Science of Beer Staling

When a Good Beer Goes Bad

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BREWING SCHOOL

Oxidation

"the stale flavor was mainly caused by oxygen uptake by the beer on its way from the storage tank to the bottle,"

Technical scope for low-oxygen operation methods in beer production. By H,-J. Manger, Frankfurt/Oder Brauwelt International 1999/1 pages 37-40

"flavor stability is not related to beer packaging but to wort preparation."

Nonoxidative Mechanism for Development of trans-2-Nonenal in Beer. By G.Lermusieau, S.Noel, C.Liegeois, and S.Collin Journal of the American Society of Brewing Chemists. Volume 57: No.1 (1999)

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Sensory changes in beer flavour during ageing

C.E.Dalgliesh *Flavour Stability*, Proceedings of the 16th European Brewery Convention (1977)

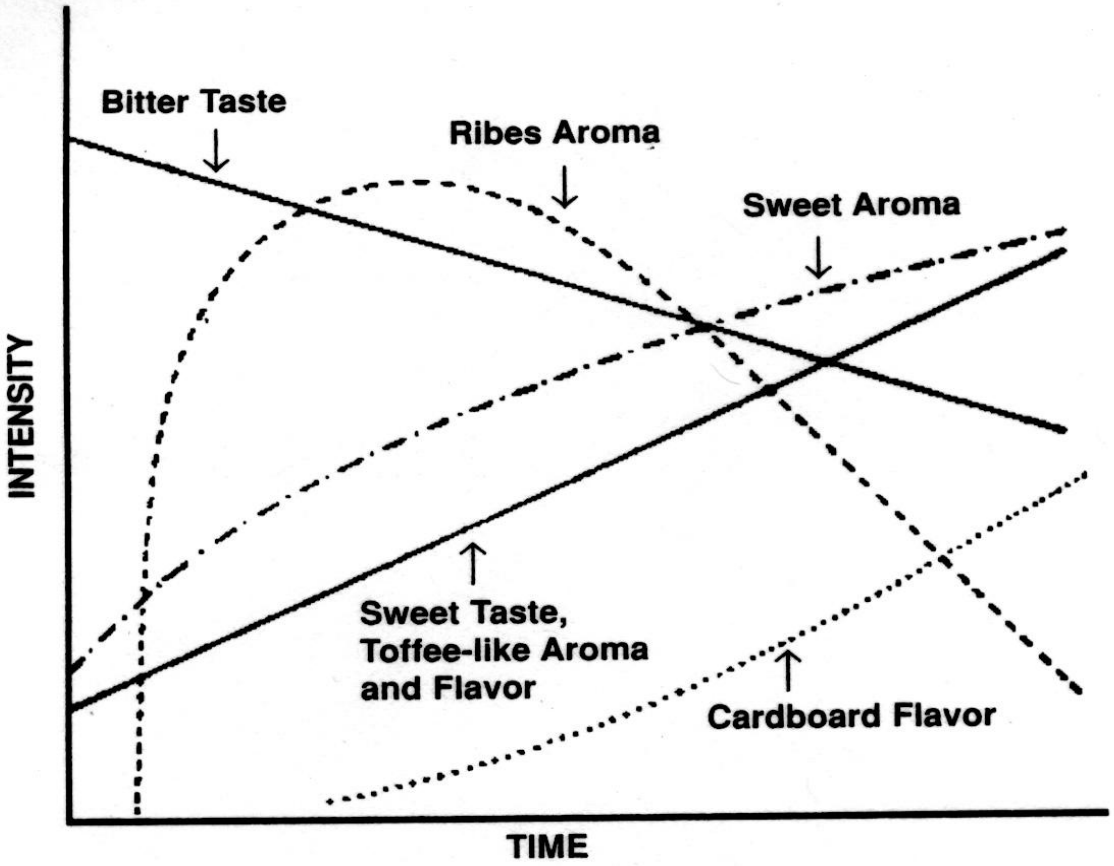
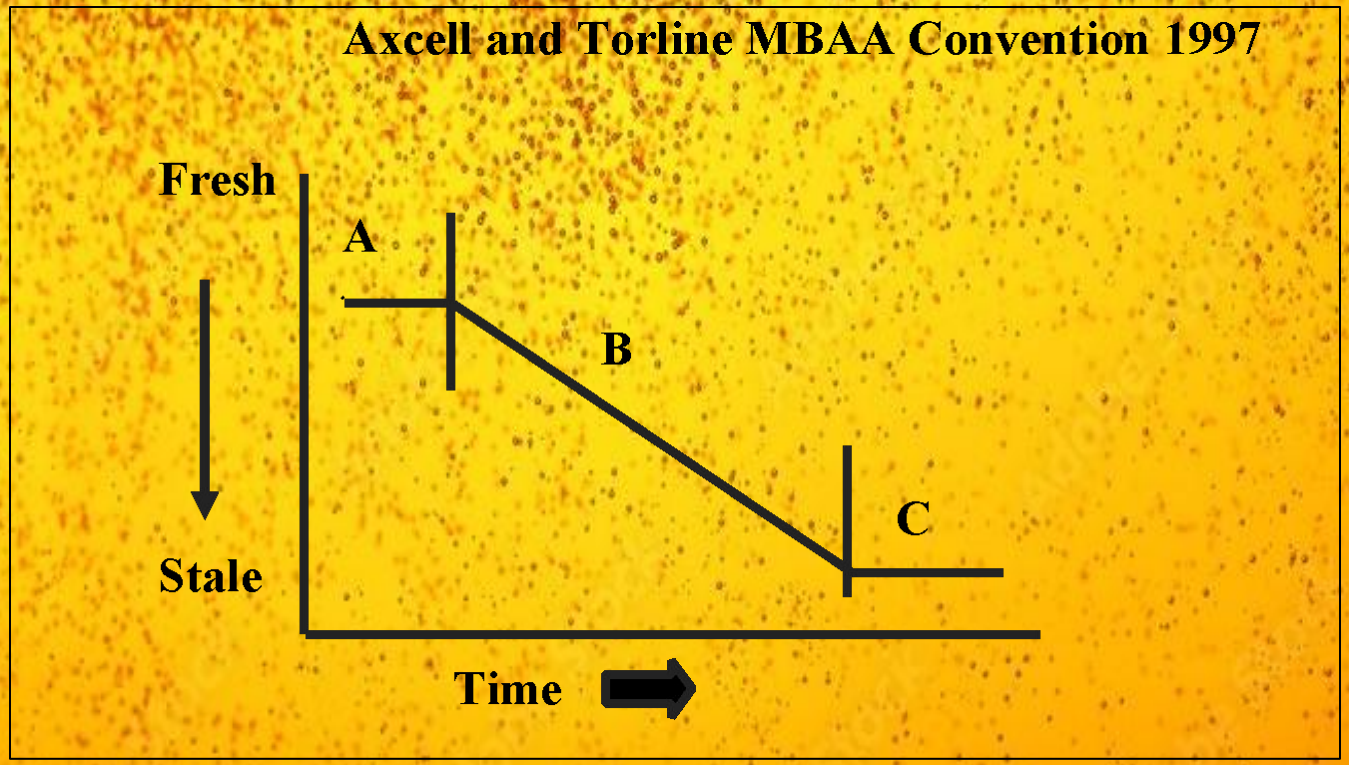


FIGURE 1

The changes in beer flavor with time in package - the Dalgliesh plot.

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Good Oxygen

- Wort aeration
  - yeast require O_2 for cell growth. Desaturation of fatty acid/lipids for healthy cell membranes
  - yeast require 5-15 ppm O_2 in wort
- Polyphenol oxidation.

