The science behind the art: hops in brewing

Joseph Wegner

Lead Chemist and Co-Owner
Gorst Valley Hops,
Mazomanie WI

Beer: Science and Art

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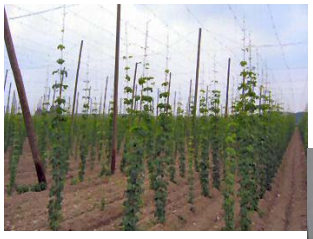
Topics of Discussion

- Quality
- Alpha and Beta Acids
- Essential Oils
- Oxidation
  - The Good
  - The Bad
  - The Ugly
- Polyphenols

From Field to Kettle





Hops Quality

- Maintain the characteristics of the freshly picked Hop cones while ensuring stability over time

Processing Effects

- Picked at peak maturity
  - Too early: low essential oil
  - Too late: poor flavors and fragile cones
- Dried to 8-12% moisture
  - Too Dry: cones disintegrate
  - Too Wet: mold and mildew
- <150°F (Quality decreases above 104°F)
  - Higher Temp = greater oxidation
  - Higher Temp = Oil loss due to volatilization

Thompson, J.F., Stone M.L., and Kranzler G.A. 1985. *Modified Air Flow Rate and Temperatre Hop Drying* in *TRANSACTIONS of the ASAE*. American Society of Agricultrual Engineers, St. Joseph, MI., Vol 28, no 4, pg 1297-1300

Optimal Storage Conditions for Hops

- Vacuum packed
  - Removes oxygen from the hops
- Oxygen barrier bag
  - Keeps oxygen from hops
  - Foil lined bags the best
- Dark storage
  - Removes energy for oxidation
- Freezer
  - Slows reactions
  - Reduces volatilization of flavor components

What happens with storage?

- Increased oxidation and loss of essential oils, alpha, and beta acids
- Hops stored for 18 months at 40ºF lost 50% of alpha and beta acids[1]
- Beers brewed with aged pellets drastically reduced beer quality[2]

[1]Peacock, Val., *The International Bitterness Unit, its Creation and What it Means* in 2009, *HOP FLAVOR AND AROMA Poceedings of the 1st International Brewers Symposium*, Shellhammer, Thomas H. ed., Master Brewers Association of the Americas, St. Paul, MN. pg 157-166.

[2] Forster, Adrian. *Influence of Hop Polyphenols on Beer Flavor* in 2009, *HOP FLAVOR AND AROMA Poceedings of the 1st International Brewers Symposium*, Shellhammer, Thomas H. ed., Master Brewers Association of the Americas, St. Paul, MN. pg 157-166.

The Acids

α-Acids
- Help preserve the beer
- Poor water solubility
- Undergo isomerization reactions
- Main bitter molecules
- Iso- α-Acids help boost foam

β-Acids
- Slightly soluble
- Not bitter, but add some flavor profile
- Oxidation products add bitterness

Types of Acids

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α-Acid

$R = CH_2CH(CH_3)_2$
$= CH_2(CH_3)_2$
$= CH(CH_3)CH_2CH_3$

β-Acid

Briggs, Dennis E., Boulton, Chris A., Brookes, Peter A. and Stevens, Roger, 2004, *Brewing Science and Practice*. CRC Press LLC, Boca Raton, FL. Pg 259

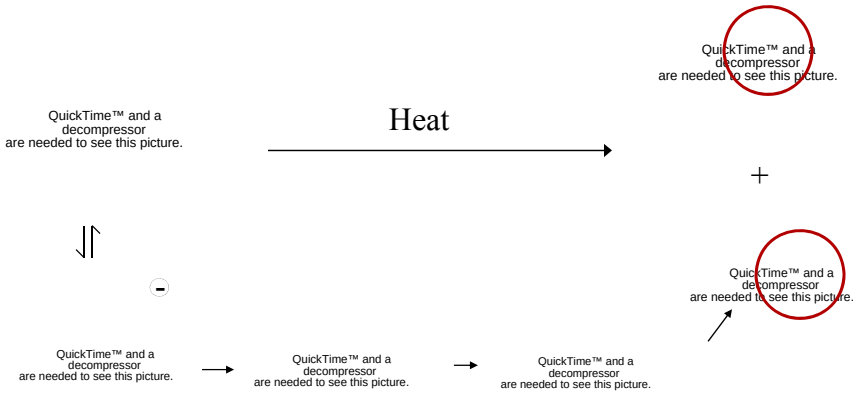
Isomer

- Chemical Definition:

Any of two or more substances that are composed of the same elements in the same proportions but differ in properties because of differences in the arrangement of atoms.

