Hop Varieties and Conditionings: New Opportunities for Special Beers

Philippe Lefèvre
Yakima Chief
Hops and Beer Flavour
Hops and Beer Flavour

Van Opstaele *et al.*, 2006
Hops and Beer Flavour

Beer Flavour

Taste (Gustatory)

Odour (Olfactory)

Van Opstaele et al., 2006
Hops and Beer Flavour

Beer Flavour

- Taste (Gustatory)
- Odour (Olfactory)
- Mouthfeel (Tactile)

Van Opstaele et al., 2006
Hops and Beer Flavour

Beer Flavour

- Taste (Gustatory)
- Odour (Olfactory)
- Mouthfeel (Tactile)

Receptors in nose, mouth and throat

Van Opstaele et al., 2006
Hops and Beer Flavour

Beer Flavour

- Odour: Olfactory
  - Receptors in nose, mouth and throat
- Bitterness
- Taste
  - Gustatory
- Mouthfeel: Tactile

Van Opstaele et al., 2006
Hops and Beer Flavour

Beer Flavour

- **Receptors in nose, mouth and throat**
- **Hop aroma**
- **Odour**
- **Taste**
- **Bitterness**
- **Mouthfeel**

- **Gustatory**
- **Olfactory**
- **Tactile**

Van Opstaele et al., 2006
Hops and Beer Flavour

Beer Flavour

Taste

Gustatory

Bitterness

Hop aroma

Odour

Olfactory

Polyphenols

Mouthfeel

Tactile

Receptors in nose, mouth and throat

Van Opstaele et al., 2006
Hop Bitterness

Beer Flavour

Taste

Gustatory

Bitterness
Hop Bitterness

Beer Flavour

Intensity → Bitterness → Quality

Gustatory

Taste
Hop Bitterness

Beer Flavour

Taste

Intensity

Bitterness

Quality

Gustatory

Many different hop-derived compounds

Hops and fresh beer
- 48 compounds (1)

Aged beer
- 57 compounds (1)

(1) Haseleu et al., 2010
Bitter Hop Compounds

α-acids

Humulones
Bitter Hop Compounds

α-acids

Humulones

β-acids

Lupulones
Bitter Hop Compounds

α-acids

Humulones

Humulone
Adhumulone

β-acids

Lupulones

Colupulone
Lupulone
Adlupulone
Bitter Hop Compounds

**α-acids**
- Humulones
  - Cohumulone
  - Humulone
  - Adhumulone

**β-acids**
- Lupulones
  - Colupulone
  - Lupulone
  - Adlupulone

**Chalcones**
- Xanthohumol
Wort Boiling: $\alpha$-Acids

Humulones $\rightarrow$ Cis-isohumulones + Trans-isohumulones
Wort Boiling: $\alpha$-Acids

- Major contribution to the bitter taste
- Varying levels and quality of bitterness
- Hop addition at the beginning of wort boiling
α-Acids & Derivatives

IAA  DHIAA  THIAA  HHIAA
Wort Boiling : $\beta$-Acids

Lupulones

Hulupones

Haseleu et al., 2010
Wort Boiling: $\beta$-Acids

Lupulones $\rightarrow$ Hulupones $\rightarrow$ Hulupinic Acid

Haseleu et al., 2010
Wort Boiling: β-Acids

Lupulones → Hulupones → Hulupinic Acid

O₂

Tricyclolupones

Haseleu et al., 2010
Wort Boiling: $\beta$-Acids

Lupulones $\xrightarrow{O_2} \text{Hulupones} \xrightarrow{} \text{Hulupinic Acid}$

- Other bitter compounds
- Also formed during ageing

Haseleu et al., 2010
Wort Boiling: Chalcones

- Compound with very well-rounded bitterness
- High $\alpha$-acids $\rightarrow$ high xanthohumol content

