MAIN FLAVOR CHANGES IN AGED SPECIALTY BEERS

DAAN SAISON
Overview

- Introduction
  - Flavor perception
  - Beer aging
  - Specialty beers
- Flavor profile aged specialty beer
- Focus on some process/product characteristics
- Conclusions
Flavor perception: Taste vs aroma

Taste

Non-volatile compounds

Aroma

Volatile compounds

Flavour: taste + aroma
Chemical background flavour

- Beer: water-ethanol mixture (5-12 v/v%) and 100s of chemical compounds
  - Every compound: own specific effect on flavour
- Taste-mouthfeel
  - Iso-\(\alpha\)-acids: bitter
  - Oligosacharides: mouthfulness
  - Polyfenols: adstringent
- Aroma
  - Esters: fruity
  - Higher alcohols: solventy, fruity
  - Aldehydes: mainly negative

BANANA
ROSE-LIKE
SOLVENT
AMANDEL, CHOCOLATE
CARDBOARD
CARAMEL
Concepts related to flavour perception

- Every compound: different flavour impact
  - Dependent on flavour, concentration in beer & ‘flavour activity’ of compound
- Flavour activity: THRESHOLD (TH)
  - Concentration needed for perception
  - Important tool: idea of contribution to flavour
## Some examples of thresholds

<table>
<thead>
<tr>
<th>Aging compound</th>
<th>TH Literature (ppb)</th>
<th>Factor difference between highest and lowest TH reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>1114, &lt;12500^c, 10000-20000^k</td>
<td>18</td>
</tr>
<tr>
<td>(E)-2-nonenal</td>
<td>0.03, &lt;0.05^c, 0.05^i, 0.11^a, 0.5^b</td>
<td>17</td>
</tr>
<tr>
<td>(E,E)-2,4-decadiënal</td>
<td>0.11, 0.3^a</td>
<td>3</td>
</tr>
<tr>
<td>2-methylbutanal</td>
<td>35^e, 45, 1250^a</td>
<td>36</td>
</tr>
<tr>
<td>3-methylbutanal</td>
<td>46^e, 56, (600)^a</td>
<td>13</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>515, 1000^j, (2000)^a</td>
<td>4</td>
</tr>
<tr>
<td>Methional</td>
<td>&lt;0.5^q, 4.2, 40^d, (250)^a</td>
<td>500</td>
</tr>
</tbody>
</table>

Very large difference between THs reported in literature

- Applied method
- Population
- Beer used - mostly pilsner beer → Different for specialty beers
Ageing of beer

- No health risks
- Colour increase
- Flavour evolution during storage
  - Not necessarily perceived as ‘bad’
- A commercialized beer: consistent, satisfy expectations
- Important problem: growing export & globalisation
Flavour during beer ageing

Fresh flavours
- Cardboard
- Solvent
- Ribes (berries, cassis, raisins, honey)
- Maillard (caramel, burnt, bread, butter)
- Sulphury
- Madeira

Aged flavours
- Honey

Storage Time
Origin of flavour evolution

- Hydrolysis of compounds with fresh flavour characteristics: ‘Fresh compounds’
  - Mainly esters
- Formation of compounds with aged flavour characteristics: ‘Ageing compounds’
  - Mainly aldehydes
- Result of many chemical reactions
  - Oxidative reactions, Maillard reactions, Strecker degradation, furanether formation, release from imine adducts, aldol condensation, β-damascenone formation, degradation of hop bitter acids, hydrolysis of esters,.....
Specialty beers

- Wide variety of specialty beers
- Key process variables vs pils
  - Top fermentation
  - Use of specialty malts
  - Use of spices/dry hopping
  - Refermentation
- Key product variables
  - Alcohol content
  - Fruity, solvent, phenolic
  - Malty, caramel, roasted
  - Hoppy, spicy, floral
  - Bitter, Sweet, sour
- Every beer will age in a different way
Aged beer flavor

- Lager beer is used as standard in most flavor stability research
- Knowledge on specialty beers is often deducted from lager beer results
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Different aging profiles after 23 months at 20°C

- Cardboard
- Madeira
- Solvent
- Sulphury
- Ribes (berries, cassis, raisins, honey)
- Maillard (caramel, burnt, bread, butter)

Legend:
- Green: Pilsner
- Blue: Specialty - Blonde
- Red: Specialty - Dark
Identification most important aging compounds

Explain aged flavor from chemical composition
Better insights in specific aged flavor notes
Solvent flavor

- Part of aged flavor profile specialty beers
- Mainly caused by furfuryl ethyl ether
- Chemical condensation reaction of
  - Furfuryl alcohol
    - Maillard reaction
    - Reduction of furfural
  - Ethanol
- Especially important in beers with high ABV and dark color
Madeira flavor

- Especially present in beers aged at room temperature for long time
Lager beer in several storage conditions

<table>
<thead>
<tr>
<th>Storage Duration</th>
<th>Temperature</th>
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</thead>
<tbody>
<tr>
<td>5 days</td>
<td>60°C</td>
</tr>
<tr>
<td>3 weeks</td>
<td>40°C</td>
</tr>
<tr>
<td>3 months</td>
<td>28°C</td>
</tr>
<tr>
<td>6 months</td>
<td>20°C</td>
</tr>
<tr>
<td>10 years</td>
<td>20°C</td>
</tr>
</tbody>
</table>

- 0: cardboard
- 1: Madeira
- 2: Maillard
- 3: solvent
- 4: ribes

Graph showing the impact of storage conditions on beer characteristics.
Madeira flavor especially present in beers aged at room temperature for long time. Mostly combined with Maillard and ribes notes.

