The science behind the art: hops in brewing

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Beer: Science and Art
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

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**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
- $<150^\circ$F (Quality decreases above $104^\circ$F)
  - Higher Temp = greater oxidation
  - Higher Temp = Oil loss due to volatilization

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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\(^2\)

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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

α-Acid
\[ R = \text{CH}_2\text{CH}(	ext{CH}_3)_2 \]
\[ = \text{CH}_2\text{CH}_3 \]
\[ = \text{CH}(	ext{CH}_3)_2\text{CH}_3 \]

β-Acid

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.


α-Acid Isomerization Reaction

Heat

**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 CO₂ 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

### Structures of Reduced Iso-Alpha Acids

<table>
<thead>
<tr>
<th>Acids</th>
<th>Production Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydro-Iso-α-Acids</td>
<td>- Produced through hydrogenation</td>
</tr>
<tr>
<td>Hexahydro-Iso-α-Acids</td>
<td>- Produced through hydrogenation and sodium borohydride reduction</td>
</tr>
<tr>
<td>Rho-Iso-α-Acids</td>
<td>- Produced through sodium borohydride reduction</td>
</tr>
</tbody>
</table>

### Foam Stabilization

- CO₂ or N₂ + CO₂
  - 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


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

<table>
<thead>
<tr>
<th>Monoterpenes</th>
<th>Sesquiterpenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myrcene</td>
<td>α-Humulene</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>β-Farnesene</td>
</tr>
<tr>
<td></td>
<td>α-Selinene</td>
</tr>
<tr>
<td></td>
<td>β-Selinene</td>
</tr>
<tr>
<td></td>
<td>β-Caryophyllene</td>
</tr>
</tbody>
</table>


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-octadien-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

Sulfur Containing Compounds

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


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 CO₂ Extraction
  - Extracts essential oils, alpha and beta acids
  - No solvent residue
- Supercritical CO₂ 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 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


Oxidation: the Bad

- Oxidation products of α-acids to not bitter
  - While oxidized β-acids are bitter, the flavor profile is not as desirable
- 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

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

3-Methylbut-2-ene-1-thiol

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

R = H or OH


Where to go for more information


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


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

Do You Have a Question?