(1) Collin et al., 2011
Hops Ageing: $\alpha$-Acids

- Very bitter compounds
- Present in old hops
Beer Ageing: Iso-α-Acids

Haseleu et al., 2010

Cis-isohumulones
Trans-isohumulones

Cis-humulinic Acids & Cis-alloisohumulones
Trans-humulinic Acids & Trans-alloisohumulones
Beer Ageing: Iso-\(\alpha\)-Acids

- Cis-isohumulones
- Trans-isohumulones
- Tricyclohumols

Other bitter compounds
Very harsh bitterness

Haseleu et al., 2010
Bitter Hop Varieties

Bitter Hop Breeding

- Intensity of bitterness $\rightarrow$ more $\alpha$-acids
- Quality of bitterness $\rightarrow$ less cohumulone
Bitter Hop Varieties

Bitter Hop Breeding
- Intensity of bitterness $\rightarrow$ more $\alpha$-acids
- Quality of bitterness $\rightarrow$ less cohumulone

Northern Brewer
Brewers Gold

Magnum
Taurus
Herkules

Cluster
Galena
Nugget

Columbus-Tomahawk-Zeus
Summit
And many others
Conclusions

- Many compounds involved (not only iso-α-acids)
  → Various levels and quality of bitterness
- Quality of hops (drying, storage, processing)
  → Important to avoid oxidized compounds
- Important shift in hop varieties
Conclusions

➤ Many compounds involved (not only iso-\(\alpha\)-acids)
   → Various levels and quality of bitterness
➤ Quality of hops (drying, storage, processing)
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➤ Important shift in hop varieties

For the Future

➤ Continue to develop products and processes which will allow to contribute to various tastes in beer
Hop Aroma

Beer Flavour

Key Points

Hop aroma

Odour

Olfactory
Hop Aroma

Beer Flavour

Key Points

Hop Composition

Hop aroma

Odour

Olfactory
Hop Aroma

Beer Flavour

- Hop aroma
- Odour

Key Points

- Hop Composition
- Hop Varieties
Hop Aroma

Key Points

- Hop Composition
- Hop Varieties
- Brewing Process

Beer Flavour

- Hop aroma
- Odour

Olfactory
Hop Aroma

Beer Flavour

Many different hop-derived compounds → Hop aroma → Odour → Olfactory

Hop Composition
Hop Aroma

Beer Flavour

- Many different hop-derived compounds
- Hop aroma
- Odour

Hop Composition

- Hop Oil

Olfactory
Hop Aroma

Beer Flavour

- Many different hop-derived compounds
  - Hop aroma
    - Odour
      - Olfactory

Hop Composition

- Hop Oil
- Glycosides
Hop Aroma

Beer Flavour

- Many different hop-derived compounds
- Hop aroma
- Odour
- Olfactory

Hop Composition

- Hop Oil
- Glycosides
- Cysteine Adducts
Hop Oil Compounds

Hydrocarbons

50-80%

- Monoterpenes: myrcene, limonene, pinene
- Sesquiterpenes: humulene, farnesene, caryophyllene
- Aliphatic hydrocarbons

Schönberger & Kostelecky, 2011
Hop Oil Compounds

**Hydrocarbons**

- **50-80%**
  - **Monoterpenes:** myrcene, limonene, pinene
  - **Sesquiterpenes:** humulene, farnesene, caryophyllene
  - **Aliphatic hydrocarbons**

**O-compounds**

- **20-50%**
  - **Monoterpene alcohols:** linalool, geraniol, nerol
  - **Sesquiterpene alcohols:** humulol, humulenol
  - **Others:** acids, alcohols, ketones, esters, aldehydes, epoxides

Schönberger & Kostelecky, 2011
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**S-compounds**
- **< 1%**
  - **Thioesters**
  - **Sulfides**
  - **Polyfunctional thiols**
  - **Others**

Schönberger & Kostelecky, 2011
Many Hop Aroma Compounds

- **Hops** → more than 400 compounds, up to 1000
- **Beer** → hundreds maybe thousands compounds
- And many transformations during brewing process

