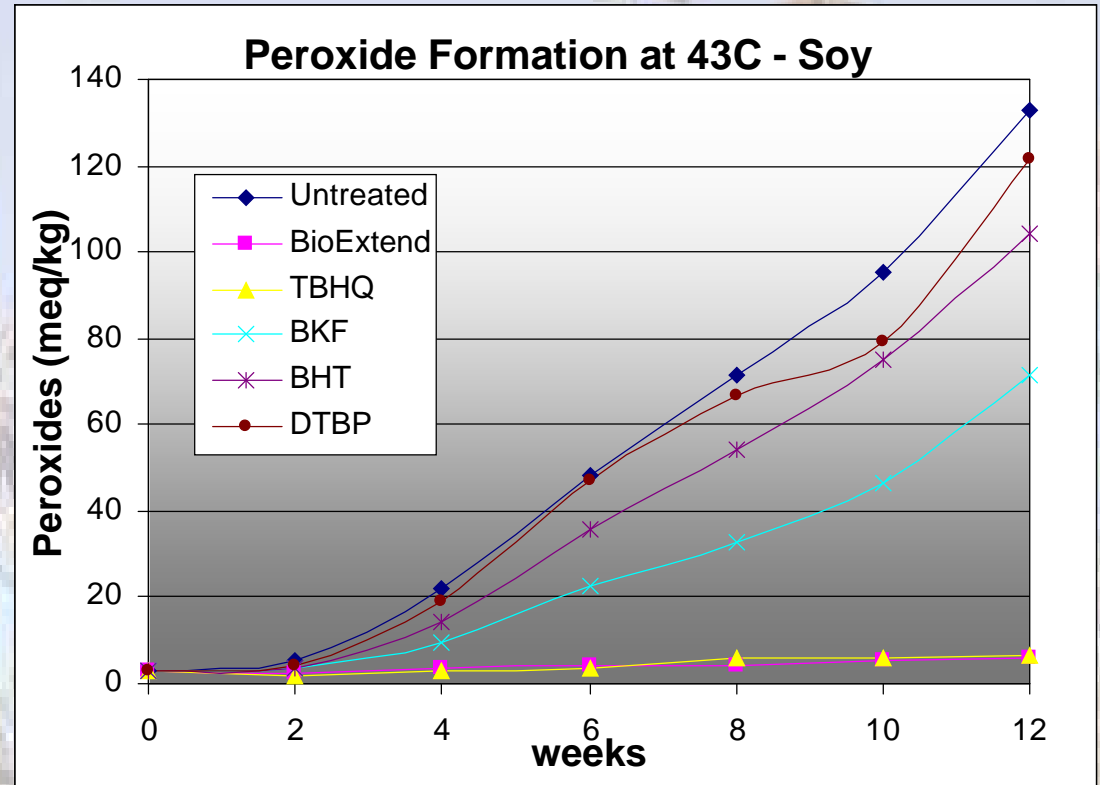
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Some Tools are Better Than Others

- Yellowness Index
 - Some samples yellowed
 - Some samples bleached
- Not a discerning tool for assessing degradation

Peroxide Value

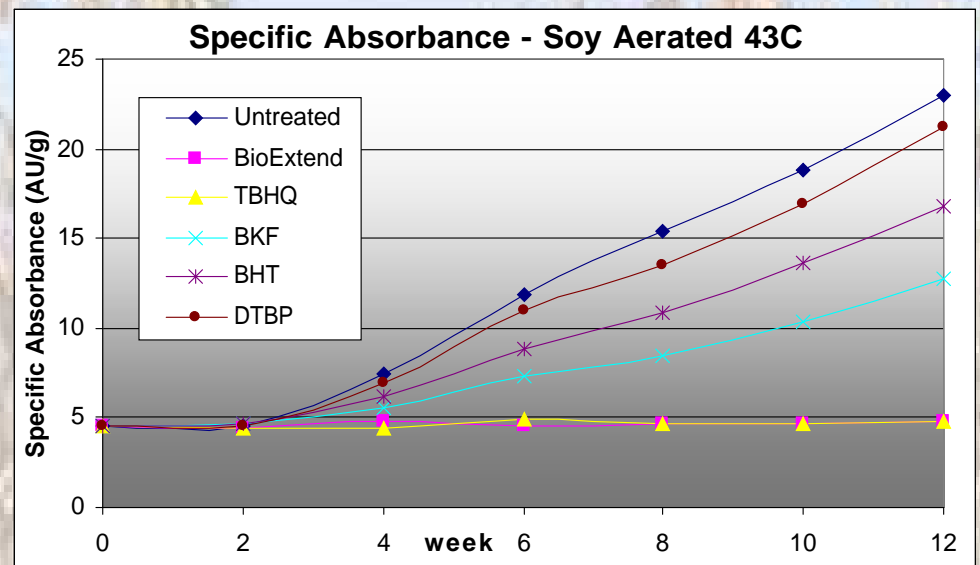
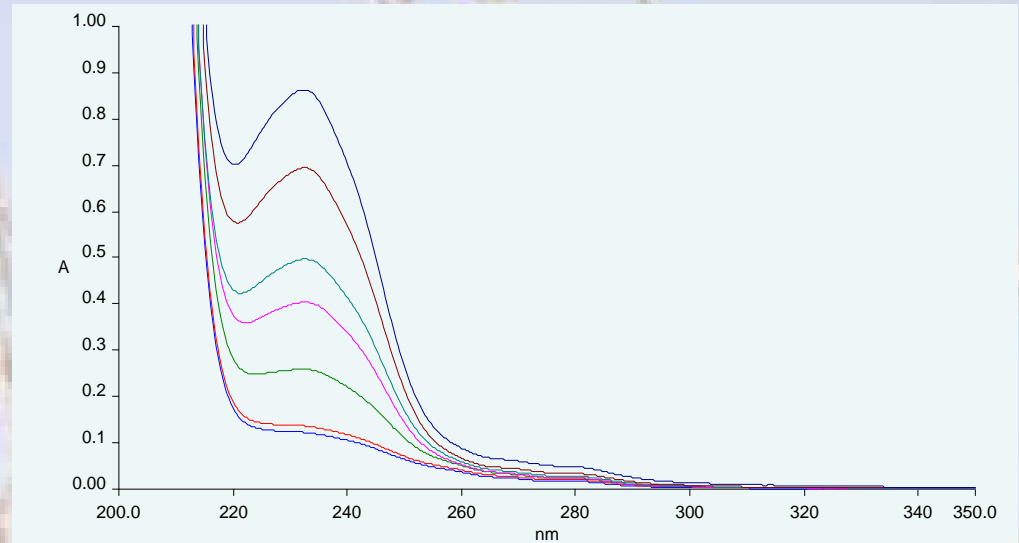
- Ambient samples increased only slightly
- At 43° C, PV showed dramatic increases, except for TBHQ and BioExtend
- Little to no dependence upon aeration (small effect seen for DTBP and untreated)



