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Evolution of Beer Aroma

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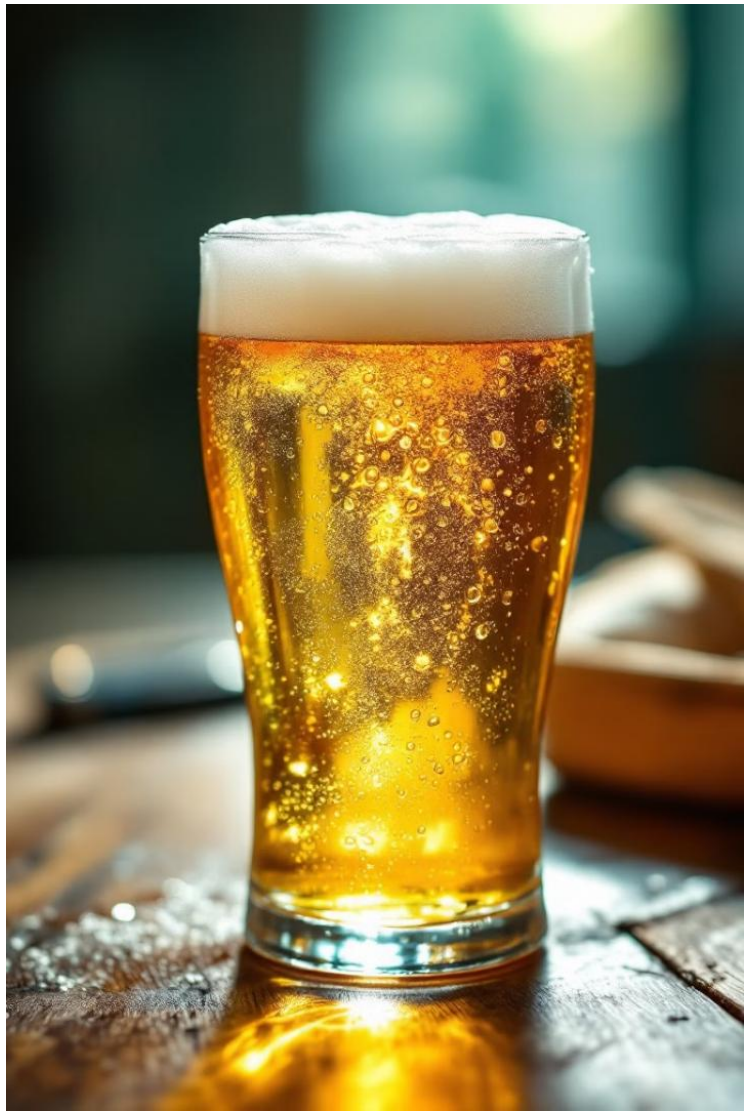
Beer Aroma

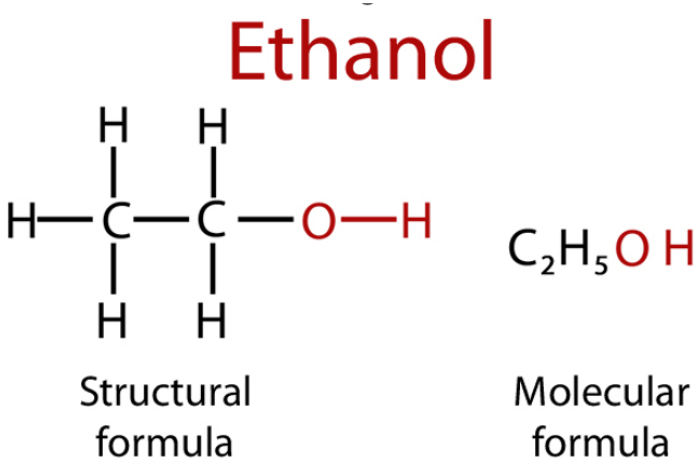


Beer aroma is a complex interplay of volatile compounds from various sources including hops, malt and yeast with its byproducts.