(1) Roberts *et al.*, 2004; (2) Schönberger, 2011
Hop Aroma Complexity

Many Hop Aroma Compounds

- **Hops** → more than 400 compounds, up to 1000 \(^{(1)}\)
- **Beer** → hundreds maybe thousands compounds \(^{(1)}\)
- And many transformations during brewing process

Synergistic Effect \(^{(2)}\)

- Very complex interaction between aroma compounds
- Threshold values depend on presence and concentration of other compounds

\(^{(1)}\) Roberts *et al.*, 2004; \(^{(2)}\) Schönberger, 2011
Hop Aroma Compounds

**Hop Aroma & Key Compounds**

- **Noble & Spicy** → oxygenated sesquiterpenoids (humulene epoxides, caryophyllene epoxide, humulenol)
- **Citrusy** → carboxylic acid esters, alcohols and ketones
- **Fruity** → terpene alcohols (linalool, geraniol, citronellol), thiols (4MMP, 3MH, 3MHA), ketones, epoxides and esters
- **Green & Grassy** → aldehydes (hexanal)

Kishimoro *et al.*, 2008; Schönberger & Kostelecky, 2011
Hop Aroma

Beer Flavour

Hop aroma

Odour

Olfactory

Hop Varieties

Traditional Hop Aroma

Specialty Hop Aroma
Traditional Hop Aroma

Historic Hops

- Saaz, Lublin, Hallertauer Mittelfrüh, Hersbrucker, Tettnanger, Spalter, Styrian Golding, East Kent Golding, Fuggle
Traditional Hop Aroma

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New Hop Varieties
- **Europe** → Tradition, Saphir, Premiant, Sládeň, Aurora, Bobek
- **United States** → Willamette, Sterling, Palisade, Mount Hood, Vanguard
Specialty Hop Aroma

History

- **Cascade** → developed in the 50’s, released in 1972
- **Development** → American craft brewing industry
- **Trend** → more emphasis on hop flavour
Specialty Hop Aroma

History
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Key Hop Varieties
- **United States** → Amarillo®, Cascade, Centennial, Chinook, Citra®, Mosaic®, Simcoe®
- **Others** → Nelson Sauvin (New Zealand), Galaxy (Australia), Southern Promise (South Africa)
Hop Aroma Evaluation

Evaluation techniques

- **Raw hops**
  - Sniffing of crushed pellets or cones

- **Simulation of boiling**
  - Hop tea

- **Simulation of dry hopping**
  - Maceration in a superfine alcohol solution

- **But never replace a brew!**
Hop Aroma Evaluation

Radar diagrams - Sterling

Overall Hop Aroma
Floral
Fruity
Spicy
Piney
Citrus
Herbal
Grassy
Cheesy
Woodsy
Onion/Garlic

Base Beer
Sterling Fresh
Sterling 2 Months

Brynildson, 2010
Hop Aroma Evaluation

Radar diagrams - Willamette

Overall Hop Aroma
Floral
Fruity
Spicy
Piney
Citrus
Herbal
Grassy
Cheesy
Woodsy
Onion/Garlic
Base Beer
Willamette Fresh
Willamette 2 Months

Brynildson, 2010
Hop Aroma Evaluation

Radar diagrams - Cascade

Brynildson, 2010
Hop Aroma Evaluation

Radar diagrams - Chinook

Overall Hop Aroma
Floral
Fruity
Spicy
Piney
Citrus
Herbal
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Onion/Garlic