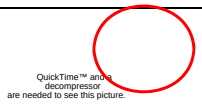
"isomer." The American HeritageÆ Dictionary of the English Language, Fourth Edition. Houghton Mifflin Company, 2004. 14 Jun. 2010. <Dictionary.com http://dictionary.reference.com/browse/isomer>.

α-Acid Isomerization Reaction



Briggs, Dennis E., Boulton, Chris A., Brookes, Peter A. and Stevens, Roger, 2004,

Iso-α-Acids

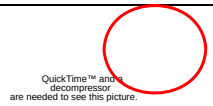


Iso-Humulone

- Highly desirable bitterness profile
- Generally the primary α-acid

Iso-Adhumulone

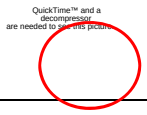
- Bitter, but the flavor is less understood
- Generally found in low concentrations



Iso-Cohumulone

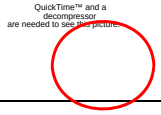
- Generally considered to be a more harsh bitter
- Lower levels in Nobel Hops

β-Acids

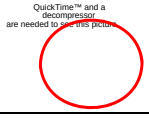


Lupulone

- Generally the highest percentage



Adlupulone



Colupulone

Isomerized Hops

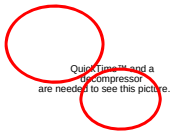
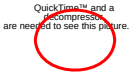
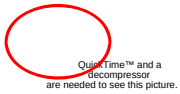
- Pellets
  - Magnesium oxide added to catalyze the reaction
  - Heated at ~50°C for up to 14 days (under vacuum storage)
  - Heating decreases the amount of essential oils
  - End of Wort boil addition
  - Often considered as "modified" products
- Liquid Extracts
  - Liquid CO_2 extract (highly purified)
  - Heated with salts under inert gasses
  - Used for post-fermentation addition

Reduced Iso-Alpha Acids

- Benefits
  - Improved foam stability
  - Similar bitter intensity
  - Improved oxidation stability
  - Reduces risk of skunky beer
- Issues
  - Considered as modified a material
  - Highly processed
  - Cost

Shellhammer, Thomas H., *Hop Components and Thei Impact on the Bitterness of Quality of Beer* in 2009, *HOP FLAVOR AND AROMA Poceedings of the 1st International Brewers Symposium*, Shellhammer, Thomas H. ed., Master Brewers Association of the Americas, St. Paul, MN.

Structures of Reduced Iso-Alpha Acids

	Tetrahydro-Iso-α-Acids ▫Produced through hydrogenation
	Hexahydro-Iso-α-Acids ▫ Produced through hydrogenation and sodium borohydride reduction
	Rho-Iso-α-Acids ▫Produced through sodium borohydride reduction

Foam Stabilization

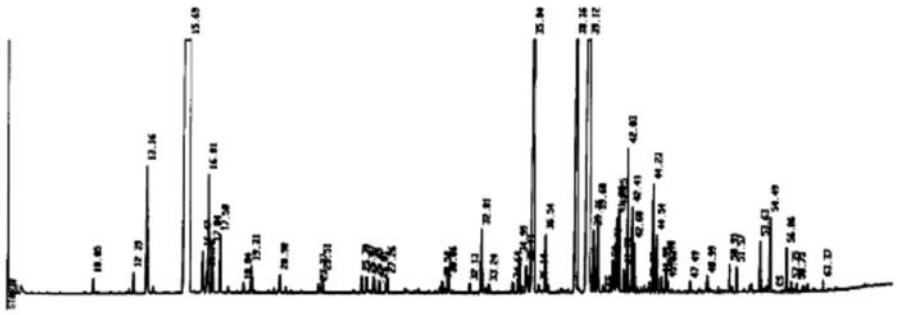
- CO_2 or N_2 + CO_2
  - Generates Foam
  - Discontinuous phase
- Water/Ethanol
  - Continuous phase
- Glyco-proteins from grains
  - Allows Foam
- Iso-acids
  - Stabilize foam
  - Higher proportion in foam than in liquid phase