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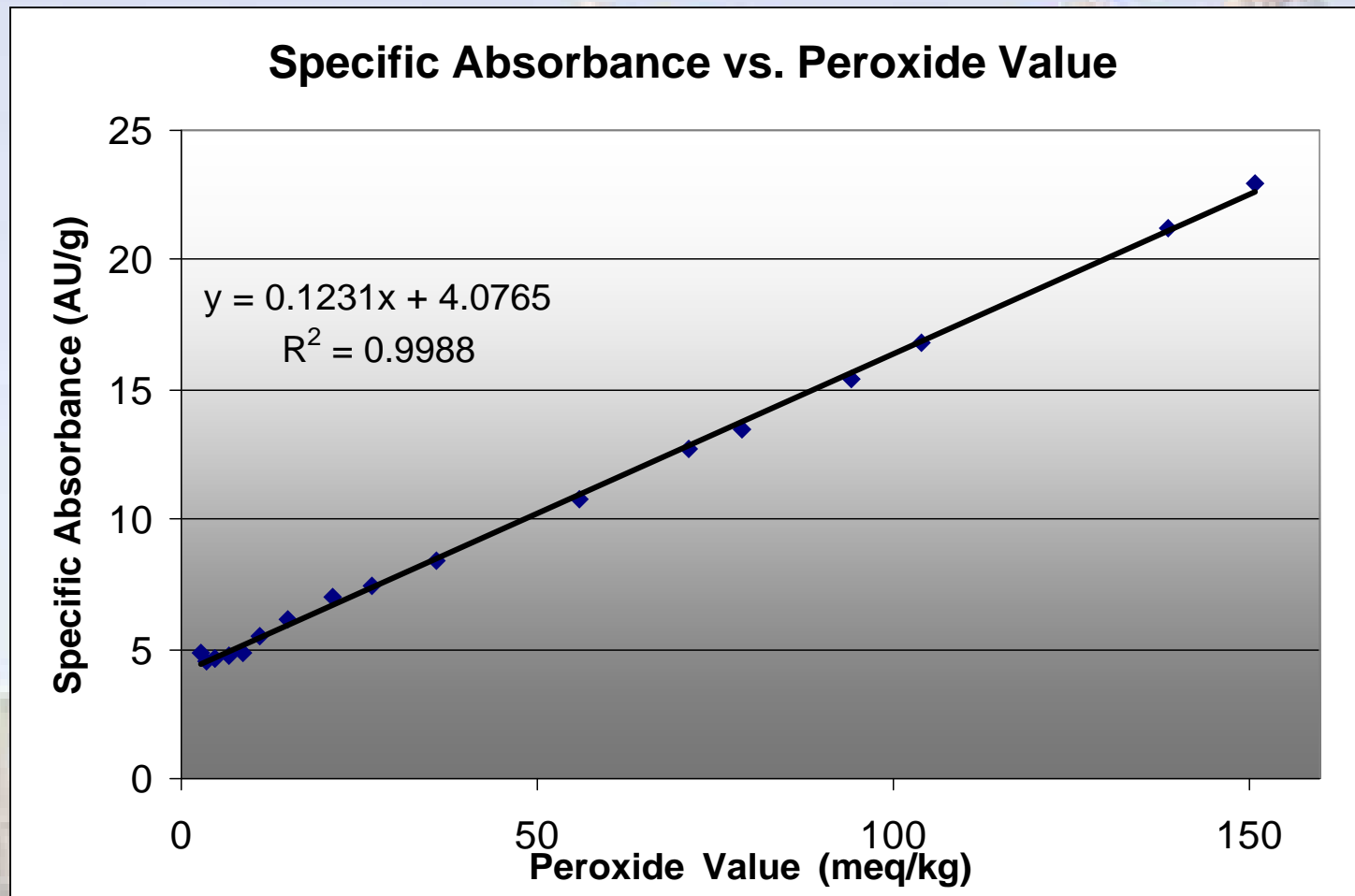
UV Absorbance at 232 nm