Base Beer
Chinook Fresh
Chinook 2 Months

Brynildson, 2010
Hop Aroma

Beer Flavour

Brewing Process

Hop aroma → Odour → Olfactory
Hop Aroma

Beer Flavour

Brewing Process

Wort Boiling & Whirlpool

Hop aroma

Odour

Olfactory
Hop Aroma

Beer Flavour

Brewing Process

Wort Boiling & Whirlpool

Fermentation & Maturation

Hop aroma

Odour

Olfactory
Hop Aroma

Beer Flavour

Brewing Process

Wort Boiling & Whirlpool

Fermentation & Maturation

Kettle, Late & Dry Aroma

Hop aroma

Odour

Olfactory
Wort Boiling & Whirlpool

Physical Elimination

- Very volatile compounds
  → Important losses with boiling vapor
- Apolar compounds
  → Losses by adsorption on trub, tank walls, etc.
Wort Boiling & Whirlpool

Chemical Transformations

- **Oxidation reactions**
  - Production of more soluble compounds

- **Examples**
  - Production of humulene epoxides
  - Production of caryophyllene epoxide
  - Production of humuladienone
  - Production of methyl isobutyl ketone

- **And many others**
Fermentation & Maturation

Physical Elimination

- Very volatile compounds
  → Losses with CO$_2$ produced during fermentation

- Apolar compounds
  → Losses by adsorption on yeast, tank walls, etc.

(1) Vermeulen et al., 2006
Fermentation & Maturation

**Physical Elimination**
- Very volatile compounds
  - Losses with CO$_2$ produced during fermentation
- Apolar compounds
  - Losses by adsorption on yeast, tank walls, etc.

**Chemical Reactions**
- Reactions with H$_2$S produced by yeast
  - Production of 3-sulfanyl-3-methylbutanol$^{(1)}$, etc.
- And others

$^{(1)}$ Vermeulen et al., 2006
Fermentation & Maturation

Enzymatic Transformations

- Biotransformation of monoterpene alcohols
  \[ \rightarrow \beta\text{-}citronellol, \text{geraniol, nerol, linalool and } \alpha\text{-}terpineol \]

(1) King & Dickinson, 2000; (2) Daenen et al., 2007; (3) Gros et al., 2012
Enzymatic Transformations

- Biotransformation of monoterpenes alcohols
  $\rightarrow \beta$-citronellol, geraniol, nerol, linalool and $\alpha$-terpineol

- Action of $\beta$-glucosidases
  $\rightarrow$ Liberation of aglycones from glycosides

- Action of $\beta$-lyases
  $\rightarrow$ Liberation of polyfunctional thiols from cysteine adducts or glutathions

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Fermentation & Maturation

Enzymatic Transformations

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- Action of $\beta$-lyases
  → Liberation of polyfunctional thiols from cysteine adducts or glutathions$^3$

- And probably others

$^1$ King & Dickinson, 2000; $^2$ Daenen et al., 2007; $^3$ Gros et al., 2012
Evolution of Process

New trends for hops use

- **Origin**
  → American craft breweries

- **Quantity**
  → Use of more hops

- **Brewing process**
  → Addition at different points of the process, through innovative techniques
  → Addition later and later in the process, to avoid oxidised compounds
Hop Aroma

Conclusions

➢ Hop composition
  → Many compounds involved → key-compounds
  → Complex interactions between them → synergy
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➢ Hop varieties
  → Development of hops with specific character
Hop Aroma

Conclusions

- Hop composition
  → Many compounds involved → key-compounds
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- Hop varieties
  → Development of hops with specific character

- Brewing process
  → Many reactions during boiling and fermentation
  → Link between hops and beer compounds?
Hop Aroma

Conclusions

- **Hop composition**
  - Many compounds involved → key-compounds
  - Complex interactions between them → synergy

- **Hop varieties**
  - Development of hops with specific character

- **Brewing process**
  - Many reactions during boiling and fermentation
  - Link between hops and beer compounds?

- **Big challenge for the future!**
Conclusion

Major role of hops on the beer flavour

- Taste → Hop bitterness
- Odour → Hop aroma
- Even with very limited quantities
- Interacting with the other ingredients
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Key points for hop flavour

- Hop variety
- Added quantity
- Point of addition and process