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Proposed Mechanisms for Stale Flavor

- Oxidation of Higher alcohols (melanoidin mediated)
- Oxidative Degradation of Isohumulones
- Oxidation of Unsaturated Fatty Acids
  - autoxidation
  - enzymic degradation (lipoxygenase)
  - photo-oxidation
- Aldol condensation of short chain aldehydes

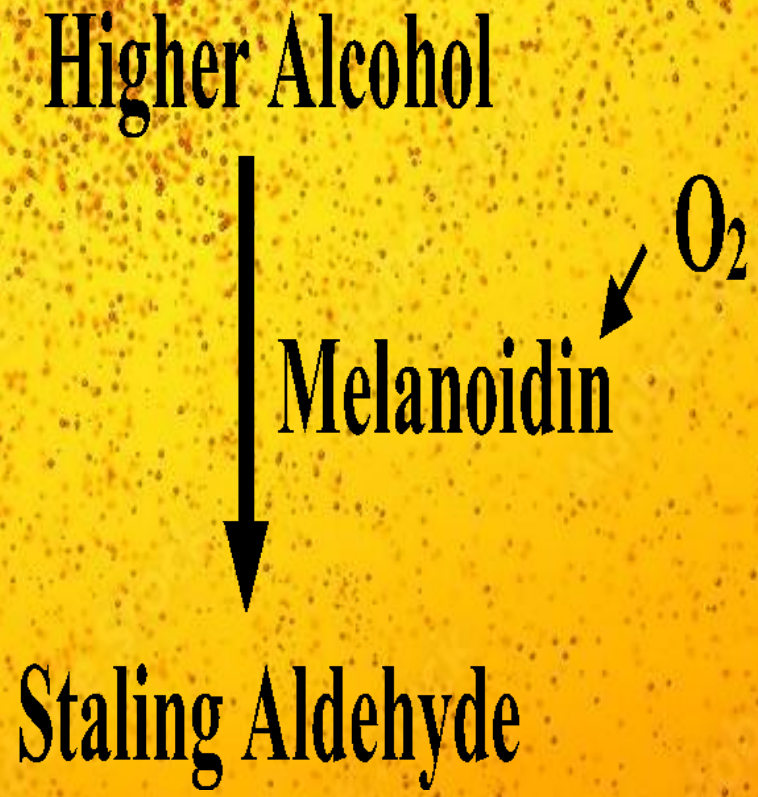
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continued

- Strecker degradation of amino acids
- Oxidation of long chain unsaturated aldehydes

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Oxidation of Higher alcohols



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Strecker Degradation of Amino Acids

Amino acid	Compound name	Character
Proline (NP)	2-acetyl-1-pyrroline	Mousy off-flavor; Bread-like
Lysine (P)	2-acetyltetrahydropyridine, 2-ethyltetrahydropyridine	Mousy off-flavor
β-Alanine (NP)	-	Wet hay/acetaldehyde flavor
Tryptophan (NP)	-	corn chip
Valine (NP)	2-methylpropanal (65-90 ppm)	Grainy, varnish, fruity
Isoleucine (NP)	2-methylbutanal (35-45 ppm)	Almond, apple-like, malty
Leucine (NP)	3-methylbutanal (46 – 56 ppm)	Malty, chocolate, cherry, almond
Methionine (NP)	Methional (42 ppm)	Cooked potatoes, worty
	dimethyltrisulfide	onion-like or skunk-like off-flavor
	3-(methylthio)propionaldehyde	
Phenylalanine (NP)	Phenylacetaldehyde (100 ppm)	Hyacinth, flowery, roses
Serine (P) Threonine (P)	4,5-Dimethyl-3-hydroxy-2(5H)-furanone or sotolon	Madeira-oxidized–curry–walnut notes, know as madeira off-flavor)
Cysteine (P)	3-methyl-2-butene-1-thiol	At higher concentrations, light-struck off-flavor lager beers