- UV Spectra and Absorbances Changed Little with Ambient Aging
- Aging at 43° C resembled PV data



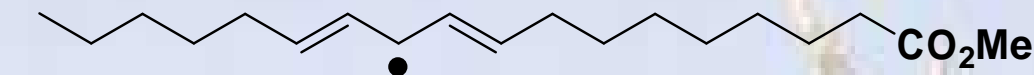
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Peroxide Value and UV Absorbance Relationship

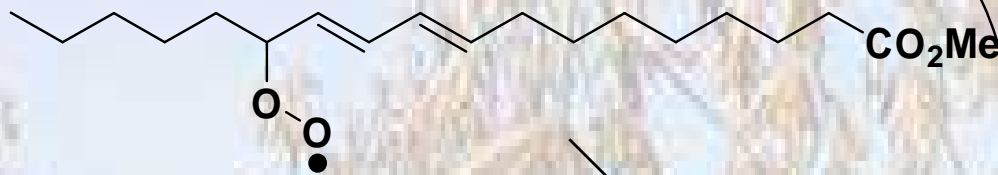


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The Propagation Phase forms both peroxides and conjugated systems

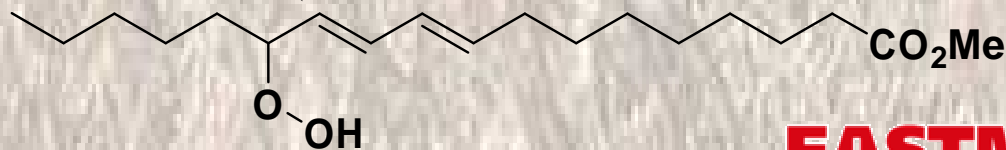


O_2 very fast



RH

$\text{R}\cdot$



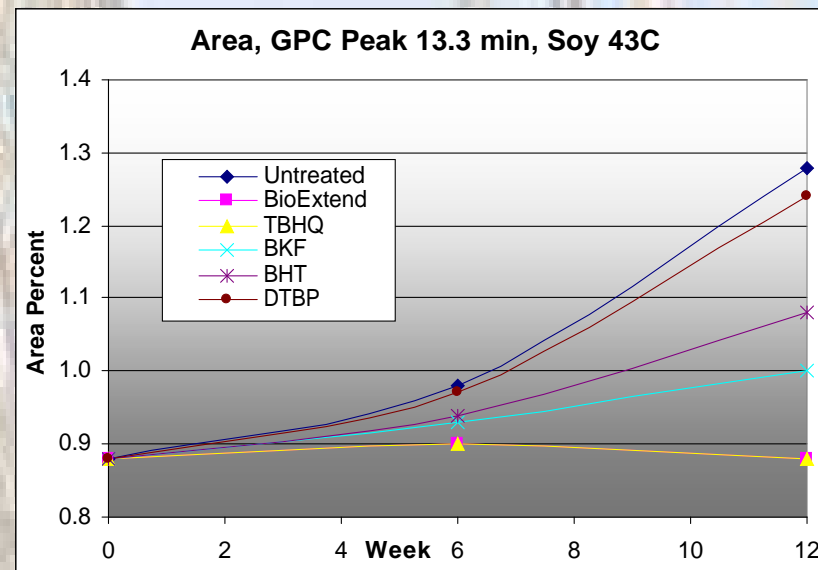
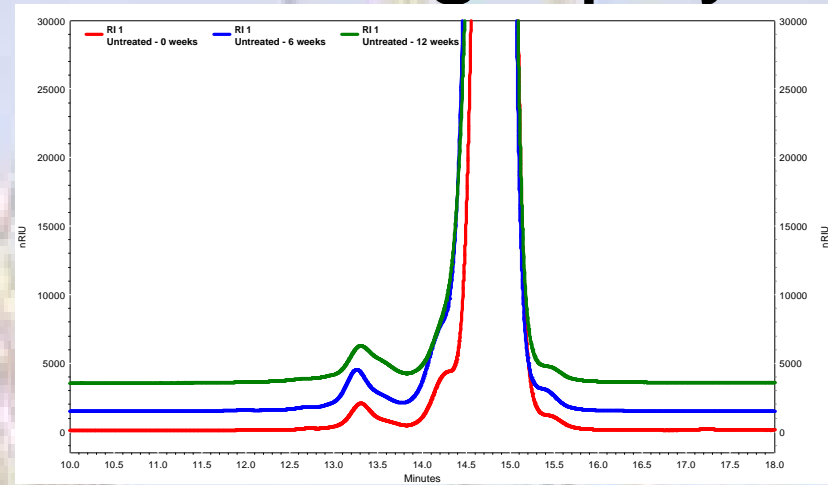
The fat radical reacts rapidly with oxygen to form the peroxy radical.

