BARTH-HAAS GROUP

BEER DIVERSIFICATION BY EFFICIENT DRY HOPPING

Georg Drexler, Brewing Solutions
**DRY HOPPING**

- Around 30-35% of US Craft Beers are IPAs (“regular”, New England/Hazy, Session, Double...)
- Lot more beers than IPAs are dry hopped (Pale Ales, some Lager/Pilsner, Experimentals etc.)
- US Craft beer: >50% dry hopped?!
- Dry hopping is very popular, but still not fully understood
- Dry hopping itself is not a unique selling proposition

=> Need and opportunities for improvement
Agenda

- Diversification – relevant hop compounds
- Efficient dry hopping
- Provoak
IMPORTANT HOP AROMA COMPOUNDS

• Linalool: „Key Aroma Compound“?

• Depends on
  – which varieties are used?
  – at which stage in the brewery?
  – at which dose rate?

• If we talk about...
  – Traditional, late hopped beer styles (low in hop aroma) – Maybe!
  – hoppy craft beers with flavour hops – NO!

• What about Thiols?
# Hop Oil Composition

440 compounds identified, 1000+ are likely!

<table>
<thead>
<tr>
<th>Substance Group</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoterpenes (myrcene, pinene etc.)</td>
<td>approx. 40 %</td>
</tr>
<tr>
<td>Sesquiterpenes (β-caryophyllene, α-humulene)</td>
<td>approx. 40 %</td>
</tr>
<tr>
<td>Carboxylicacid-esters (methyl-esters)</td>
<td>approx. 15 %</td>
</tr>
<tr>
<td>Carboxylicacids</td>
<td>approx. 1 %</td>
</tr>
<tr>
<td>Monoterpenoxides (linalool, geraniol etc.)</td>
<td>approx. 1 %</td>
</tr>
<tr>
<td>Sesquiterpenoxides (humullenol II, humulen epoxides)</td>
<td>approx. 1 %</td>
</tr>
<tr>
<td>Aldehydes, Ketones (hexenal, epoxydecenal, undecanone, octadienone)</td>
<td>approx. 1 %</td>
</tr>
<tr>
<td>Aliphatic hydrocarbons</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>Sulfur containing compounds (4-MMP, 3-MMP, 3-MH...)</td>
<td>&lt; 0.1 %</td>
</tr>
<tr>
<td>Glycosidically bound aroma compounds</td>
<td>?</td>
</tr>
</tbody>
</table>
What are Thiols?

- Thiols and Mercaptans are organosulfur compounds that contain a sulfur-hydrogen bond
- In form of aldehydes, ketones and esters: fruity and pleasant
- “Mercapto” relates to the ability to bind mercury (II) ions (capturing Mercury)
- Thermally unstable (?)
- Aromatic compounds with unique properties in wine, milk, cheese, vegetables, fruits... and HOPS!
**IMPORTANT AND FRUITY THIOLS**

- **4 ng/L**
  - 4-Mercaptomethylpentan-2-one = **4MMP** = 4S4M2Pone

- **60 ng/L**
  - 3-Mercaptohexan-1-ol = **3MH** = 3SHol

- **0.8-4 ng/L**
  - 3-Mercaptohexylacetate = **3MHA** = 3SHA

*Images of fruits and vegetables are used to illustrate the thiols.*

31.05.2019
IMPORTANT AND FRUITY THIOLS

3-Mercapto-octanal = 3MO = 3SOal

3-Mercapto-4-methylpentan-1-ol = 3MMP = 3S4MPol

4-Mercapto-4-methylpentan-2-ol (4MMPOH)?
box tree, cat pee
Range in wines (ng/L): 0-40
Odor threshold (ng/L) : 0.8

Found in Hallertau Blanc, Nelson Sauvin, Mosaic and Amarillo
4MMP — Recent Studies

- Flavour threshold as low as 1.5 ng/l
- In beers up to 150 ng/l (Dagan 2018)
- 4MMP concentrations in European and US cultivars from <1 to 114 µg/kg (Reglitz; Steinhaus 2017):
  - high in US varieties as Citra, Mosaic etc.
  - low in classic European varieties
- Stable concentration from cones to pellets
- Optimum extraction time for dry-hopping process is ~4 days
- Strong decline of 4MMP concentration with beer aging (Reglitz; Steinhaus 2018)
FREE THIOLS IN HOPS