Hot Side Aeration

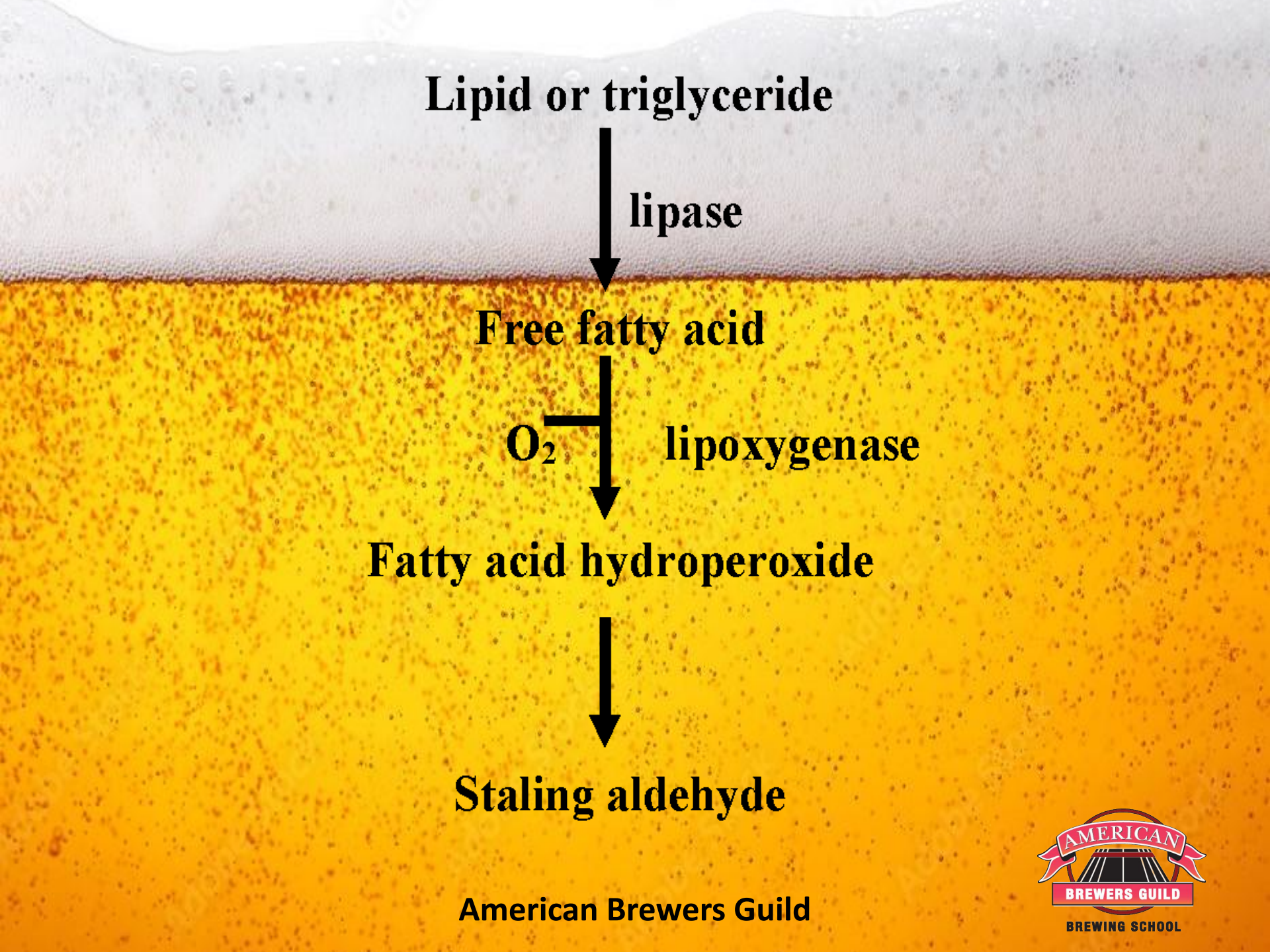
- Beer packaged with DO_2 levels below 10 ppb still eventually show signs of staling.
- It is proposed that oxygen pickup in the mill, mash tun, wort-separation, boiling, and whirlpool results in the formation of stale beer flavor pre-cursors.