The peroxy radical reacts with another fat molecule to form the hydroperoxide; the double bonds in the hydroperoxide rearrange to form a conjugated system.

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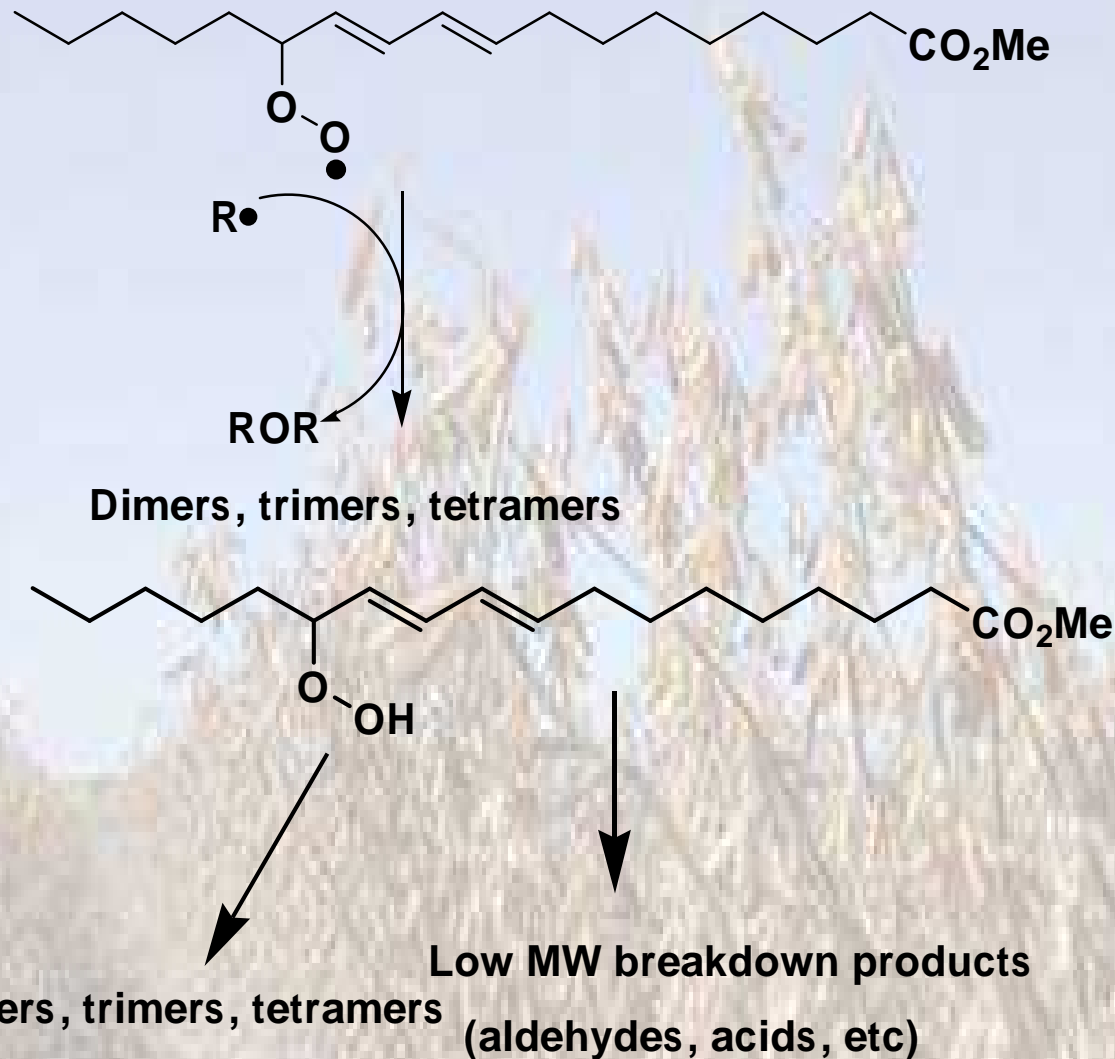
Gel Permeation Chromatography

- Peaks of higher MW species increase at 43° C
- Changes are only small (0.14-0.3%)



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GPC as a Measure of Oxidation Termination

