How to increase oxidative stability in fats and oils

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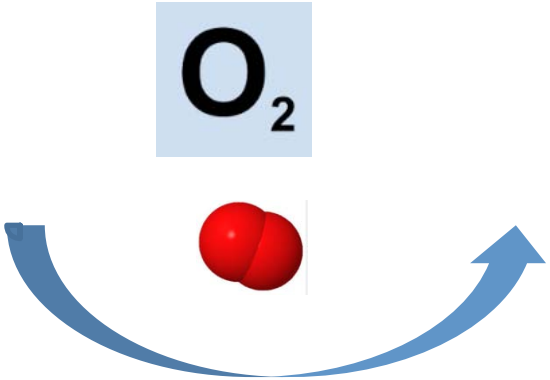
Mechanisms of lipid oxidation



Effects of lipid oxidation

- Flavor Quality Loss
  - Rancid flavor
  - Changes of color and texture
  - Consumer Acceptance
  - Economic loss
- Nutritional Quality Loss
  - Essential Fatty Acids
  - Vitamins
- Health Risks
  - Growth Retardation
  - Heart Diseases

Mechanisms of lipid oxidation

- **Autoxidation**
- Singlet oxygen oxidation
- Enzyme related oxidation
- **Deep fat frying**

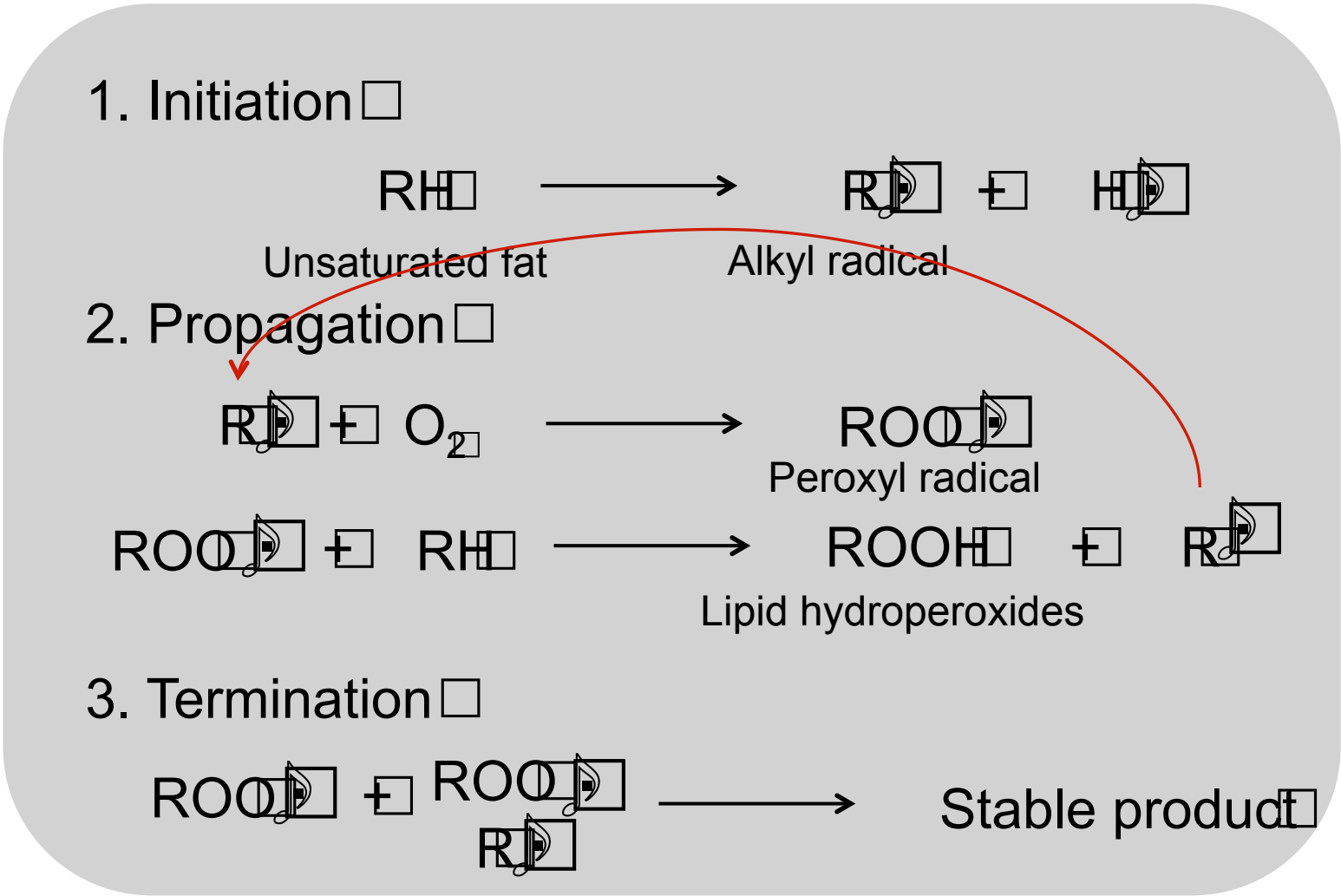
Autoxidation

Lipid compounds become radicals first and then react with triplet oxygen.

Autoxidation : free radical chain reactions.

