That Fabulous Hop Stink

The dirty secret about your hop chemistry you need to know

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Production and Brewing Science

Hopnology

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TOPICS

- Quality Parameters
- Production and Processing
- Aroma Components
- Extraction During Brewing
- Tips for Handling Opened Hops

Who is Hopnology?

- Scientists, Business Analysts, Market Specialists, and Industry Experts
- Lecturers at the Siebel Institute
- Business Builders, Food Scientists, and Farmers
- Pioneers in hop and beer aroma chemistry
- 20 years experience in hop production and craft beer business
- Creators of AromaSmart© hop technology

Hops Quality

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

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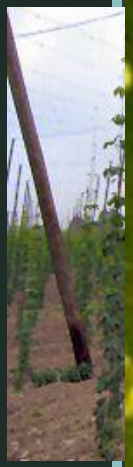
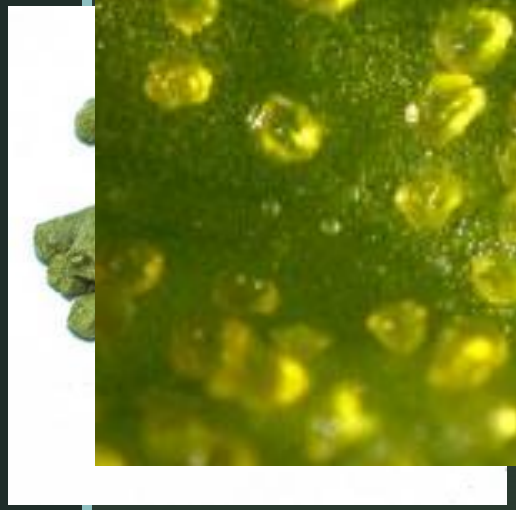
From Field to Kettle



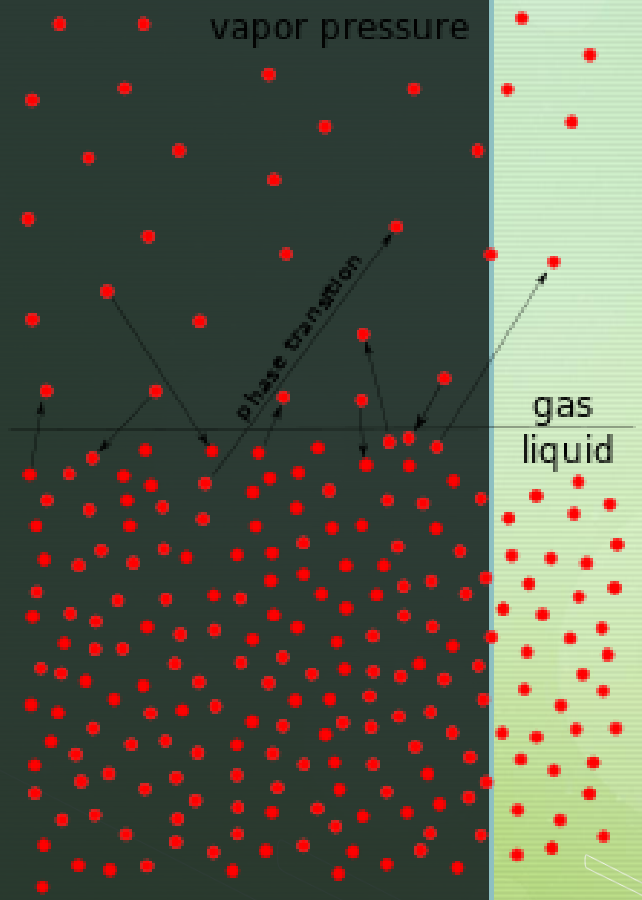


Aromatic Issues

- Aromatics are very volatile, heat sensitive, and susceptible to oxidative damage
- Processing issues responsible for damaging aroma profile
  - Improper drying
  - Overheated or improper pelletizing
    - Incorrect pellet density
  - Incorrect packaging
  - Poor storage conditions

Vapor Pressure

Pressure exerted by a vapor in thermodynamic equilibrium with its condensed phase at a given temperature in a closed system