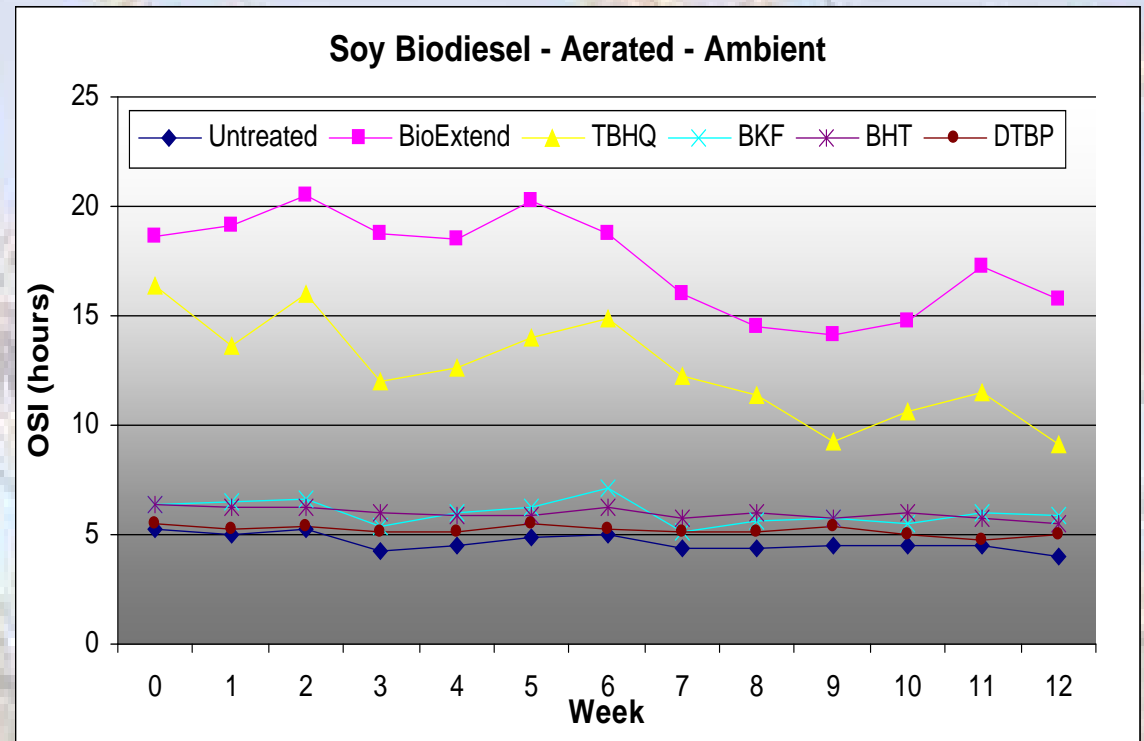


Reaction of the peroxy radical with a fat radical, or decomposition of the hydroperoxide results in termination of the cycle. The products of the termination reactions are high molecular weight compounds or potentially corrosive compounds.

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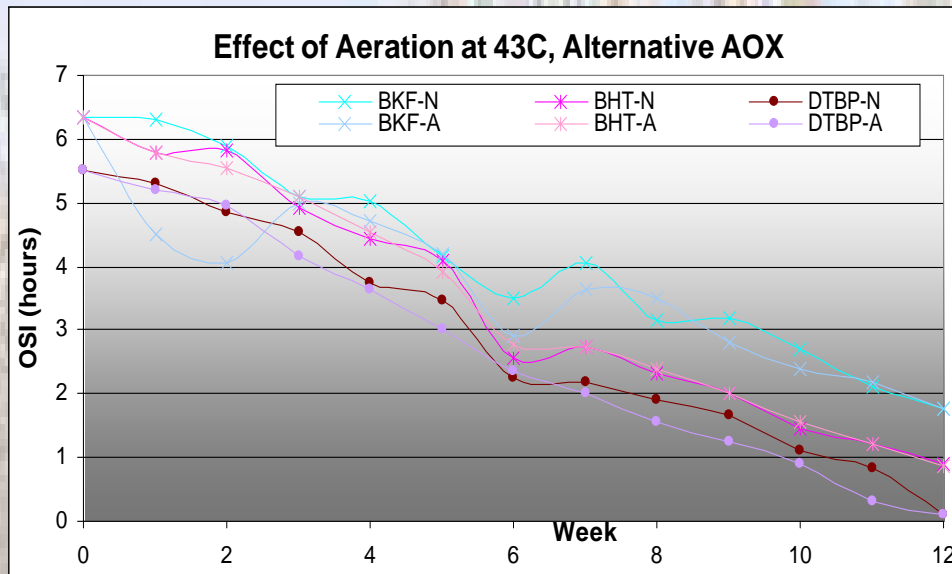
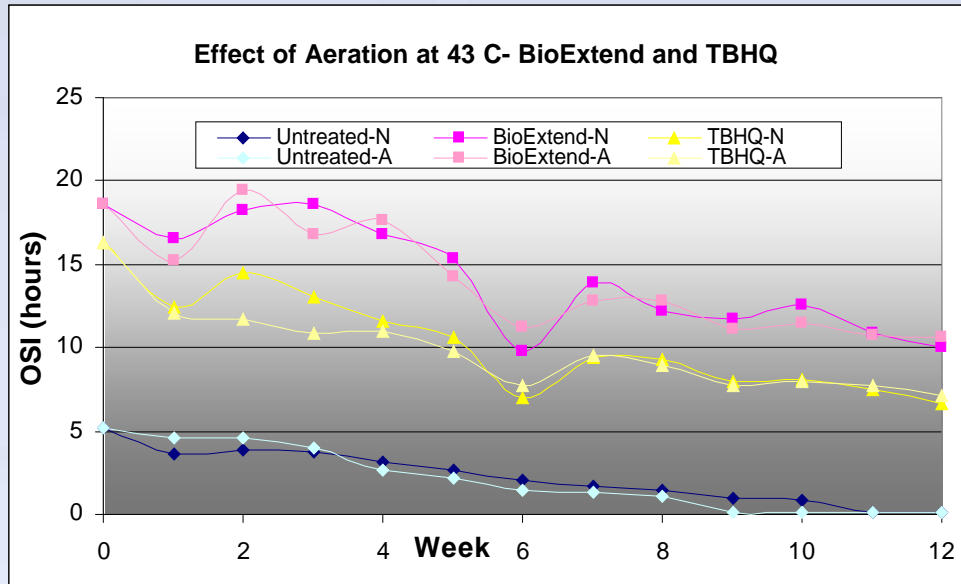
OSI is the premier tool