1. Initiation : radical formation
2. Propagation : radical chain reaction
3. Termination: non- radical formation

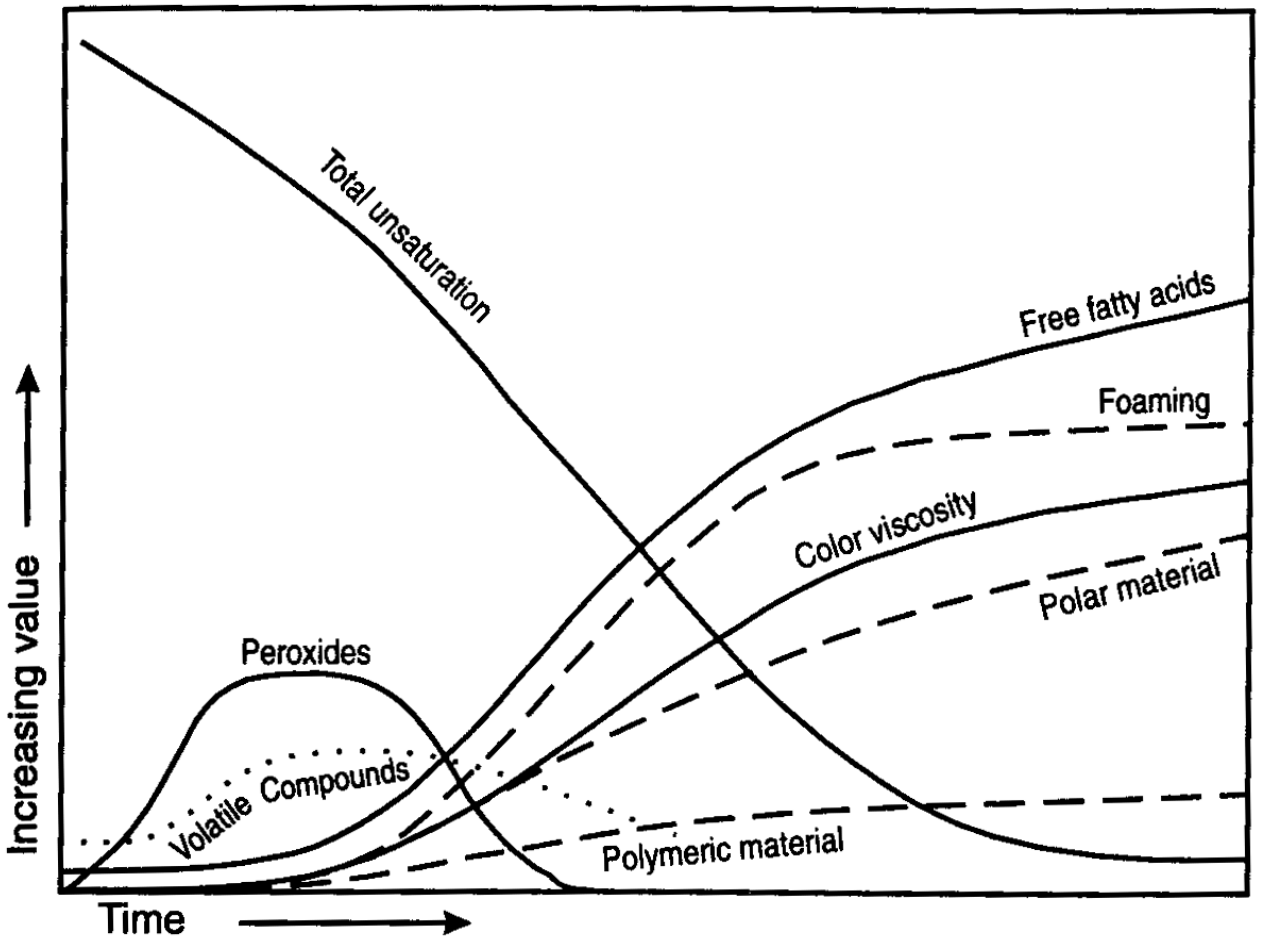
Autoxidation



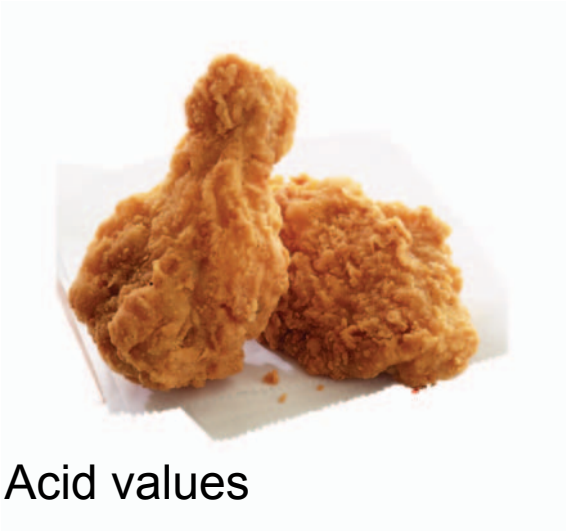
Deep-fat frying

Deep-Fat Frying is a process of immersing food in hot oil so that the flavors and the juices are retained in a crisp crust of food by simultaneous heat and mass transfer.