In this presentation an overwiev of the evolution of beer arom is presented.

It will also give you insight into the biotransformations of aromatic components and their influence on beer aroma.

Ethanol



Ethanol, the second most abundant component in beer after water, plays a crucial role in beer aroma. It is produced during fermentaiton by the yeast.

Its aroma directly contributes to the overall flavor profile, while also influencing the volatility and solubility of other aroma compounds.

Aroma

Ethanol's own aroma is characterized as sharp, slightly sweet and warm aroma, adding a distinct note to the beer's flavor.

Influence on Other Compounds

Ethanol affects the vapor pressure, solubility, and reactions of other volatile compounds, impacting their contribution to the final aroma.

Malt

Barley malt, the primary raw material in brewing, undergoes a process called mashing, where enzymes break down its constituents like beta-glucans, proteins, dextrins and starch. This process releases volatile compounds that contribute to the malty, worty aroma of beer.
Volatiles derived from oxidation of lipid precursors, volatiles formed in the Maillard reaction, aliphatic sulphur compounds and phenols.

1 Malty Aroma

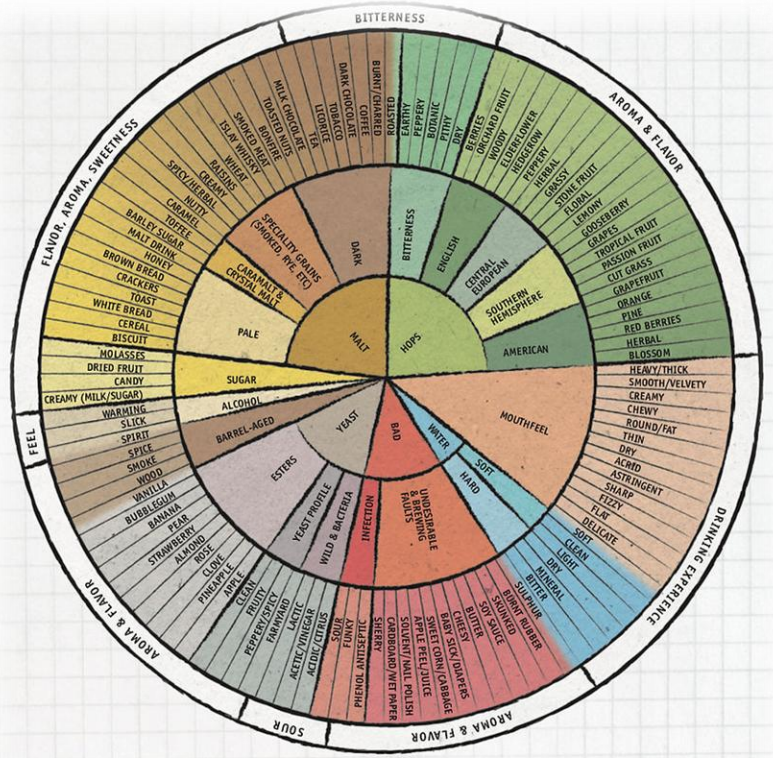
Volatiles from malt contribute to the characteristic malty, worthy, and husky aroma of beer.

2 Aromas

Roasted, Smoky, Coffee, Toffee, Bready, Fruity/Nutty Malty,Sweet Caramel Aromas

3 Flavor Wheel

Acording to the beer flavour wheel, developed by dr. Meilgaard, which became a standard around the world, flavours from barley can be divided into cereal, caramelized (roasted), and phenolic flavors.



Taken from the book **Craft Beer World**
by Mark Dredge

Dimethyl sulphide (DMS)

highly volatile compound that can overwhelm other aromas in beer, even at very low concentrations.

It originates from S-methylmethionine (SMM), a precursor found in barley. SMM is pulled into the wort during mashing and lautering and as the wort is heated the SMM degrades and is converted into DMS.

DMS can be reduced or eliminated through vigorous wort boiling, as SMM is heat-sensitive.