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Continued

- Lipids in the Mash oxidize
- Melanoidins form in the kettle and decoction mashes
- Iso α acids oxidize in the kettle and whirlpool

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Enzymic Lipid Oxidation

- Survive for a few minutes in an infusion mash
- Lipoxygenase enzyme activity is important but largely dependant on substrate concentration (lipid and O_2) rather than enzyme concentration
- Non enzymic route is more likely (Bamforth)

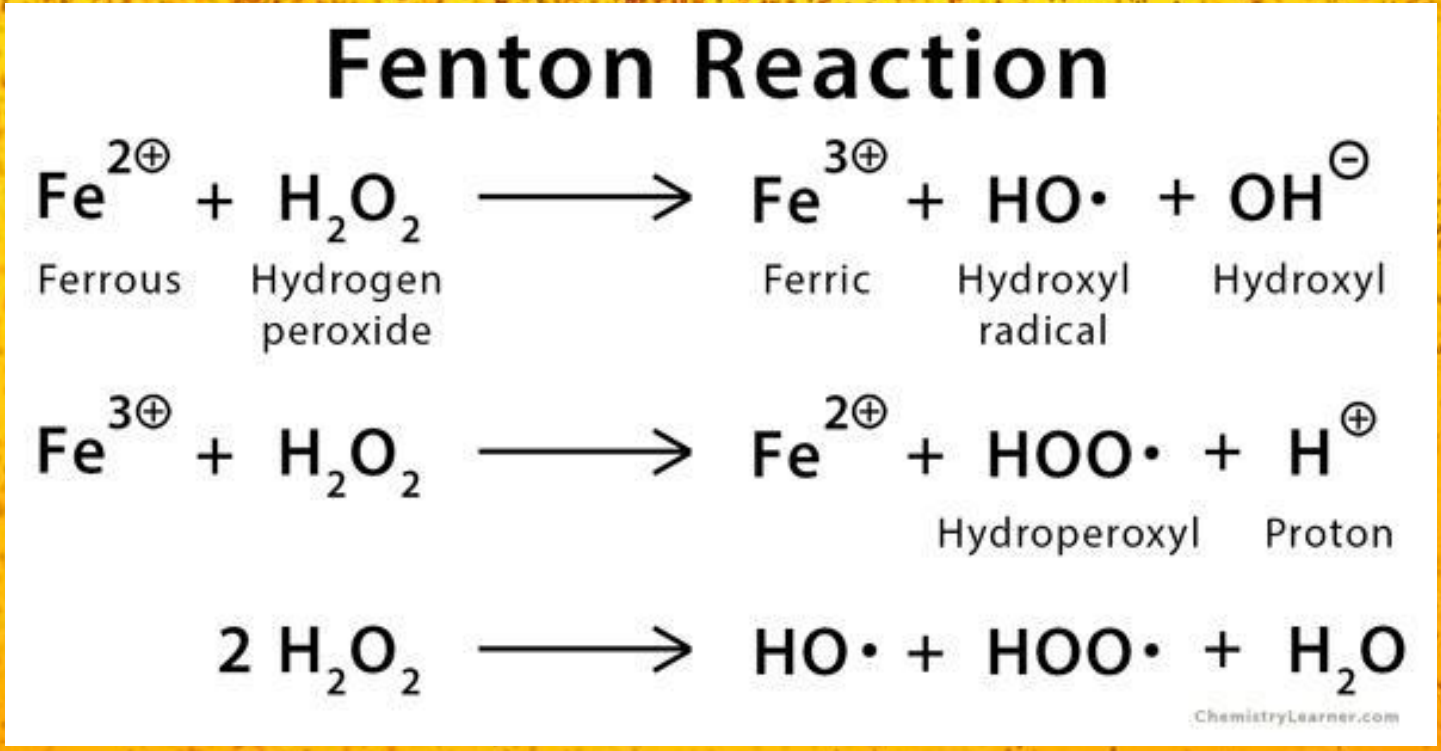
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Non Enzymic Oxidation