Changes in volatile and non-volatile during frying



Measuring parameters for deep fat frying products



Acid values

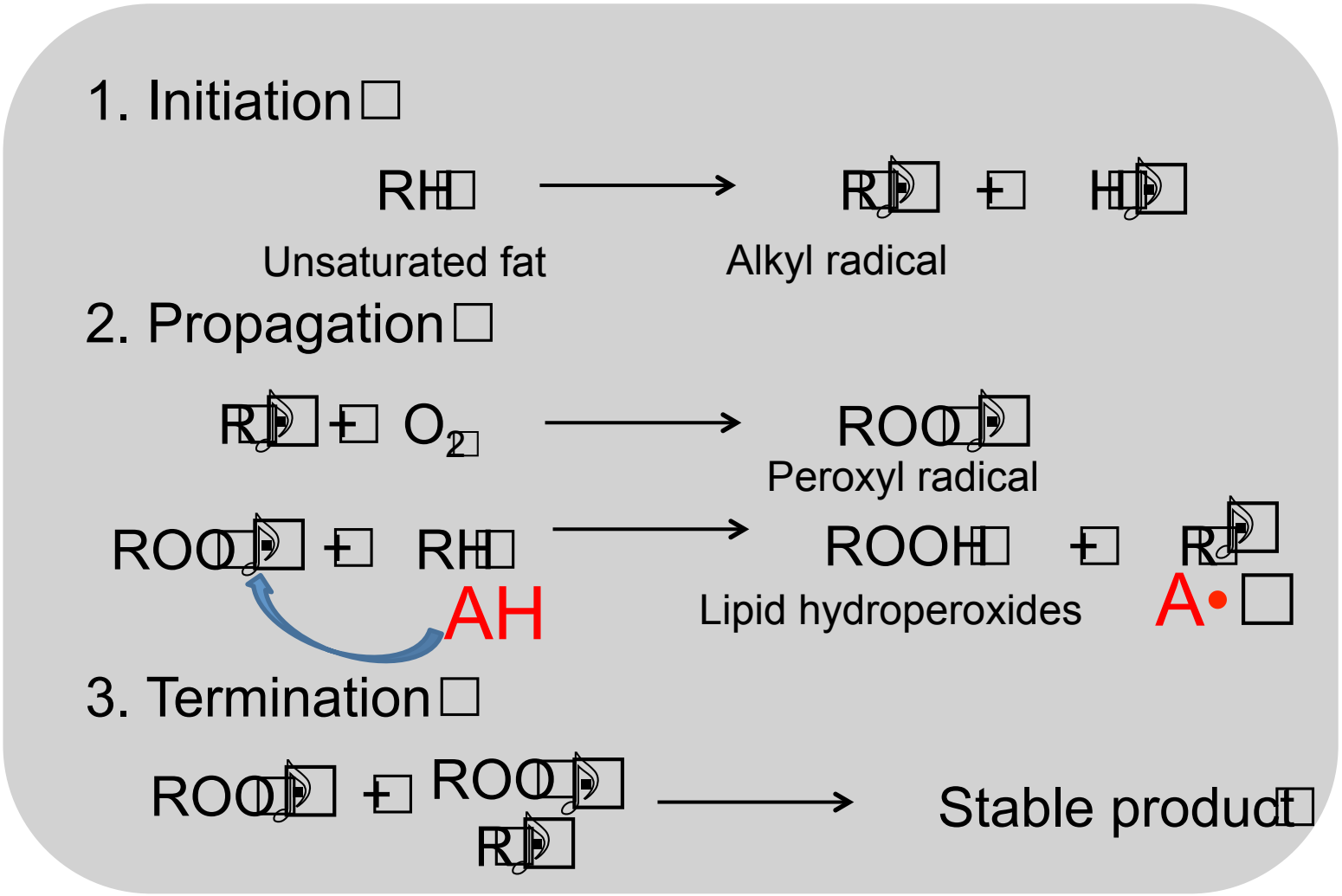
Total polar materials (TPM)

Mechanisms of antioxidants

Types of antioxidants

- Hydrogen donating compounds (Free radical scavengers)
- Singlet oxygen quenchers
- Metal chelators
- Enzymatic antioxidants
- Oxygen scavengers

Hydrogen donating antioxidants during autoxidation



Antioxidant mechanisms of hydrogen donating compounds :

chemical point of views

- One-electron reduction potential (mV)
- Bond dissociation enthalpy (kcal/mol) between carbon and hydrogen

One-electron reduction potential of s elected compounds (mV)

$HO\cdot, H^+ / H_2O$	2310
$RO\cdot, H^+ / ROH$	1600
$ROO\cdot, H^+ / ROOH$	1000
Astaxanthin	970
$H_2O_2/ 2H^+, O_2\cdot^-$	940
$GS\cdot/GS^-$ (Glutathione)	920
beta-carotene	840
Kaempferol	750
Hesperidin	720
Luteolin	600
Rutin	600
$PUFA\cdot, H^+ / PUFA$	600

Good Antioxidants
< 600 mV

Ferulic acid	595
Catechin	570
Chlorogenic acid	550
Caffeic acid	534
$Catechol\cdot, H^+ / Catechol$	530
α-Tocopheroxyl $\cdot, H^+$ /α-Tocopherol	480
Trolox	480
Myricetin	360
Quercetin	330
$H_2O_2, H^+ / H_2O, HO\cdot$	320
$Ascorbate^-\cdot, H^+$ / Ascorbate	282
$O_2/ O_2\text{-}\cdot$	-330
RSSR/ RSSR-$\cdot$ (GSH)	-1500
H_2O / e^{-aq}	-2870

Bond dissociation enthalpy of selected compounds (kcal/mol)

Ascorbic acid	69, 83
Dehydroascorbic acid	71
alpha-tocopherol	77.1, 78.87, 79.30
beta-tocopherol	80.20
gamma-tocopherol	80.04, 80.10
delta-tocopherol	81.62, 82.20
BHA	77.20
Biacylic hydrogen at C11 in linoleic acid	75-80
Allyic hydrogen at C8 or C14 in linoleic acid	88
Alkyl hydrogen at C17 or C18 in linoleic acid	101

BHT	80
Cafferic acid	81.21
Myricetin	81.48
catecol	81.80, 82.82
Quercetin	81.98
Rutin	82.15
Hesperidin	82.65
Hydroperoxides	87.49
Phenol	90.40
Ethanol	105.40
H_2O	118.00