Dimethyl sulfoxide (DMSO) is another source of DMS. DMSO transformation to DMS during fermentation.

Calm fermentation positively effects on formation of DMS, which is why light lagers are more susceptible to this off-flavor.

The odor detection threshold:

- the lowest concentration of a certain odor compound that is perceivable by the human sense of smell.
- more important than the concentration level of a particular component.

flavor threshold of DMS is < 20ppb

Hops

despite being a minor ingredient is essential for beer's bitterness and aroma. Their complex chemistry has been studied for decades, revealing a wealth of volatile compounds that contribute to the unique flavor profile of beer.

Bitterness and Aroma

Hops are added to boiling wort to provide bitterness and aroma to the final product.

Isomerization

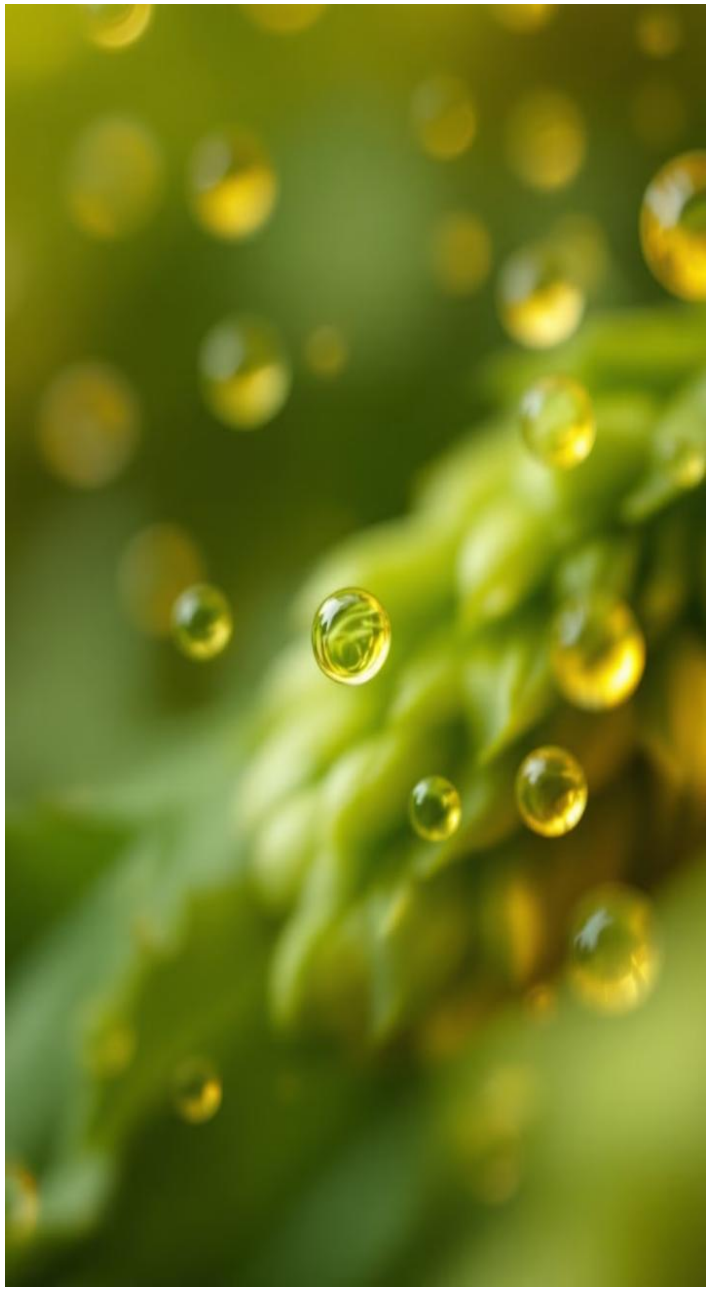
Boiling the wort causes the isomerization of hop alpha-acids, contributing to bitterness.

