Hop Quality – A Brewer’s Perspective

Thomas H. Shellhammer Ph.D.
Nor’Wester Professor of Fermentation Science
Oregon State University, Corvallis, Oregon, USA

How is beer made?

- Barley
- Hops
- Yeast
- Water

Barley Malting

- Steeping - grain hydration
- Germination – kernel modification
  - Enzymes produced that will be used by brewers
- Kilning – color & aroma

Inside the brewery

Mashing ➔ Boiling ➔ Fermenting ➔ Finishing ➔ Packaging
Mashing

Large copper kettle

From M. Jackson. 1993. Beer Companion

Boiling

Hops

humulus lupulus

From Krones Inc. 2001. The Way to Good Beer
Lupulin glands

Fermentation
Finishing
- Maturation
- Carbonation
- Filtration
- Packaging

Where are hops added?

**On the hot side**
- To boiling wort
  - At the beginning (primarily for bitterness)
  - At the end (primarily for aroma)
  - After boiling but right before cooling (just aroma)

**On the cold side – dry hopping**
- To beer
  - Solely for aroma

Lupulin glands

Hops composition

<table>
<thead>
<tr>
<th>Principle Components</th>
<th>Concentration (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose + lignin</td>
<td>40.0 - 50.0</td>
</tr>
<tr>
<td>Protein</td>
<td>15.0</td>
</tr>
<tr>
<td>Alpha acids</td>
<td>2.0 - 17.0</td>
</tr>
<tr>
<td>Beta acids</td>
<td>2.0 - 10.0</td>
</tr>
<tr>
<td>Water</td>
<td>8.0 - 12.0</td>
</tr>
<tr>
<td>Minerals</td>
<td>8.0</td>
</tr>
<tr>
<td>Polyphenols and tannins</td>
<td>3.0 - 6.0</td>
</tr>
<tr>
<td>Lipids and fatty acids</td>
<td>1.0 - 5.0</td>
</tr>
<tr>
<td>Hop oil</td>
<td>0.5 - 3.0</td>
</tr>
<tr>
<td>Monosaccharides</td>
<td>2.0</td>
</tr>
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<td>Pectin</td>
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Hop Acids – \( \alpha \) & \( \beta \) Acids

The most important reaction in hop chemistry?

Analysis of hop resins – in hops

- Conductometric
- Spectrophotometric
- HPLC

Lead conductance value for measuring alpha acids in hops

![Conductometric titration of \( \alpha \)-acids. Stevens, 1987](image_url)
UV spectra for methanol extracts of hops

The Hop Storage Index (HSI)

\[ (HSI) = \frac{A_{275}}{A_{325}} \]

Figure 1. Typical spectra of alkaline methanol solutions obtained from hops in various stages of deterioration. \( A_{275} \) decreases as hop acids are oxidized and \( A_{325} \) increases as oxidation products accumulate, resulting in proportional increases in \( A_{275}/A_{325} \).

Hop Deterioration During Storage

Figure 2. Relationship of deterioration of hop acids to increase of \( A_{275}/A_{325} \). Nine varieties stored 3, 6, and 10 months are represented. The arrow at \( A_{275}/A_{325} = 0.24 \) is the average initial value for all varieties. Lupulin was held at elevated temperatures until no further change took place in its absorption spectrum: \( A_{275}/A_{325} = 2.5 \) and represents 100% loss.

Lickens, et al., 1970
Bittering can stay constant during storage

![Graph showing the effect of storage on bittering value](image)

**The IBU analysis**

Liquid-Liquid extraction of bitter compounds from beer

<table>
<thead>
<tr>
<th>Strong Acid</th>
<th>Non-Polar Solvent</th>
<th>Beer</th>
</tr>
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</table>
| Adds excess hydrogen ions to solution – protonating all carboxylic acid functional groups | When functional groups are charged at a lower pH they are more non-polar | Bitter compounds
Iso alpha acids
Oxidized hop acids
Polyphenols
Non-bitter compounds
Alpha acids |

3 N Hydrochloric Acid + 2,2,4 trimethylpentane + Beer

Measure the absorbance at 275 nm
Absorbance @ 275 x 50 = Bittering Units

1 BU ≠ 1 ppm iso-alpha acid

**Extraction removes more than just Isos**

<table>
<thead>
<tr>
<th>STORAGE TEMPERATURE</th>
<th>ALPH A ACIDS IN HOPS</th>
<th>ISO-ALPHA ACIDS IN BEER</th>
<th>BEER IBUs</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20°F</td>
<td>3.22%</td>
<td>19.8 ppm</td>
<td>13.5</td>
</tr>
<tr>
<td>25°F</td>
<td>2.91%</td>
<td>18.1 ppm</td>
<td>12.0</td>
</tr>
<tr>
<td>45°F</td>
<td>1.71%</td>
<td>14.4 ppm</td>
<td>13.5</td>
</tr>
<tr>
<td>70°F</td>
<td>0.41%</td>
<td>2.9 ppm</td>
<td>11.0</td>
</tr>
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Brews made with an identical amount of cone hops stored 18 months at different temperatures

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Peacock, 1998

**Abused hops still produce bitter beer**

Isos Acid
Non-Polar Phase - TMP
Iso-Alpha Acids
Alpha Acids
Oxidized hop acids
Polyphenols