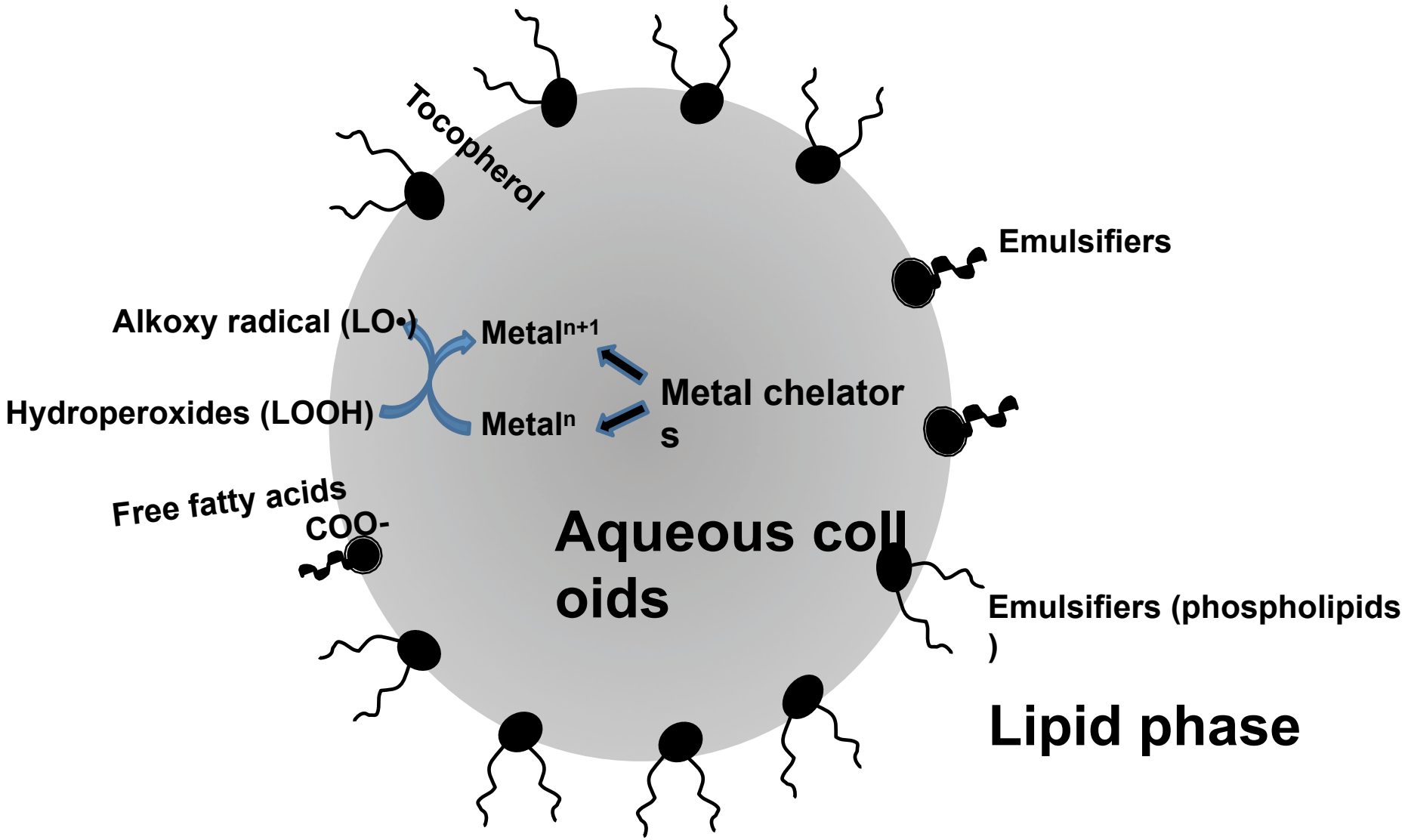
Good Antioxidants
< 75-80 kcal/mol

Physical point of view

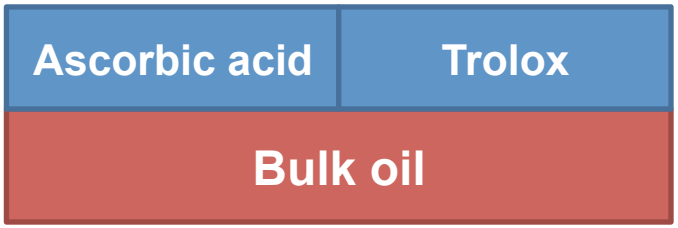
- Food matrix

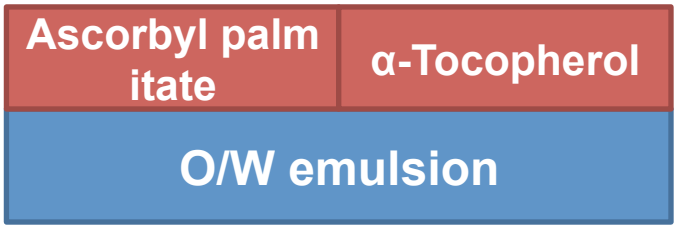
- Location for lipid oxidation

Interfacial phenomena for lipid oxidation



Antioxidant polar paradox theory



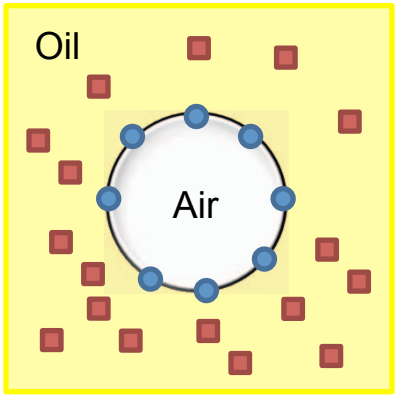


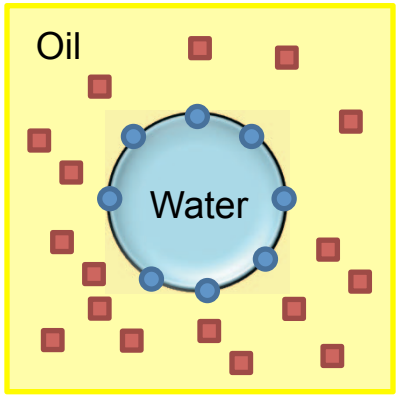
- Polar antioxidants (ascorbic acid, trolox) are more effective in less polar media (bulk oils).

- Nonpolar antioxidants (ascorbyl palmitate, α-tocopherol) are more effective in relatively more polar media (oil-in-water emulsions).