Essential Oils

Hop cones contain essential oils (0.5 to 4.0 rel %) , which are responsible for the aromatic qualities of hops.

Hop Essential Oils: A Chemical Symphony

Hop essential oil is a complex mixture of volatile compounds, primarily hydrocarbons, oxygen-bearing compounds and sulfur-containing compounds.



Hydrocarbons

The most abundant group (aprox. 75% of the total oil), includ. monoterpenes, sesquiterpenes and aliphatic hydrocarbons. Low solubility in water, also low boiling point

Oxygen-bearing Compounds

Present in smaller amounts (up to 25 %), are crucial for beer aroma, including alcohols, aldehydes, ketones, acids, esters, and epoxides.

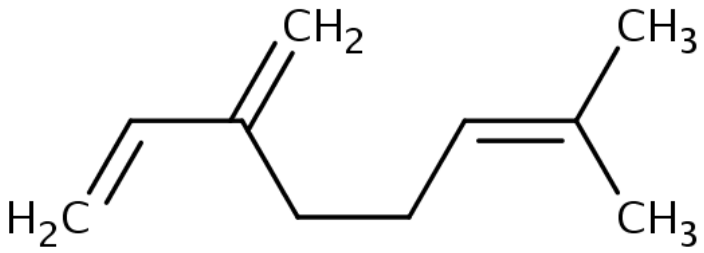
Sulfur-containing Compounds

Present in trace amounts, can significantly impact beer aroma, often contributing to off-flavors. In traces, but their odour threshold is very low - 0.007 ppb (4MMP)

Myrcene: The Dominant Hydrocarbon

Myrcene, a monoterpene, is the most abundant component in hop essential oil. While it contributes to the fresh hop aroma, it is generally undesirable in beer due to its sharp smell and low solubility.

Present in hops in high concentrations (up to 75% in hops) would not pass the brewing process and do not contribute much to the final beer aroma due to the evaporization, degradation or chemical reactions. Can have sedating or „couchlock“ effect.



1

Discovery

Myrcene was first isolated from bay oil in 1895.

2

Aroma

Myrcene is responsible for the fresh hop aroma, but its sharp smell is often undesirable in beer.

3

Solubility

Myrcene's low solubility in water means it is easily lost during the boiling process.

Concentration range in hop oil (rel. %): 10-75
Odour threshold in beer (ppb): 50-200

Linalool: The Floral Delight

Linalool, a monoterpene alcohol, is a key contributor to the floral aroma of beer. Despite its low concentration in hops, its low odor threshold - down to 2 ppb in most lagers makes it a very noticeable component in a beer's aroma

1

Floral Aroma

Linalool contributes to the floral aroma of beer, a desirable characteristic for many beer styles.

2

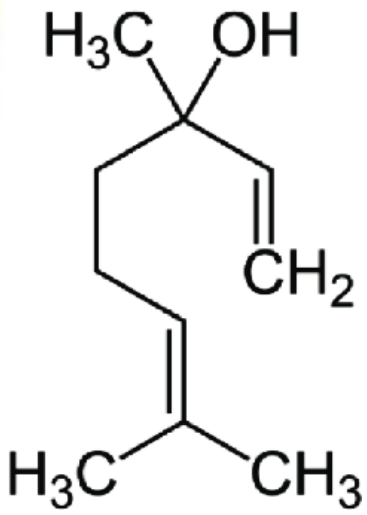
Hop Quality

Linalool levels in hops are often used as an indicator of hop quality.

3

Degradation

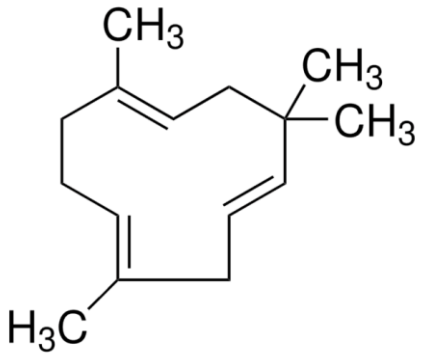
Free linalool in beer degrades rapidly, making its contribution dependent on the timing of hopping.