Chemical background:

Not result of one or some specific compounds. Result of many aging compounds. Throughout aged beers with pronounced Madeira flavor, high concentrations of following compounds were found: 2-furfuryl ethyl ether, Acetaldehyde, Diacetyl, Strecker aldehydes, (E)-2-nonenal.

Diagram:

- 5 days 60°C
- 3 weeks 40°C
- 3 months 28°C
- 6 months 20°C
- 10 years 20°C

Cardboard, solvent, Maillard, ribes.
Decline of fruitiness in top fermented beers

- Significant decrease of acetate esters, mainly iso-amyl acetate during storage (Neven et al., 1997)
  - Chemical hydrolysis
  - Enzymatic hydrolysis
    - Only unpasteurised or bottle conditioned beers
    - Esterases released by yeast as a result of autolysis

- Effect on flavor
  - Less fruitiness perception
  - Less masking of aged flavors
Masking effect fruitiness of beer

- Isoamyl acetate (IAA) is important contributor to fruitiness
- TH pilsner with endogenous conc 475 ppb IAA
- TH same pilsner with extra added 300 ppb IAA
- Fresh flavor influences perception of aged flavors
  - Lager: flavor less outspoken – aged flavor notes perceived quicker
  - Specialty: often complex flavor
    - takes longer to perceive aged flavor
    - Decline of fresh flavor important

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<th>TH</th>
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<tr>
<td>2-methylbutanal</td>
<td>45 ppb</td>
</tr>
<tr>
<td>Methional</td>
<td>4.2 ppb</td>
</tr>
<tr>
<td>Phenylacetaldehyde</td>
<td>105 ppb</td>
</tr>
</tbody>
</table>

- $x^3 \rightarrow 157$ ppb
- $x^{1.4} \rightarrow 5.8$ ppb
- $x^1 \rightarrow 110$ ppb
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Use of specialty malts

- Dark beers are suggested to age better
  - Suggestion that aged flavors are formed less
- Introduces large pool of precursors aging reactions
  - Several aging reactions will deliver more aging compounds
- Beers with prominent flavor of specialty malts
  - More complex background: aged flavor less apparent
  - Increase of flavor TH of aging compounds
  - Aging adds complexity, not necessarily rejected
Alcohol content

- Not a lot of research
- Is precursor for some aging reactions (e.g., Furfuryl ethyl ether)
- If assumptions need to be made, it may be that aged flavor is mostly perceived as less disturbing in higher alcohol beers
  - Mostly, higher ABV beers are more complex at the start
  - Ethanol has been shown to increase aldehyde retention in low-alcohol beers (Perpète & Collin, 2000)
  - Alcohol can mask harshness and gives beer more roundness
Refermentation

- Addition of fermentable sugars and yeast to bottle
- Assumed to have a protective effect
  - Hypothesised as natural defence against oxygen
  - Overall not very clear
- Study effect of refermentation on beer aging
  - Referment aged beers
Refermentation of aged beers (0.3°P; 1 mio cells/mL)

**Lager**

- Madeira
- Solvent
- Ribes
- Maillard
- Sulphury

**Ale**

- Madeira
- Solvent
- Ribes
- Maillard
- Sulphury

**Flavour evolution**

<table>
<thead>
<tr>
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<th>Ageing</th>
<th>RF</th>
</tr>
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<tr>
<td>Cardboard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
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</tr>
<tr>
<td>Ribes</td>
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<td></td>
</tr>
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<td>Maillard</td>
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<td></td>
</tr>
<tr>
<td>Sulphury</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madeira</td>
<td></td>
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</tr>
</tbody>
</table>
Concentration evolution aged +RF

- **3-methylbutanal**
  - Fresh
  - Aged
  - Aged + refermented

- **Furfural**
  - Concentration (ppb)

- **2-Furfurylethylether**
  - Concentration (ppb)

**Yeast cell**

**CARBONYL COMPOUND**
- HIGH flavour activity
- Precursor of ageing reaction

**NAD(P)H**

**NAD(P)^+**

**Reducing enzyme**

**CORRESPONDING ALCOHOL**
- LOW flavour activity
- Relatively unreactive
Ageing after RF and yeast addition

- Pilsner beer: all aged 6 months at 20°C
  - NORMAL ageing
  - Ageing after RF (1 million cells/mL; 3 g/L sucrose)
  - Ageing after YEAST ADDITION (1 million cells/mL)

- Tasting results

![Graph showing overall score and ageing intensity for Initial, Aged, RF, and Yeast samples.](image)
Ageing with different yeast amounts

- Ageing pilsner beer (6 months 20°C) after addition of different yeast amounts
- Only 10,000 cells/mL: much better ageing
Conclusions

- Every specialty beer will age differently
  - Result of different ratios of chemical compounds
  - Dependent on precursors and storage conditions
- Compared to lager beer more chance on
  - Solvent, Maillard and Madeira flavors
  - Large effect of reduced fruitiness on aged flavor profile
- Yeast can reduce aged flavor compounds
- Refermentation has protective effect
  - Also in absence sugar
  - In low yeast cell concentrations