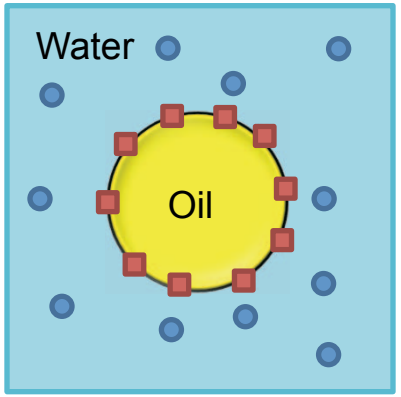
Antioxidant polar paradox theory

Bulk oil





O/W emulsion



Polar antioxidant

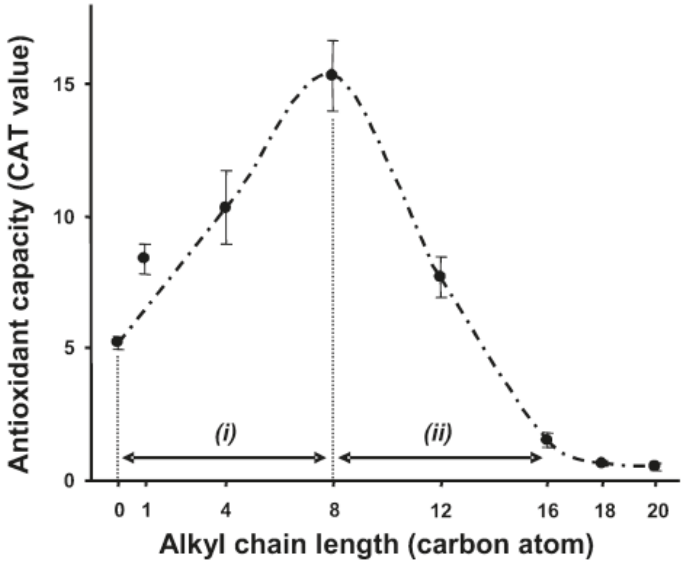
Non-polar antioxidant

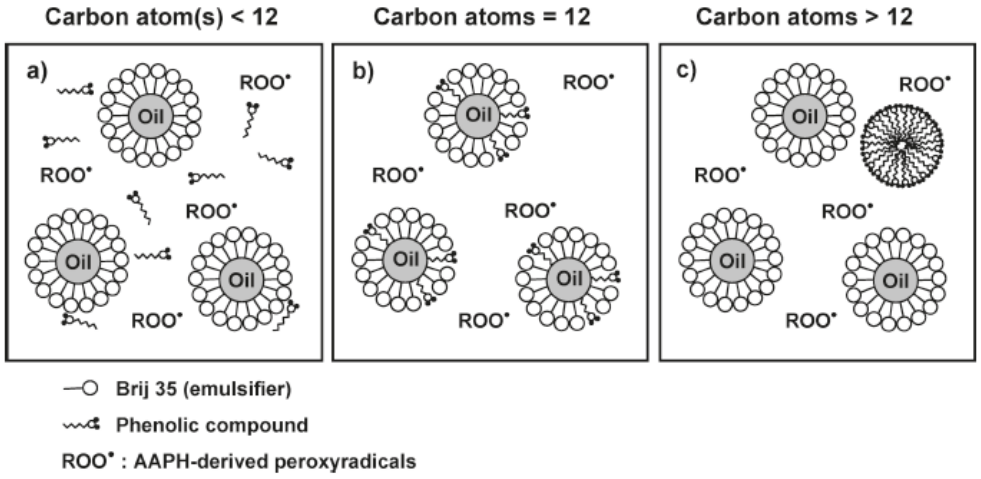
(Frankel *et al*., 1994)

Re-evaluation of antioxidant pola r paradox theory

In O/W emulsion systems

Cut-off theory of phenolipid antioxidants

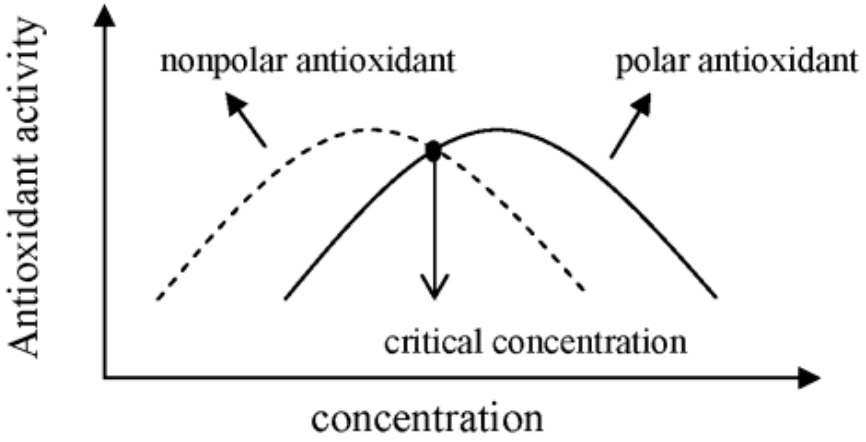


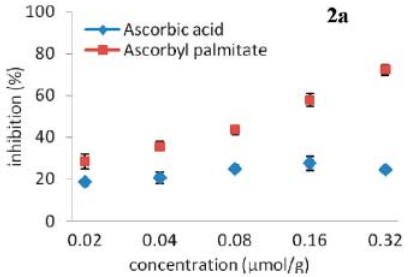


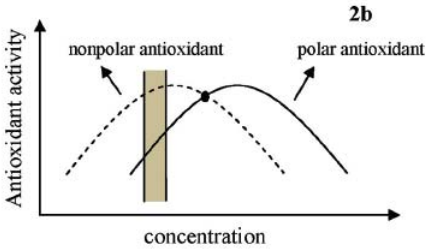
(Laguerre *et al*., 2010; Lucas *et a*l., 2010)

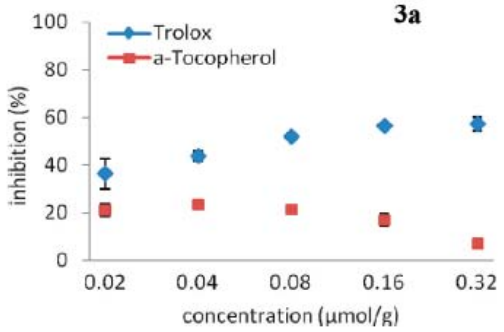
Re-evaluation of antioxidant pola r paradox theory