- Metal ions, light, enzymes in the mash can create super reactive forms of oxygen
- These then oxidize mash components including
  - lipids
  - polyphenols
  - proteins

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Fenton Reaction




Free fatty acid
superoxide
O_2
peroxide
hydroxyl
Fatty acid hydroperoxide
Staling aldehyde

Linoleic acid – (E)-2-nonenal

- Gives brewers something to focus on in determining mechanisms, however staling is a complex issue and there are many other important reactions contributing.
- Most reactions have been demonstrated on the laboratory scale, but remain unproved on production beers

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Dry Hop Compounds

Some of the volatile aroma compounds that contribute significantly to dry-hop flavour in dry-hopped beers include

- Mono and sesquiterpenes: myrcene, humulene and caryophyllene
- Terpene alcohols: linalool, geraniol, nerol and β-citronellol.
- Esters: 2-methylbutyl isobutanoate, isobutyl isobutyrate, isoamyl isobutyrate
- Sulphur containing thiol compounds (3-mercapto-1-hexanol and 4-mercapto-4-methyl-2-pentanone)

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Dry Hopping

Beer is a biochemical soup with thousands of reactants.

- Esters break down and reform Some reduce, others increase.
- Thiols increase then degrade
- Unfiltered beer contains live yeast providing a mechanism to mop up oxygen, but autolysis releases enzymes that catalyse staling reactions reactions

Dry Hopping

- Brewers report loss of dry hop aroma rapidly after packaging
- Depends on O_2 content but more importantly on storage temperature
- β Damascenone (berry like) in one experiment increased 80x after 5 days at 40 C
- Monoterpenes (linalool, myrcene etc) reduce by up to 80% in 3 months at room temperature

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Thiols

Oxidation of Thiols

- Some thiols increase in concentration during beer aging. Thiols bound to amino acids are released increasing their appearance in beer
- Others develop an antioxidant role reacting with radical oxgen to help mask stale aldehydes

Terpenes

Oxidation of Terpenes

- Small monoterpenes such as myrcene disappear fastest due to oxidation reactions which happen faster at warm temperatures
- Larger sesquiterpenes and their oxidative components disappear more slowly
- Terpenes polymerize, isomerize and degrade all causing changes in aroma profile
- Storage at room temperature dramatically increases the rate of these reactions.

Measuring Oxidation Potential

- **Measure the relative oxidizing/reducing potential (ReDox)**
  - Indicator Time Test
  - electron spin resonance
- **Directly measure a range of specific stale compounds or precursors**
  - Gas / high performance liquid chromatography
  - spectrophometric methods

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Forcing Test

- Expose a sample of beer to harsh conditions ie extreme heat and extreme cold
- Used to test microbiological stability
- Different reactions occur due to high heat compared with extended warm storage

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Prevention of Stale Beer Flavor?