Non Polar Phase - Beer

Alpha Acids
Oxidized hop acids
Polyphenols
Correlation between total IAA & IBU

\[ y = 1.2x + 2.0 \]

\[ R^2 = 0.905 \]

BU increase due to hop polyphenols

Terminology

**Chromatography**

The method of separation

**Chromatograph**

The instrument of separation

**Chromatogram**

The visual output of the separation

Alpha and Iso-Alpa Acids by HPLC
HPLC Process Flow

High Performance Liquid Chromatography

- Atmospheric pressure separation
- Separation variables can be manipulated based on target analyte
- Non-volatile analysis

Beer Sample

Correlation between total IAA & IBU
**Hop acids quality**

- Total alpha acids are important
- HSI is important
- Cohumulone – not important
  - Shellhammer’s opinion
- The IBU measures more than Isos
  - 1 BU ≠ 1 ppm Iso alpha acids

**Hops composition**

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**Mt. Hood Maturity Study (Probasco)**

- Alpha Acids (%)
- Total Oil
- Cone Appearance and Completeness
- Alpha Acids (%)
- Total Oil
### Hop Oil Composition

**Hop Oil Compounds of Interest**

<table>
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<tr>
<th>Compound Name</th>
<th>Classification</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene</td>
<td>Hydrocarbon, Monoterpene</td>
<td>Pine</td>
</tr>
<tr>
<td>β-pinene</td>
<td>Hydrocarbon, Monoterpene</td>
<td>Coniferous Pine, woody</td>
</tr>
<tr>
<td>β-Mycene</td>
<td>Hydrocarbon, Monoterpene</td>
<td>Green, balsam, slightly metallic</td>
</tr>
<tr>
<td>Limonene</td>
<td>Hydrocarbon, Monoterpene</td>
<td>Citrus, Orange</td>
</tr>
<tr>
<td>p-cymene</td>
<td>Hydrocarbon, Monoterpene</td>
<td>Like Orange</td>
</tr>
<tr>
<td>Caryophyllene</td>
<td>Hydrocarbon, Sesquiterpene</td>
<td>Woody, Carrot</td>
</tr>
<tr>
<td>E, β-Farnesene</td>
<td>Hydrocarbon, Sesquiterpene</td>
<td>Green, woody, weedy, herbal, pine and gin</td>
</tr>
<tr>
<td>Humulene</td>
<td>Hydrocarbon, Sesquiterpene</td>
<td>Woody</td>
</tr>
<tr>
<td>Methyl heptanoate</td>
<td>Oxygenated, Ester</td>
<td>Sweet, fruity, peach, apricot, green, berry</td>
</tr>
<tr>
<td>Geraniol</td>
<td>Oxygenated, Monoterpene Alchool</td>
<td>Sweet floral, perfumy</td>
</tr>
<tr>
<td>Linalool</td>
<td>Oxygenated, Monoterpene Alchool</td>
<td>Floral, Orange</td>
</tr>
<tr>
<td>Citronellol</td>
<td>Oxygenated, Monoterpene Alchool</td>
<td>Floral, Rose Citrus</td>
</tr>
<tr>
<td>Farnesol</td>
<td>Oxygenated, Sesquiterpene Alchool</td>
<td>Spicy</td>
</tr>
<tr>
<td>Citral</td>
<td>Oxygenated, other</td>
<td>Sweet Citrus</td>
</tr>
<tr>
<td>Geranyl Acetate</td>
<td>Oxygenated, Monoterpene or ester</td>
<td>Floral, Sweet Citrus</td>
</tr>
<tr>
<td>Humulene Epoxyide I</td>
<td>Oxygenated, Epoxyide</td>
<td>Hay-like</td>
</tr>
<tr>
<td>Humulene Epoxyide 2</td>
<td>Oxygenated, Epoxyide</td>
<td>Cedar, Lime</td>
</tr>
</tbody>
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### Harvest Timeline

**Harvest Dates by Farm and Year**

- **Early**
- **Typical**
- **Late**

- **Willamette**
  - F1 2010
  - F1 2011
  - F2 2010
  - F2 2011

- **Cascade**
  - F1 2010
  - F1 2011
  - F2 2010
  - F2 2011

- **Harvest Timeline**

- **Note**: The major hydrocarbons group of compounds do not survive browndettle boil nor fermentation and are therefore unimportant to beer flavor. The oxidation products group of compounds are thought to be the “noble aroma,” herbal, and spicy beer flavor contributions. The floral and citrus groups contribute similar flavors to finished beer.
Preliminary brewing: Cascade

- Typical harvest hops = apple, apricot/peach, and sweaty/onion/garlic notes.
- Late harvest hops = higher melon and floral notes.

Timing of hop addition and flavor impact

- Bitterness a function of alpha and boil time
- Aromatic level is a function of volatilization

<table>
<thead>
<tr>
<th>Hop Addition</th>
<th>Floral</th>
<th>Citrus</th>
<th>Spicy</th>
<th>Resinous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kettle hop</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Late hop</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Dry hop</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
</tr>
</tbody>
</table>
Oil quantity and quality

- Maturity influences both
- Hop processing influences both
  - Drying
  - Pelletizing
  - Storage conditions
- Hop aroma is tied to hop oil