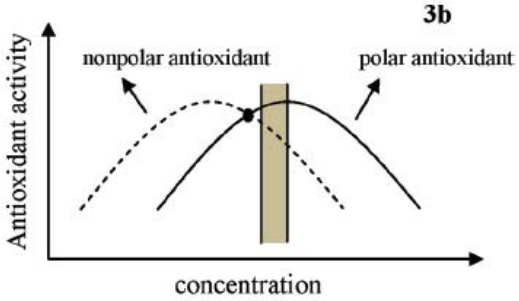
In bulk oil systems











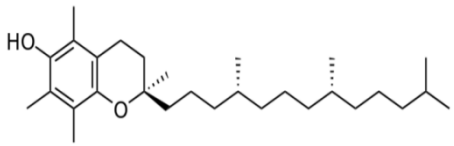
(Shahidi and Zhong, 2011)

Role of moisture on lipid oxidat ion

Effects of moisture on lipophilic anti oxidant properties in bulk oils

- Lipophilic antioxidant (α-tocopherol)

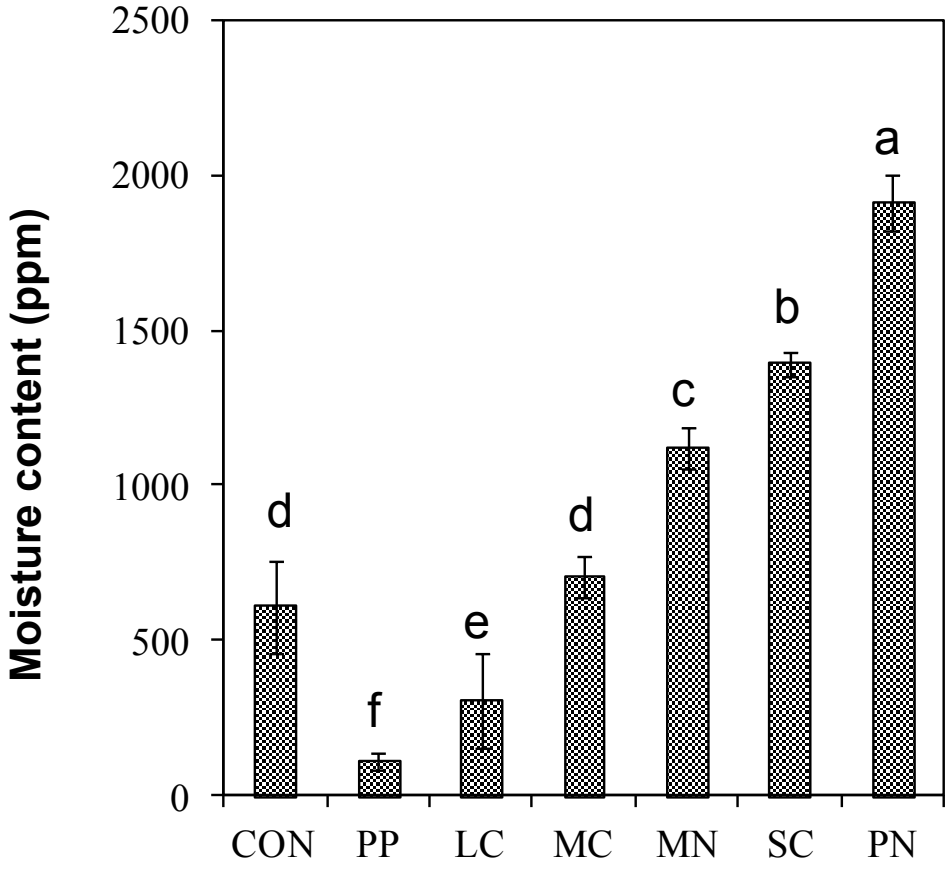
α-Tocopherol



- Lipid soluble antioxidant
- Vitamin E,
  inhibition of lipid oxidation
- Donate phenolic hydrogen atom

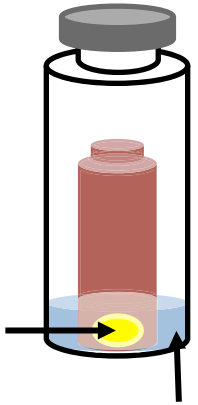
(Kim *et al.*, 2015a)

Moisture content in oils



Relative humidity ↑ , Moisture content ↑

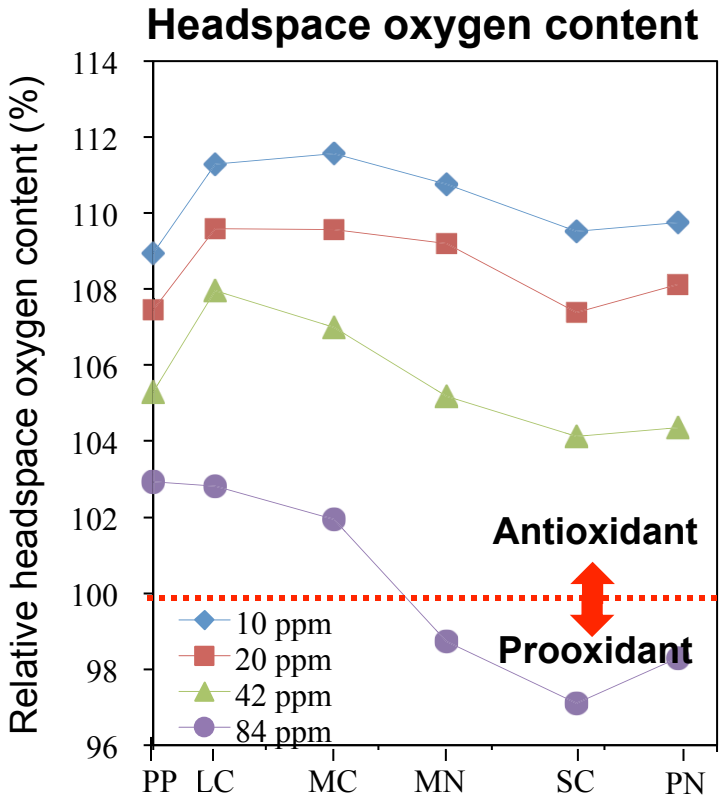
Double vial sys tems can regul ate the moistur e content in oil s.