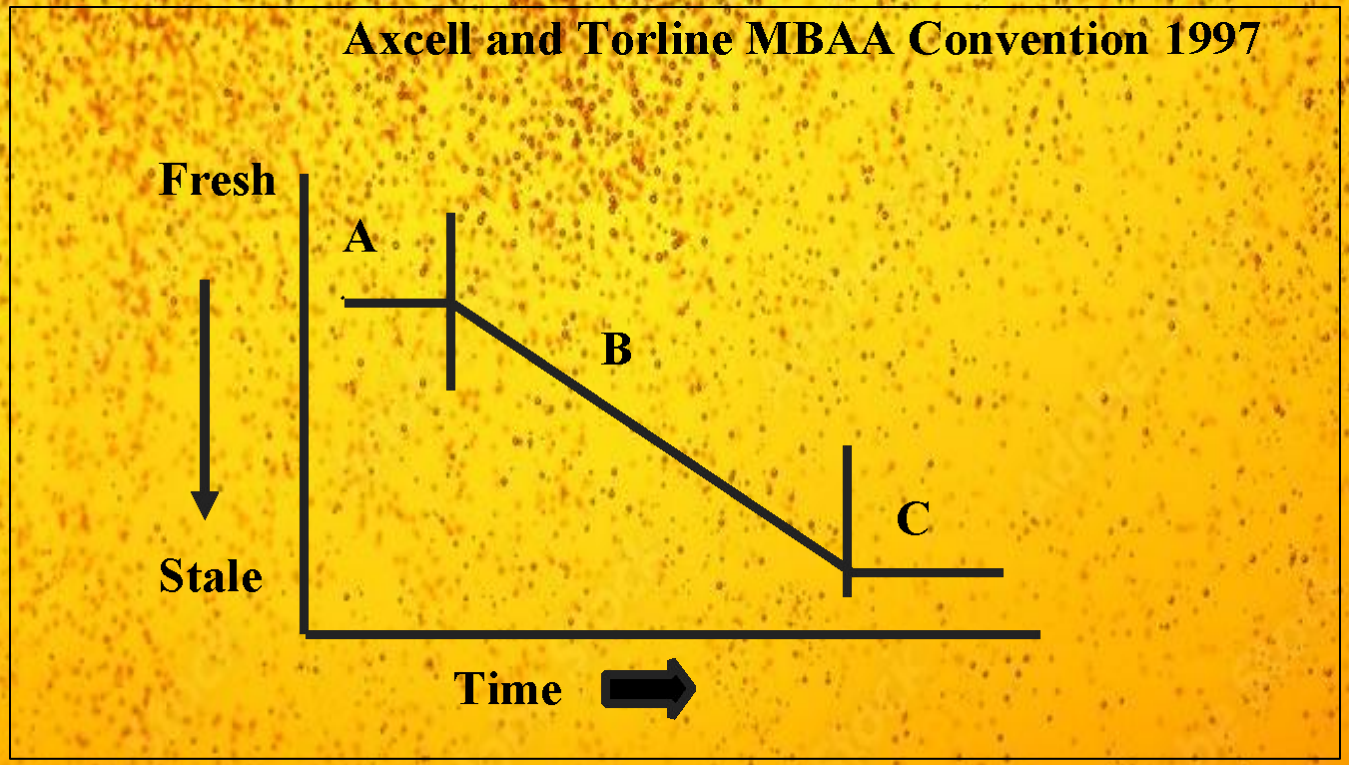
Pre-Cursors to stale beer flavor are

Melanoidins, lipids, higher alcohols, isohumulones, phenols, polyphenols, amino acids, esters, proteins, ie malt, hops and yeast

and are present at up to 10,000 times the concentrations of the stale flavors they result in.

(1 million seconds is 12 days, 1 billion seconds is 32 years, and 1 trillion seconds is 317 centuries)

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Brewing Education

Postponement of Stale Beer Flavor
Stalling the staling

- **Anti Oxidants**
  - Added to beer
    - **Bisulfite SO_2**
    - **ascorbic acid**
    - **enzymes**
  - Naturally Occurring
    - **polyphenols**
    - **phenolic acids**
    - **yeast**

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Order of Magnitude Improvements unlikely through brewhouse design

Most modern brewhouses already have the following attributes

- bottom fill
- thinner mashes
- gentle agitation
- clear wort production
- shorter boil times
- rapid wort cooling
- low shear pumping

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Big Brewer's Approach

- Low O_2 packaging
- Control of Distribution network
- Refrigerated storage and transport
- Regional production
- Fast turnover

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Colour Darkens due to Oxidation



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What Can I Do?

- De-Aerated water to chase beer through pipes and hoses
- Purge air from bright beer tank
- Flush the filter with deaerated water or CO_2

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And In the Brewhouse
"Good Brewing Practice"

- Quality Raw Materials
- Minimize Wort Splashing
- Don't Over-Boil Wort
- Gentle Transfers
- Maintain Plant (Pump Seals)

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Expected O_2 levels throughout the Brewery

- Wort 5-15 ppm
- End of Fermentation <10 ppb
- Beer in Bright Tank 10-100 ppb
- Packaged Beer 40-200 ppb

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