Essential oils

- 0.03-2% of hop mass
- Over 300 constituents have been identified
- Comprised of:
  - Hydrocarbons (Terpenes)
  - Oxygenated compounds
  - Sulfur containing compounds

Ting, Patrick L., Kay, Susan, and Ryder, David. The Occurrence and Nature of Kettle Hop Flavor. In: Shellhammer, Thomas H. ed., 2009, *HOP FLAVOR AND AROMA Poceedings of the 1st International Brewers Symposium*, Master Brewers Association of the Americas, St. Paul, MN. Pg 25-26

Example Chromatogram Slide



Kenny, S., subcommittee chair, 2004 "Determination of Hop Essential Oils by Capillary Gas Chromatography" American Society of Brewing Chemists. p180

Primary Hydrocarbons in Hops Oil

Monoterpenes	Sesquiterpenes
Myrcene	α-Humulene
	β-Farnesene
β-Pinene	α-Selinene
	β -Selinene
	β-Caryophyllene

Priest, Fergus G. and Stewart, Graham G. ed., 2006, *Handbook of Brewing,* CRS Press, Boca Raton, FL. Pg 198

Main Terpenes of Hops Oil

Myrcene
- Low negative effect on aroma (typically pungent)
- Typically the highest concentration oil
- Oxidation products add to flavor profile

β-pinene
- Pine or citrus notes
- Generally low concentration

β-caryophyllene
- Woody fragrance
- Oxidation products desirable

α-humulene
- Most desirable component in Nobel hops
- Known as the main characteristics smell of hops
- Oxidation products also desirable

Oxygenated Fraction of Hops Oil
Examples

- Alcohols
  - Linalool ⇒ floral
  - Geraniol⇒floral
  - (Z)-3-hexene-1-ol ⇒ green
- Ketones
  - beta-ionone ⇒ floral
  - (Z)-1,5-ocatadien-3-one ⇒ green
- Esters
  - 2-phenylethyl-3-methylbutanoate ⇒ floral
  - Ethyl-3-methylbutanoate ⇒ citrus
  - 2-methylpropanoate ⇒ citrus
- Aldehydes
  - (Z)-3-hexanal ⇒ green
  - (E,Z)-2,6-nonadienal ⇒ green

Kishimoto,Toru. *Investigations of Hop-Derived Odor-Active Components in Beer* in 2009, *HOP FLAVOR AND AROMA Poceedings of the 1st International Brewers Symposium*, Shellhammer, Thomas H. ed., Master Brewers Association of the Americas, St. Paul, MN. pg 157-166.

Sulfur Containing Compounds

- Mainly due to the use of elemental sulfur as an antifungal agent in the field
- Negative impact on flavor

QuickTime™ and a decompressor are needed to see this picture.

Dimethyl disulfide

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Dimethyl trisulfide

Priest, Fergus G. and Stewart, Graham G. ed., 2006, *Handbook of Brewing*, CRS Press, Boca Raton, FL. pg 200.

Methods of Extraction

- Steam Distillation
  - Essential oils extracted
  - Oil quality is process dependent
- Vacuum Steam Distillation
  - Lower temp than steam distillation
- Vacuum Distillation
- Solvent Extraction
- Liquid CO_2 Extraction
  - Extracts essential oils, alpha and beta acids
  - No solvent residue
- Supercritical CO_2 Extraction
  - Increased pressure can extract undesirable compounds

Oxidation

- Chemical Definition:

1. The combination of a substance with oxygen.

2. A reaction in which the atoms in an element lose electrons and the valence of the element is correspondingly increased.

"oxidation." The American HeritageÆ Dictionary of the English Language, Fourth Edition. Houghton Mifflin Company, 2004. 14 Jun. 2010. <Dictionary.com http://dictionary.reference.com/browse/oxidation>.