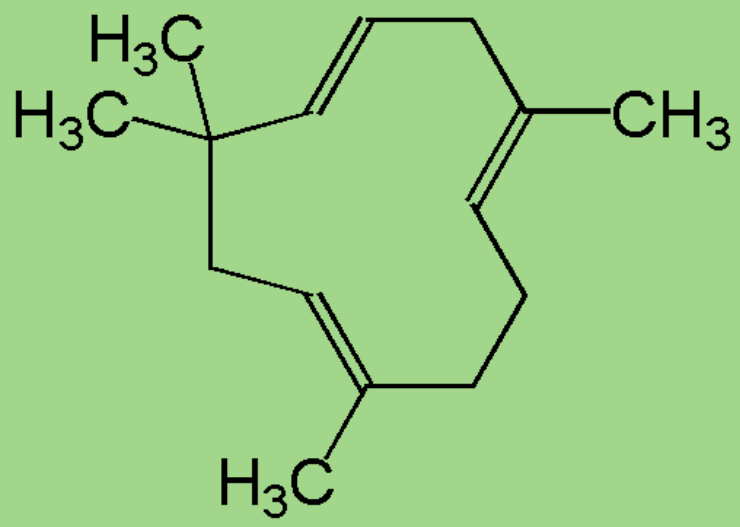
- Boiling point

  Pressure from molecule vapor equals the atmospheric pressure

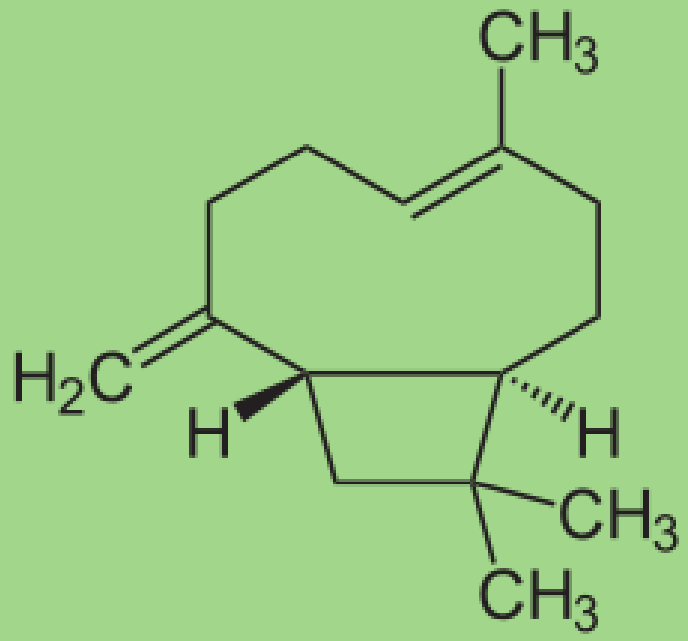
Essential Oils, but….

- Four main oils
  - Humulene
    - Primary oil responsible for “hoppy” nose
  - Caryophyllene
    - Similar to Humulene and closely related to oils found in citrus and marijuana
  - Farnesene
    - Typically found is small amounts, has a grassy, green apple aroma (higher in some varieties like Sterling and Tettnanger)
  - Myrcene
    - Comprises the majority of the oil fraction, ranges from floral to metallic depending on concentration

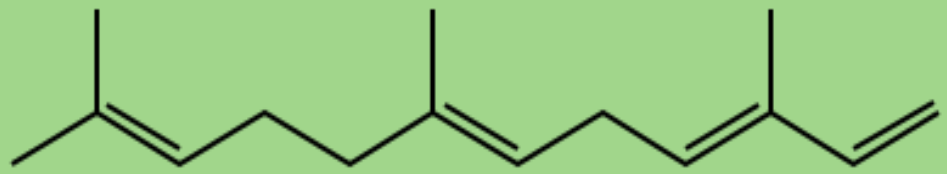
Know Your Oils



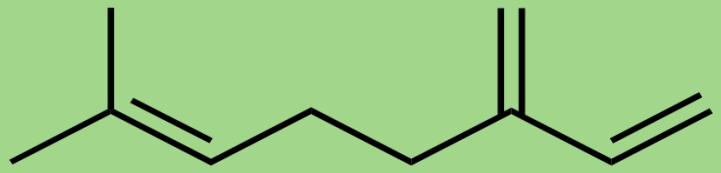
Humulene



Caryophylene



Farnesene



Myrcene

High Oil ≠ Big Hop Aroma

- 2015 OSU study shows absolutely no link between high oil content and dry hop aroma
  - Also shows no correlation between myrcene, humulene, or caryophyllene and dry hop aroma
- Individual levels of linalool and geraniol also show NO correlation to dry hop aroma

Where's the Stink Then?

- OSU study shows that dry hop aroma is correlated with:
  - Farnesene content
  - Linalool:geraniol ratio
  - Beta damascone
  - Geranyl acetate
  - Terpen-4-ol
- What do all of these compounds have in common?