Data from various studies of Collin et al and Dagan et al

μg/kg

4-mercapto-4-methylpentan-2-on  3-mercaptohexan-1-ol
3-mercaptohexyl-acetate  3-mercapto-4-methylpentan-1-ol

31.05.2019
SUMMARY ON THIOLS

• Different Thiols exhibit fruity flavours
• Thiols interact and change flavour quality
• Thiols can become unpleasant, depending on concentration, ratio, beer matrix, etc.
• Free Thiols in “New World Hops”
• Looking for the right hop variety will help to diversify
• Comprehensive data of all meaningful hop varieties is needed (incl. checking harvest dates)
• Behaviour during fermentation/dry hopping not fully understood
Agenda

- Diversification – relevant hop compounds
- Efficient dry hopping
- Provoak
Dry Hopping

- A crucial process step for the production of many (craft) beers
- Part of the most popular craft beer style recipes (IPA, Pale Ale, Hazy IPA...)
- Still a question mark for many brewers
- Hops as (the most?) important flavour contributor
Factors influencing Hop Aroma

- variety
time of harvest
crop year, kilning

Point of addition
solubility/
evaporation

adsorption/
transformation/
interactions

dry hopping
(with/out yeast)
duration, temp, agitation, etc.

aroma in hops

hoppy aroma in beer

Harvest
Brewhouse
Fermentation
Lagering

plus.....filtration....bottling...storage
Dry hopping highly depends on:

- Wettability and swelling properties
- Particle size and distribution
- Temperature
- Ethanol concentration
- Process type (static - dynamic)
- Contact time
- Oil concentration (variety, enrichment)
- Tank geometry and scale
Hop Varieties & Products

• All hop varieties and types can be used
• Hop Cones ("flowers"): contact area, oxygen
• Hop Pellets: homogeneous, better utilisation
• Hop Powder: difficult dosing
• Hop Oils/Emulsions: best yield, less beer losses; oil is insoluble => emulsion
Swelling properties depend on...

• Pelletization process
• Percentage of coarse fraction („green“ material)

Volume increase:

• Up to 1000%
• Severe beer losses without retention
• Key indicator for dry hopping equipment (hop bags, etc.)
INCREASE IN EFFICIENCY (VARIETY & PRODUCT)

In terms of varieties or products, dry hopping efficiency could be increased by:

• The usage of Hop Varieties with high oil contents (0.4-4 ml/100g)
• Enriched Hop Pellets (Type 45): reduce beer losses by up to 50%
• Hop oil products: excellent utilisation (up to 100%)
=> no beer losses at all
**PHA Products**

- **PHA Classics**
  - Rose
  - Myrcen
  - Citrusy
  - Sylvan
  - Spicy
  - Floral
  - Herbal
  - Custom Products
  - Create a versatile flavour and aroma palate; often used as a mixture

- **PHA Varietals**
  - Hersbrucker
  - Cascade
  - Perle
  - Mt. Hood
  - Golding
  - Tradition
  - Other Varieties
  - Late hopping character, strong taste impact

- **PHA Topnotes**
  - Hersbrucker
  - Cascade
  - Perle
  - Mt. Hood
  - Golding
  - Tradition
  - Other Varieties
  - Dry hopping character; highly volatile components of specific hop oil → more effect on aroma and less on taste
**SUBSTITUTION OF DRY HOPPING WITH PHA PRODUCTS**

- Pale Ale as base beer
- Fermentation: Yeast WL001
- 25 IBU
- 2 beers: Cascade and Target
- Addition of PHAs to beers was 0%, 25%, 50% and 75%

![Diagram showing the substitution of dry hopping with PHA products.](image-url)
SUBSTITUTION OF DRY HOPPING WITH PHA PRODUCTS

• Sensory evaluation of beers with 0%-75% PHAs against beer 100% (100% dry hopped with pellets)
  ➔ Triangle tests, for example:

  ![Triangle test diagram]

  Sample A  Sample B  Sample C
  Beer 100%  Beer 25% + PHAs  Beer 100%

• Analysis of hop aroma compounds of selected beers (VLB) plus analyses of colour, total polyphenols and foam