- Improvements in OSI of 0.25-13 hours were observed with addition of 200 ppm antioxidant
- At ambient conditions, only small losses in OSI are observed



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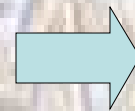
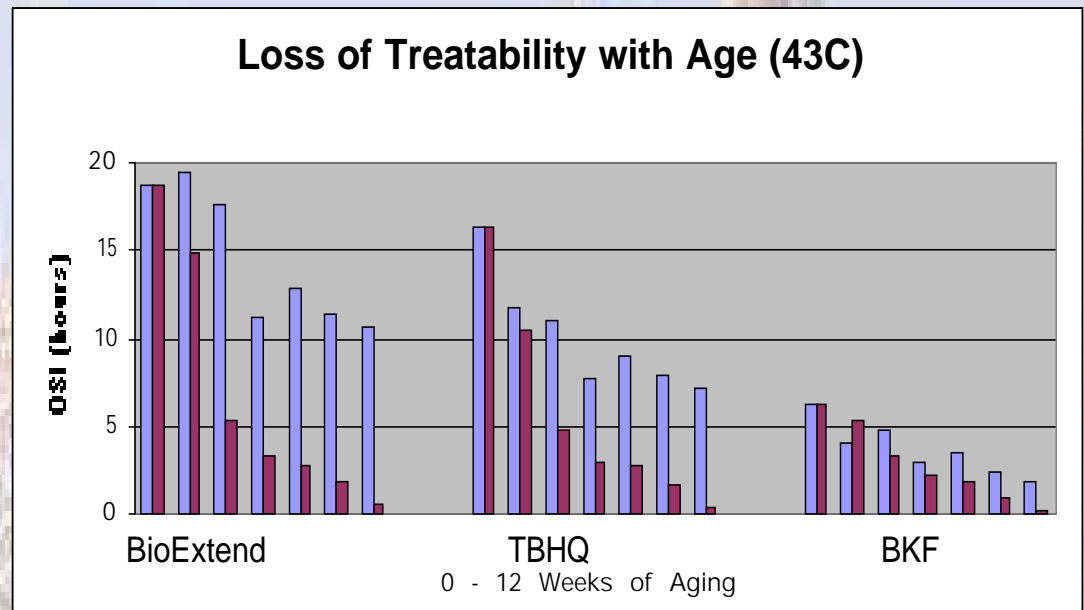
Degradation of OSI at 43° C



- All antioxidant-treated samples show significant degradation
- Light lines are aerated; darker lines are not aerated
- Aeration effect is observed only in untreated and DTBP-treated samples

All antioxidants show diminished efficacy when added to aged biodiesel

- Effect is minimal with ambient aged biodiesel
- No effect of aeration observed in antioxidants evaluated
- Blue—Fresh biodiesel treated, then aged at 43° C
- Red—Biodiesel aged at 43° C, then treated with antioxidant

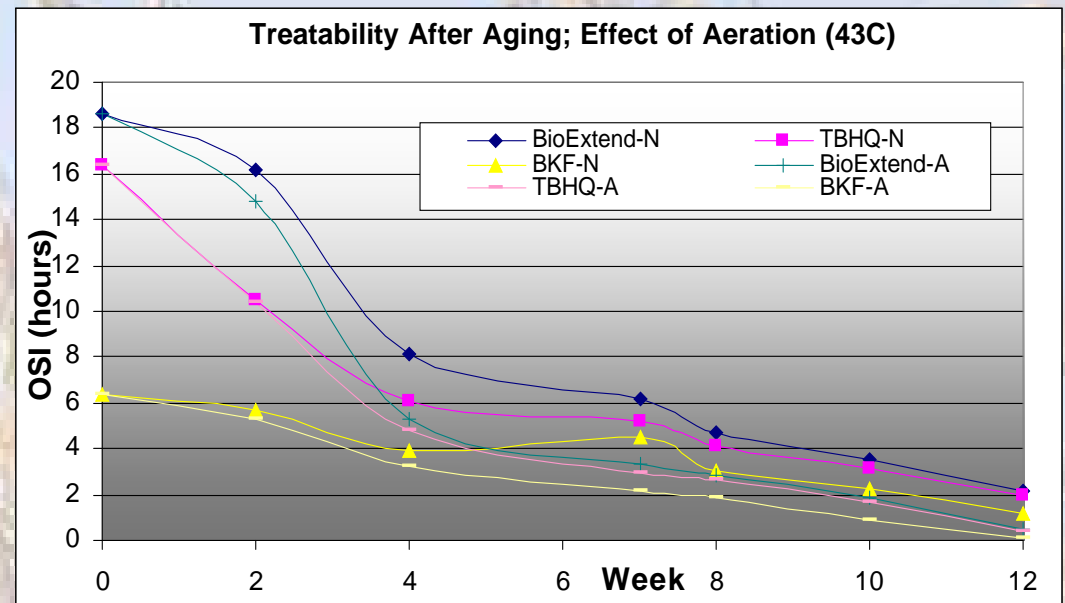


It is critical that antioxidants be added to freshly produced biodiesel

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Aeration is detrimental to "treat-after" effectiveness