Highly volatile, low human threshold, sensitive to harvest timing and storage conditions, extremely sensitive to heat destruction

Fruity and Floral

Compound	Characteristic	Taste threshold	Boiling Point
linalool	floral (lavender like), citrusy	180 ppb	199°C
geraniol	rose like	40-75 ppb	230°C
B-ionone	Woody, berry, floral, green and fruity	40 ppb	127°C
citronellol	floral rose waxy geranium oil powdery	40ppb	225°C
ethyl 2-methyl-butanoate	berry, grape, pineapple, mango and cherry notes	0.2ppb	133°C
nerol	lemon, bitter, green and fruity	300ppb	227°C
nonanal	citrus, cucumber and melon rindy,	6-12ppb	193°C
octanal	peely citrus orange	5-45ppb	172°C

www.cschi.cz/odour/files/world/Tresholds%20table.pdf

Herbal and Pine

Compound	Characteristic	Taste threshold	Boiling Point
α-pinene	Woody, piney and terpentine-like	6ppb odor	155°C
β-pinene	Woody, piney and terpentine-like with slight mint	140ppb odor	164°C
α-caryophyllene	Woody spicy earthy	210ppb	268°C
α-humulene	Woody, herbal, spicy	120ppb	276°C
farnesene	Fresh green vegetative with celery	2ppm	206°C
myrcene	Woody, vegetative, citrus, fruity with tropical mango	30-200ppb	167°C

Tropical and Dank

Compound	Characteristic	Taste threshold	Boiling point
4-mercapto-4-methylpentan-2-one	black currant, passionfruit, gooseberry, lychee, guava	3 ppt	181 °C
3-mercaptohexan-1-ol	passion fruit, tropical fruit, guava, sulfurous, grapefruit in dilution	60 ppt	198 °C
3-mercaptohexylacetate	tropical fruit, passion fruit, black currant	4 ppt	186 °C
(e,z)-1,3,5-undecatriene	pineapple	0.2 ppb	206 °C

Predominately found in Simcoe, Summit, Apollo, Topaz, CTZ

Oxidation Definition

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 can be 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

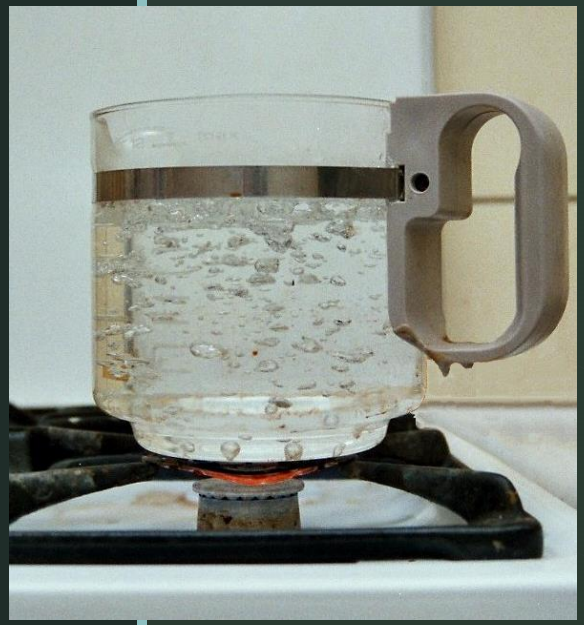
Yang, Xiaogen, Lederer, Cindy, McDaniel, Mina, and Deinzer, Max. Hydrolysis "Products of Caryophyllene Oxide in Hops and Beer". *J. Agric. Food Chem*. 1993, 41, 2082-2085

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.

The Boil



- Highly volatile compounds lost from the water phase
  - Myrcene levels are reduced by ½ every 5 minutes during boil
- Extraction of low volatiles
  - Allows oxidation of compounds such as humulene and caryophyllene, to generate odor complexity

End of Boil / Whirlpool

- Linalool extraction is late boil and whirlpool gives highest extraction (can increase during fermentation)
  - Remember about yeast transformation…
- Small amounts of low boiling point compounds maintained, less than dry hopping

https://beersensoryscience.wordpress.com/2012/02/16/linalool-fresh-and-floral-hop-aroma/

Dry Hopping

- Essential for capturing low boiling point compounds
- Extraction is temperature dependent
  - @ 23°C extractions are complete in four hours
  - @1°C hydrocarbon extractions peak in 3 days
  - Longer times do not increase the amount of extraction

Wolfe, Peter Harold, A Study of Factors Affecting the Extraction of Flavor When Dry Hopping Beer Oregon State University, 2012

Primary or Secondary?

- Citronellol and nerol can be metabolized by yeast
- Vigorous CO2 scrubs aroma compounds
  - Super intense head space aroma?
- Secondary additions to keep very delicate aromas
  - Mandarin, froot loops, bright citrus
- Increase of linalool, geraniol, nerol during aging
  - Acid hydrolysis of glutamates

Tips for Storing Opened Hops

- Store in a cold place out of light
  - <32°F best
- If possible purge hops with CO_2 or Nitrogen
- Vacuum sealing is best
  - However, if that is not available storing pellets in a 5 gallon pail purged with CO_2 and sealed will help reduce oxidation

Summary

- Building flavor profiles requires understanding how aroma components act in brewing conditions
- Flavor is complex and influenced by oxidation and evaporation of aroma components
- Maintain the quality of the hops so that you can achieve reproducible results
- Demand quality production, processing, traceability

Where to go for more information

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

Questions

- On-line classes
- Podcasts
- Research
- Consulting
- Speaking

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