(Kerner, Master Thesis TUM, 2016)
Substitution of Dry Hopping with PHA Products

• It was possible to a certain degree to substitute hops used for dry hopping by adding PHA Topnotes (up to 75%)
• Depends on the beer style and the hop varieties used
• No influence on the colour or foam by the addition of PHAs
• Reduction of polyphenols
  → no polyphenols added by the use of PHAs
• Feasible for all traditional hops (including Cascade), but more challenging for dry hopping regimes with Citra/Mosaic or similar
• Trials are necessary for each beer to find the appropriated PHA combination and dose rate
EXTRACTION DURING DRY HOPPING: STATIC VS. DYNAMIC

• **Static Extraction:**
  
  — Diffusion only (Brownian Motion)
  
  — Slow and inefficient
    (decrease in concentration gradients: particle ↔ solvent)

• **Dynamic Extraction:**
  
  — Forced distribution through fluid and molecular dynamics
    (according to Fick’s laws)
  
  — More efficient
    (higher concentration gradient over time: particle ↔ solvent)
  
  — Faster extraction of unwanted compounds (IBU, pH, Mouthfeel)
Layer Formation

- In tanks: layering will occur depending on aroma component and geometry.
- For reproducible results, mixing or recirculation before filling is crucial.

Mixing / Blending Considerations

- Beta Myrcene
  - 585 ppb
  - 342 ppb
  - 310 ppb

- Linalool
  - 129 ppb
  - 142 ppb
  - 136 ppb

Thomas P. Nielsen - Sierra Nevada Brewing Company - R&D
PROCESS TECHNOLOGY - TIME OF ADDITION

Fermentation:

• CO₂ stripping of undesired aroma components
• Forced agitation during primary fermentation
• High temperatures – good solution of oils
• Biotransformation of aroma components
• Yeast cannot be reused
• Oxygen scavenging (yeast)
• Microbiological safety
• Higher ester formation
• Low ethanol in beginning (extraction/solubility!)
• Medium extraction yield
PROCESS TECHNOLOGY - TIME OF ADDITION

Maturation (diacetyl rest / yeast harvested)

- Less CO$_2$ stripping / flotation
- Less agitation
- High temperatures
- Still active yeast present (oxygen!)
- Lower biotransformation
- Low ester formation
- Ethanol present (good extraction)
- High extraction yield
PROCESS TECHNOLOGY - TIME OF ADDITION

Lagering:

• No CO2 stripping
• No agitation
• Low temperatures (after cool crash)
• No active yeast present
• Highest ethanol concentration
• Mostly operated with bypass equipment
PROCESS TECHNOLOGY — HOPS IN

• Direct / Manual addition, loose or in bag or net
• Hop Slurry with DA water or beer (e. g. Rolec DryHopnik)
• CO₂ blow (e. g. Hop Cannon)
• Hop Percolation / Hop Bag (e. g. BrauKon HopGun, Torpedo)
PROCESS TECHNOLOGY — HOPS OUT

- Standpipe, Racking arm (beer losses!)
- Sieving (Pipe Strainers)
- Centrifuge
- Decanter
- Pre-clarification with Candle Filter or Centrifugal Discharge Filter without filter aid
- Filtration with filter aids: (saturated) membrane and sheet filters better than Kieselguhr (?!)

[Image of beer bottles]
CONCLUSIONS DRY HOPPING

Parameters to look at in order to improve the dry hopping process:

• Choice of product (Raw Hops, Pellet Type, Extracts/Oils)
• Point of Addition
• Duration of Dry Hopping
• Special Equipment
• Oxygen Uptake
• Interactions like synergistic effects => trials & tastings
**CONSISTENT HOP AROMA?**

- There are several possibilities for hop addition calculations
- There is no guarantee to get the same hop aroma in beer every time:
  - deviation in aroma of raw hops from year to year (crop to crop)
  - different hop growing regions and even hop gardens show different aroma of raw hops
  - even if the amount of dosed hop oils is the same: the composition of the hop oil might be different
  - there are interactions between hop oils and other beer compounds which may lead to variations of the aroma in the final beer
  - changes in the brewing process has an impact on the hop aroma in beer
BARTH-HAAS GROUP

PROVOAK

BREWERS’ INSPIRATION
**BACKGROUND BARREL AGING**

- Traditional method to increase aroma complexity of mostly wines and spirits
- For beer mostly pitched casks were used (except: Belgium, GB)
- Increasing popularity in craft brewing (Barley Wines, Dubbels, Ice-Bocks, Imperials)
- Aroma impact highly depends on type of wood, toasting, aging time and pre-usage
**Background Barrel Aging**

- Limited to some beer styles (high ABV and Color)
- Long maturation time (minimum 4-6 weeks, mostly several months)
- Barrels: cost intensive (Bourbon, Sherry, etc.)
- Hard to clean → microbiological hazards
- Single use for each beer style
- Product exposed to oxidation (Hop aroma!)
- High storage cost and know-how intensive

**Solutions in Wine Industry:**

- tank maturation with wooden staves, cubes, chips, powder
WHAT IS PROVOAK?