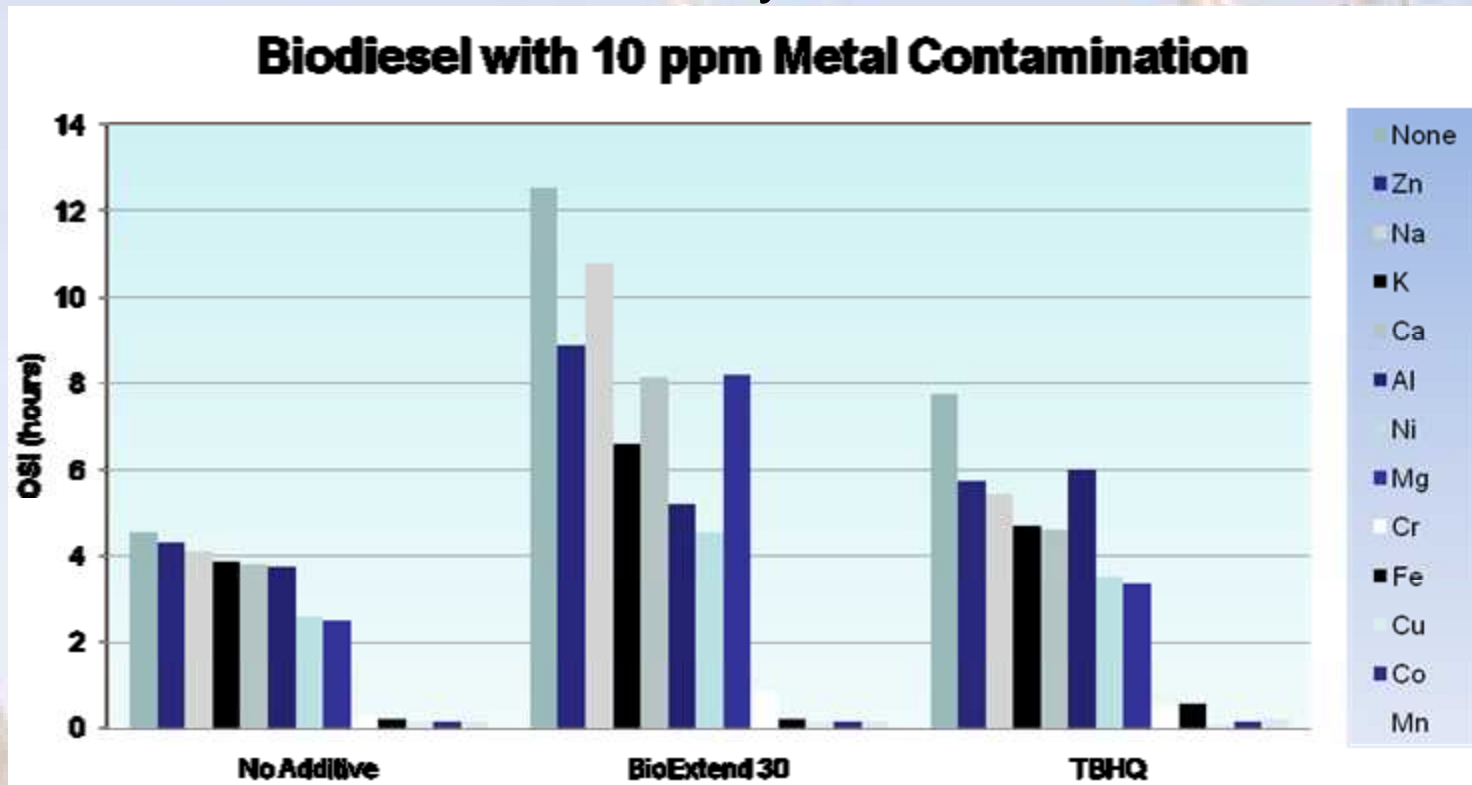
- All antioxidants evaluated show more loss in treatability with aeration
- After 4 weeks, the synergistic improvement typical of the chelator in BioExtend is lost
- Synergist important in metal-mediated initiation phase



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Metals Ion Contamination Study—

