Changes in the concentration of hop volatiles in beer during fermentation by S. cerevesiae

Grant Ruehle
Chemist, New Belgium Brewing Co.
Hop Aroma

• Understanding still relatively vague at levels used in modern craft brewing

• A strong correlation between analytical and sensory data remains elusive
  – Schieberle et al\textsuperscript{1} showed linalool alone correlated to hop perception
  – Teagle\textsuperscript{2} showed correlation of myrcene to “hoppiness”
Dry Hop aroma

• Hops used at very high rates (250-500g/hL)
• Dynamics of transfer and transformation not well understood under these circumstances
• Trace components? (thiols in particular)
• What process parameters control aroma transfer?
Impact of yeast on hop aroma

• Biotransformation\(^{1,2,3}\)
  – Geraniol/citronellol\(^4\)
  – geranyl acetate/geraniol\(^5\)
  – \(\beta\)-glucosidase release of Glycosides\(^6\)
  – \(\beta\)-lyase release of cysteine conjugated thiols\(^7\)

• Adsorption?
  – Iso-\(\alpha\)-acids on yeast cell wall
  – Loss of other terpenes?
What next?

• How much more can Hop Aroma be probed with GC-MS?
• Impact of sulfur compounds on “American hop aroma”
  – Sulfur specific detection, qTOF, mercuric extraction, derivitization
• Multivariate data techniques
  – Metabolomics approach
Experiment

• How are the most abundant terpenes impacted by the presence of yeast?
• How can desired aroma be controlled with dwell time?
Quantification of volatiles

- Gerstel MPS auto sampler
- Supelco DVB/CAR/PDMS SPME fiber
- Agilent 7890A GC and 5975C MSD
Aliphatic terpenes

- **Myrcene**
  - Solubility 5.6mg/L in water
  - Vapor pressure 7.17mmHg @25°C
- **Limonene**
  - 13.8mg/L
  - 0.198mmHg
- **Caryophyllene**
  - <1mg/L
  - 0.013mmHg
- **α-Humululene**
  - <1mg/L
  - 0.008 mmHg
Oxygenated Terpenes

- **Linalool**
  - 320mg/L
  - 0.016mmHg

- **Geraniol**
  - 686mg/L
  - 0.021mmHg

- **Nerol**
  - 809mg/L
  - 0.013mmHg

- **Citronellol**
  - Unavailable
  - 0.020mmHg
Dry hopping

- Pellets added to beer in maturation
  - 1.8L beer in 2L media flask
  - Yeast removed by centrifuge
  - Maintained at 20°C
  - 250g/hL equivalent of Cascade pellets

- Analysis performed every hour
Linalool, Nerol

- Rapidly reach saturation
- Little change seen thereafter
Geraniol, Citronellol

- Opposite trends
- Biotransformation?
  - No yeast present
Myrcene, Limonene

- Similar trends
- Limonene levels relatively low
Humulene, and Caryophyllene

- Slower transfer than oxygenated terpenes
- Very similar behavior
- Reach relatively high levels
Hopping on active yeast

- Pelletized Cascade hops added 12h after knock out
- 1.8L fermenting beer in 2L media flask In triplicate
- 30mL sample taken every 24h
  - yeast removed by centrifugation
Linalool and Nerol

- Quickly reach max concentration
- Linalool has similar max as in dry hopping
- Begin to decrease thereafter
- Nerol reaches half the concentration as in dry hopping
Geraniol and Citronellol

- Lower levels of both compounds than in dry hopping
- Difference most notable with geraniol
Myrcene and Limonene

• No evidence of myrcene transfer from pellets
  – Residual levels commonly seen from brewhouse
• Myrcene decreases throughout
• Limonene does transfer
• Falls off similar to other compounds
Humulene and Caryophyllene

- Slower transfer into beer and loss from beer than other compounds
- Much lower levels than in dry hopping
Myrcene

• Behavior on vs off yeast
• Mechanism of loss during fermentation?
Humulene

- Lower max concentration on yeast
- Increases for 50 hours during fermentation
Linalool

- Quickly reaches max concentration
- Decreases from that point
- CO₂ stripping during fermentation?
Conclusions

• Differences between hopping on and off yeast largest in aliphatic components
  – Myrcene most pronounced
  – Mechanism of myrcene loss not obvious

• Compounds lost during fermentation
  – Result of CO$_2$ stripping?
  – Hop addition after high kreuzen likely advantageous
Thank you for your attention.
Citations