Project Target:
• Fresh, intense dry-hopping aroma combined with the pleasant body and mouthfeel of barrel aging

Development Scope:
• Easy-to-dose pelletized product
• Dual purpose product without downsides
• Cost and time efficient barrel aging character
• Suitable for late and dry-hopping
• Fits modern dry-hopping processes (dwell time)
• No limitation in ABV, Color or Beer Style
PROVOAK FACTS

Products:
• US Style (toasted) and EU Style (untoasted)

Dosage and dwell time:
• ~3 ml Oil per hl for around 7 days (if static)

Disclosure (patent pending):
• 100 % natural, food grade product, consisting of hops and wooden components.
• All hops produced got US and JP norms
• Not in conformity with German purity law
• Labeling: oak aged, oak flavoured, oaked, „auf Holz gelagert“
US STYLE & EU STYLE CHARACTER

OAK AGEING & HOP AROMA

DRY HOPPING PELLET

Complex and noble flavours with both hops and oak for innovative beers.

US-STYLE:
intense, sweet hop aroma - paired with the typical heavy notes of toasted oak casks
red berries  dried fruit  bourbon
oranges  full-bodied  barrique
wild berries  vanilla

EU-STYLE:
fruity and light hop aroma - paired with typical woody notes of untoasted oak casks
tangerines  wine-like  pineapples
oranges  tannic
grapes  oaky

APPLICATION:
similar handling compared to dry-hopping with hop pellets without the disadvantages of barrel ageing (oxidation, labor-intensive, costs)

DOSAGE:
proven oak is dosed according to the hop oil concentration comparable to dry-hopping (3-6 mL Oil/hL)

CONTACT TIME:
approx. 1 week if dosed during lagering

DUAL PURPOSE PRODUCT:
one product - one pellet - one dose with two aroma components: hops and oak

100% NATURAL AND FOOD GRADE PRODUCT
PROVOAK MUNICH BROWN BEER AT BRAU 2018

PROVOAK
MUNICH BROWN

NEW

Taste - out of the box

wild berries
red currants
oranges
vanilla
barrique
bourbon

WHIRLPOOL
40 µL/L

DRYHOPPING
14,5 µL/L

IBU
AKL
6,3 %
Comments from our Tasting at BRAU Beviale 2018:
strong woody flavour, combined with fruity and berry character:

cherry, strawberry, dried fruit mango, guava, gooseberry, banana wood woody aromatic vegetal, citrusy Black currant oak, menthol jasmine, lily herbal, spicy smokey, woody woody, caramel herbal woody jasmine tea, apricot strawberr
woody woody, woody aromatic sweet fruits, woody aromatic woody aromatic, red berries liquorisch, barrel aged, malty woody, spicy, ripe orange liquorice, cassis, woody sweet, smokey orange, green pepper, raspberry woody woody honey, grapefruit sweet fruits, tobacco, woody sl woody, citrus okay, toasty woody, caramel, berry woody, raspberry spicy herbal woody cream caramel quince, peach honey, lemon, juniper red berries, sweet fruits honey, sweet fruits, oak woody, sweet, fruit woody, sweet fruit, leather herbal, caramel red berries blueberry, tobacco cassis tangerine, honey, peach red berries, sweet fruits herbal, spicy, cream caramel caramel, herbal woody, smoky menthol, green grassy, red berries cassis, woody woody, smoky, caramel Cognac, barrique, leather honey, aromatic, woody woody, red berries jasmine, oak, tobacco woody juniper smoke woody, spicy, herbal woody coffee, smokey sweet fruits tropical fruits, grape, woody woody woody, vegetal woody aromatic, cream caramel woody awet fruits, grassy ginger, fennel, artichoke barrique, lychee, plum, vanilla berries woody, fruity smokey, cherry, vanilla red berries
THANKS TO...

...all the ambitious researchers,
...all passionate brewers in love with hops
...our Brewing Solutions Team!

WE HELP YOU TO FIND THE HOP AROMA YOU ARE LOOKING FOR!

CONTACT US VIA
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