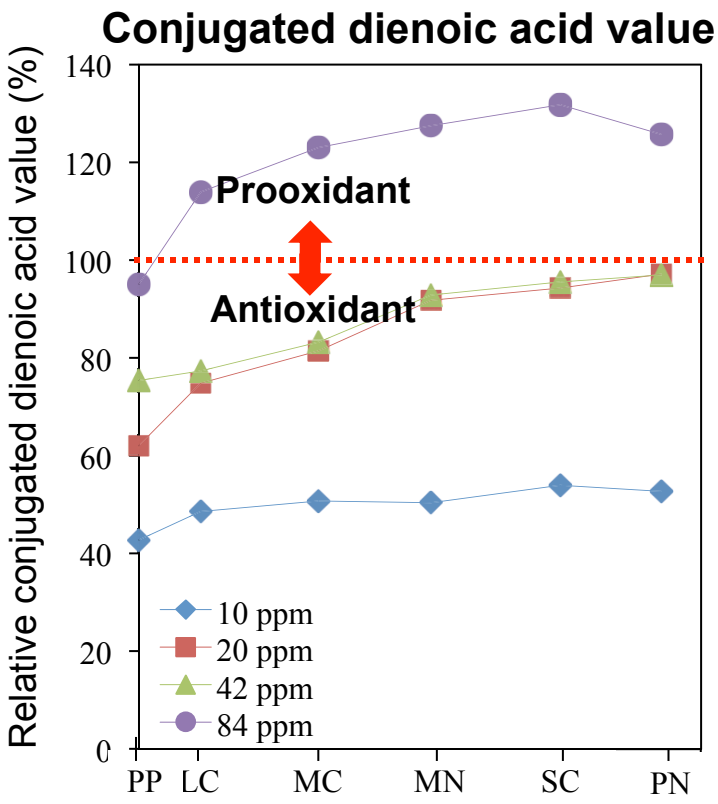


0.5 g
Stripped oil
with antioxidant

1 g
Salt solution

Relation of antioxidant properties α-tocopherol under relative humidity

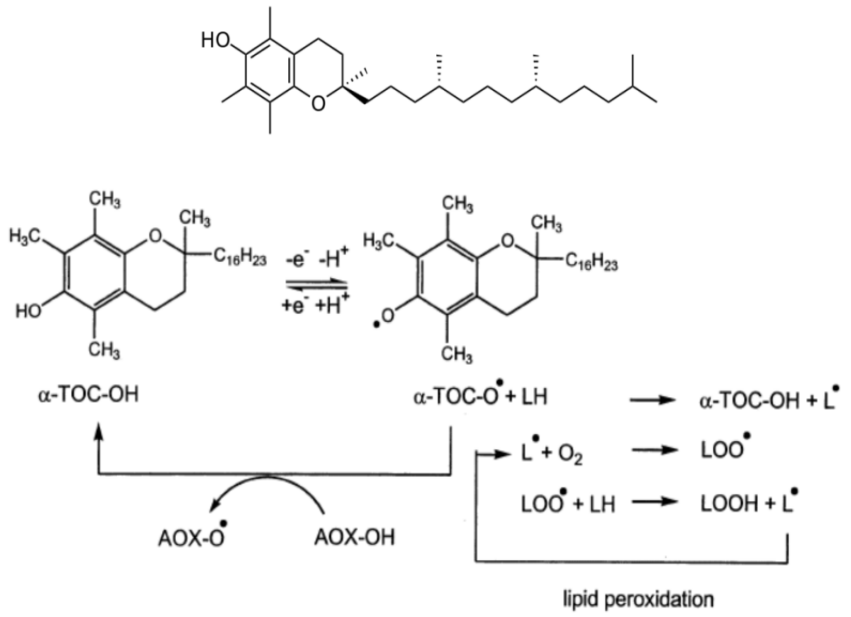




1. Headspace oxygen content prooxidant properties over MN (RH 52%)
2. Conjugated dienoic acid value prooxidant properties over LC (RH 11%)

Why does α-tocopherol accelerate oxidation?

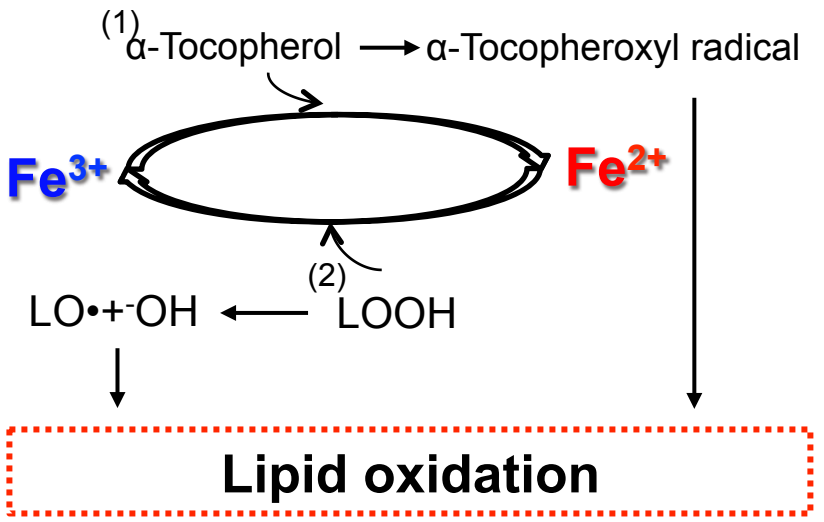
1. Generation of tocopheroxyl radical



LOO• + α-TOH → LOOH + α-TO•

Lipid peroxyl radical — *α-Tocopherol* — *Lipid hydroperoxide* — *α-Tocopheroxyl radical*