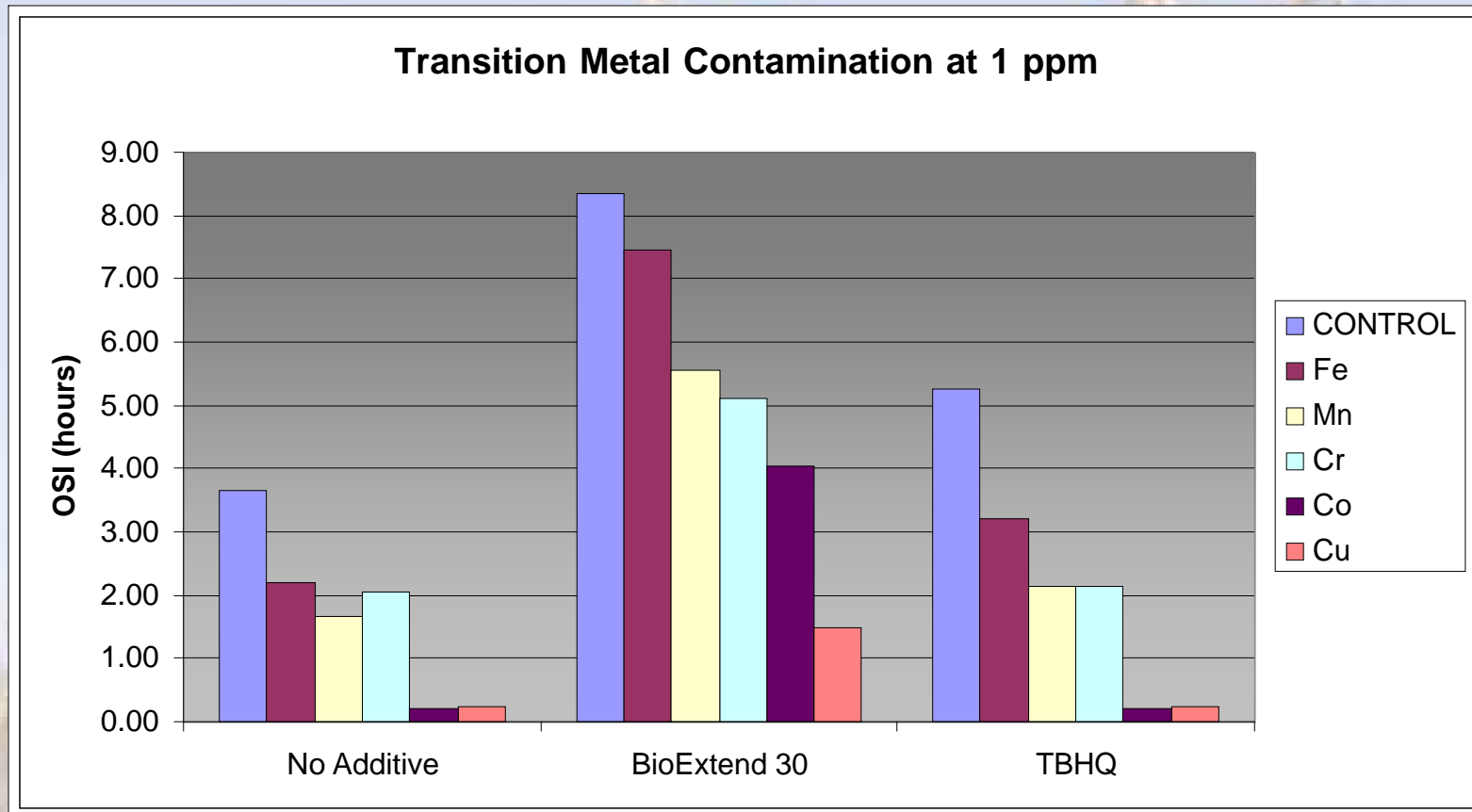
Metals were screened at 10 ppm. Antioxidants were added at 200 ppm active. Some metal ions had dramatic effect on the OSI, while others had only a small effect.



- Metals common as materials of construction, being present in hard water, or as process catalysts were included
- Transition metals have the greatest effect on OSI

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Transition metals, even at 1 ppm, can have a significant detrimental effect on OSI. A metal chelator improves the OSI performance over the antioxidant alone.



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week	0	1	2
OSI			
Control	4.7	0.15	
TBHQ Treated	17.65	0.2	
BioExtend Treated	19.5	0.2	
Peroxide Value			
Control	4.05	137.03	351.4
Control without UV			6.2
TBHQ Treated	3.84	81.18	333.9
BioExtend Treated	3.39	83.99	325
Yellowness Index			
Control	84.11	22.2	14.1
Control without UV			86.9
TBHQ Treated		38.1	17.8
BioExtend Treated		38.9	17.7

UV Exposure is Extremely Catalytic to Oxidation

- Exposure for two weeks in UVB Cabinet—extreme exposure
- All samples bleached, as measured by Yellowness Index
- Peroxide Values show highly oxidized product
- OSI reduced to near zero
- OSI not improved with antioxidant

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Conclusions

- Oxidation of biodiesel is a complex process with many factors playing a role
 - UV Exposure
 - Metal Ion Contamination
 - Storage Temperature
 - Air
 - Timing of Antioxidant Addition
- Understanding these factors and taking appropriate precautions are key to ensuring oxidative stability quality

Conclusions

Oxidative Stability is best ensured by:

- Eliminating potential for UV Exposure
- Eliminating contact with leachable metals, especially transition metals
- Using an effective antioxidant
 - Choosing an antioxidant with a metal chelator
 - BioExtend 30 > TBHQ > BKF > BHT > DTBP
- Adding antioxidant to freshly produced biodiesel
- Avoiding holding product at elevated temperature with air contact—especially if not stabilized

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