Oxidation: the Good

- Convert low odor oils into compounds with floral, citrus, and spicy notes
  - Caryophyllene oxide
  - Humulene epoxides hydrolyze (break apart in the presence of water) to products with favorable characteristics
  - Myrcene oxidation products improve the flavor of myrcene
- Converts beta-acids into bittering agents
  - The oxidized beta-acids increase as the alpha-acids decrease

Yang, Xiaogen, Lederer, Cindy, McDaniel, Mina, and Deinzer, Max. Hydrolysis "Products of Caryophyllene Oxide in Hops and Beer". *J. Agric. Food Chem.* 1993, 41, 2082-2085

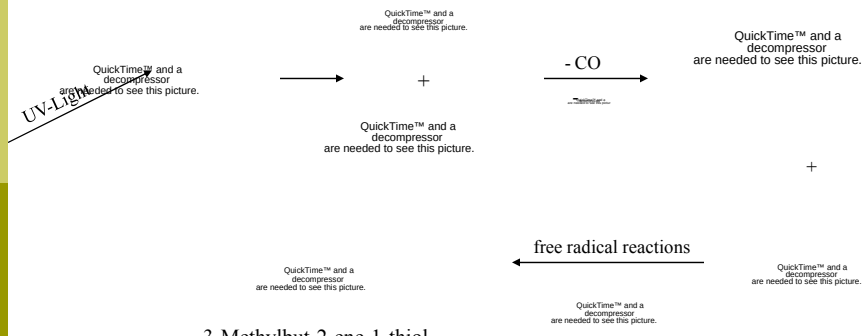
Oxidation: the Bad

- Oxidation products of α-acids to not bitter
  - While oxidized β-acids are bitter, the flavor profile is not as desireable
- Changes flavor/smell profile of hops over time (in storage)
  - Some oil oxidation products have off odors
  - Aged hops sometimes have a "cheesy" odor

Oxidation: the Ugly

Skunky Beer Flavor

- The reaction of UV light, iso-humulone, and riboflavin (vitamin B2)



3-Methylbut-2-ene-1-thiol

Burns, Colin S. et al. ÑMechanism for Formation of the Lightstruck Flavor in Beer Revealed by Time-Resolved Electron Paramagnetic Resonance.Ó*Chem. Eur. J.* v7, No. 21. WILEY-VCH, Weinheim. 2001.

Skunky Beer Protection

- Store in the dark
  - Dark glass
  - Boxes/ refrigerators/ closets
- Use reduced iso-α-acids
  - Remove sites for reactions with light
  - Remove oxidation sites

Polyphenols

- Proanthocyanidins (PAs)
  - Also known as Condensed Tannins
  - Flavan-3-ol oligomers and polymers
  - Antioxidants
- General toxicity against fungi, yeast, and bacteria
- High affinity for proteins
  - Can lead to haze with storage
- Add to bitterness profile

General Structure of Hop PAs

QuickTime™ and a
decompressor
are needed to see this picture.

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R = H or OH

Li, Hui-Jing and Deinzer, Max L., 2009, *Polyphenolic compounds in Hops* in HOP FLAVOR AND AROMA Proceedings of the 1st International Brewers Symposium. Master Brewers Association of the Americas., St. Paul MN, pg 103

Where to go for more information

Shellhammer, Thomas H. ed., 2009, *HOP FLAVOR AND AROMA Poceedings of the 1st International Brewers Symposium*, Master Brewers Association of the Americas, St. Paul, MN.

Priest, Fergus G. and Stewart, Graham G. ed., 2006, *Handbook of Brewing,* CRS Press, Boca Raton, FL.

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Bamforth, Charles, 2003, *BEER TAP INTO THE ART AND SCIENCE OF BREWING, Second Edition*. Oxford University Press, New York, New York.

Briggs, Dennis E., Boulton, Chris A., Brookes, Peter A. and Stevens, Roger, 2004, *Brewing Science and Practice*. CRC Press LLC, Boca Raton, FL.

Compendium of BREWING RESEARCH HOPS 1977-2006., 2007, American Society of Brewing Chemists, St. Paul, MN

Lermusieau, G. and Collin S. *Chapter 5 Hop Aroma Extraction and Analysis* in *Molecular Methods of Plant Analysis. Analysis of Taste and Aroma.* Jackson J.F. and Linskiens, H.F. Springer-Verlag, Berlin, Germany, 2002

Johnston, Charles. http://www.brewerschoice.net.au/html/hop%20varieties.htm,

Things to Think About

- How were your hops processed?
- Quality of the dried hops and hops extracts?
- How are your hops stored?
  - Before you purchase them?
  - After you purchase them?
- Effect of the timing of the hops addition?
- How do you store the finished beer?

Questions