2. Effects of prooxidative irons



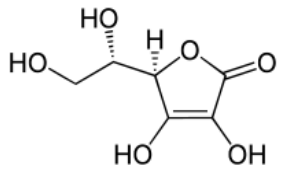
(Bingcan *et al.*, 2012)

- High water solubility of iron

Effects of moisture on hydrophilic a ntioxidant properties in bulk oils

Hydrophilic antioxidant (ascorbic acid)

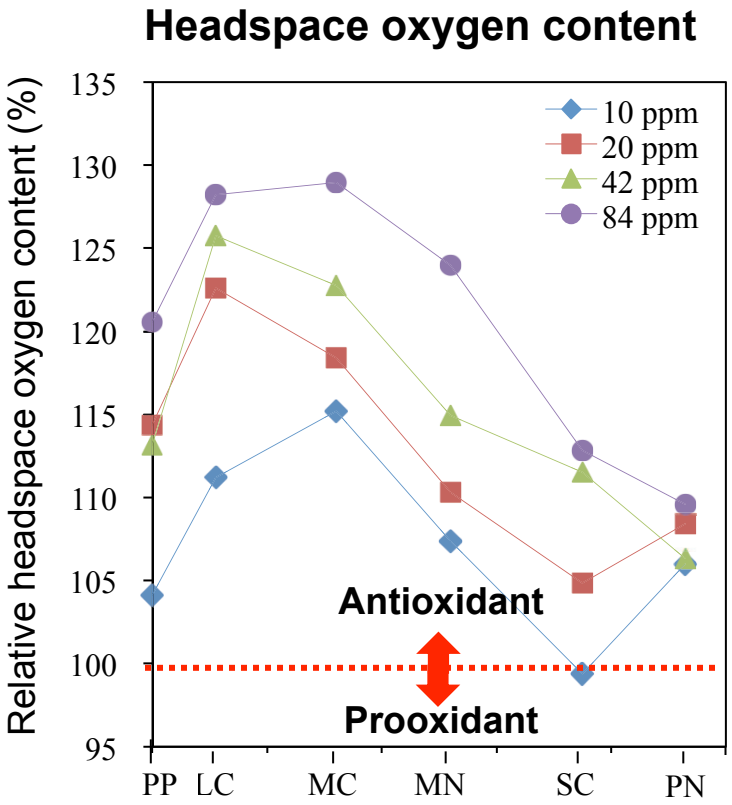
Ascorbic acid

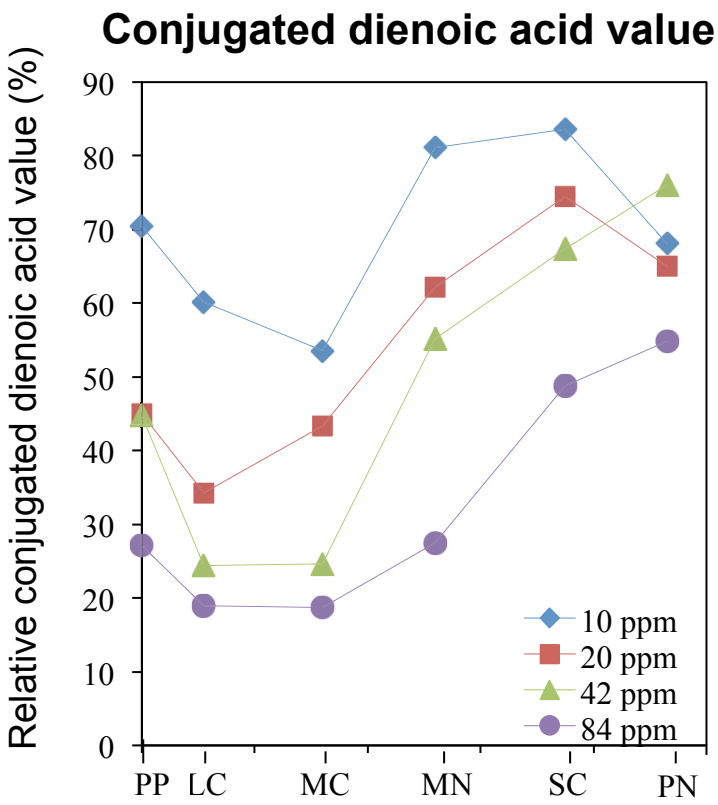


- Water soluble antioxidant
- Vitamin C,
  Naturally occur organic compound with antioxidant

(Kim *et al.*, 2015b)

Relation of antioxidant properties ascorbic acid Under relative humidity





1. Headspace oxygen content, Conjugated dienoic acid value
⇒ Antioxidant properties (except samples with 10 ppm ascorbic acid under SC condition)
2. Slope pattern changes (10 and 20 ppm)
⇒ Balance point between concentration of ascorbic acid and moisture content

Conclusion

Just addition of antioxidants does not secure the e xtension of shelf-life of oils.

Considering

- food matrix including bulk oil or emulsion

- moisture content in food matrix

- polarity of antioxidants

- other microenvironments and procedures

Suggested ways to improve oxidative sta bility in bulk oils (including palm oils)

- Keep moisture content in the middle range

- Control the contents of transition metals

- Balance the contents of lipophilic antioxidants in cluding tocopherols and tocotrienols

Acknowledgement

Alumni

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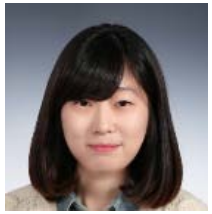
Current students



Yi BR, Oh SM, Ka HJ, Park JH, Jeong JY, Song JH, Lee CK, Kim SY

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Thank you for your attention !

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