Concentration range in hop oil (rel. %): 0,2-1,3
Odour threshold in beer (ppb): < 2

Alpha-Humulene: The Hoppy Essence

Alpha-humulene, a sesquiterpene, is another important contributor to the hoppy aroma of beer. Its high boiling point allows it to survive the brewing process and contribute to the final flavor.



Hoppy Aroma

Alpha-humulene contributes to the hoppy aroma of beer, a key characteristic for many beer styles.

Boiling Point

Its high boiling point allows alpha-humulene to survive the brewing process and contribute to the final flavor.

Concentration range in hop oil (rel. %): 10-40

Odour threshold in beer (ppb): 120

Brewing Value

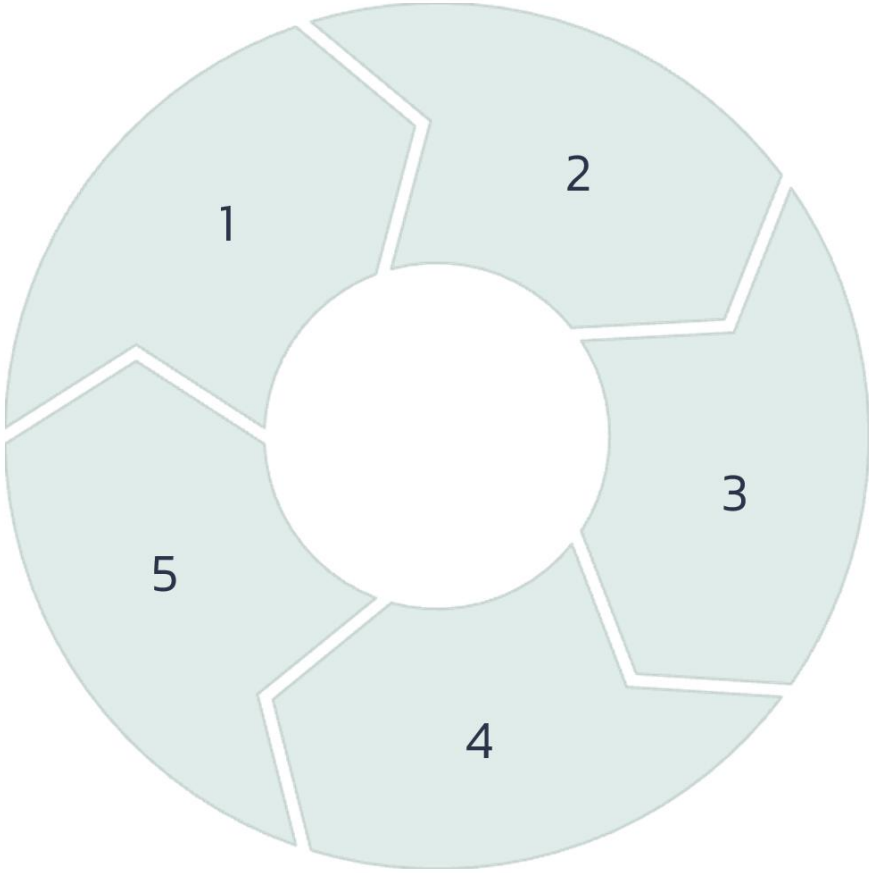
The exact brewing value of alpha-humulene is still under investigation.

Other Aroma Compounds: A Diverse Palette

In addition to myrcene, linalool, and alpha-humulene a wide range of other compounds (over 1000) contribute to the complex aroma profile of beer. These include aldehydes, ketones, acids, esters, and sulfur-containing compounds.

Aldehydes

Contribute to grassy notes



Ketones

Contribute to fruity and floral notes

Acids

Contribute to sour and tart notes

Sulfur Compounds

Can contribute to off-flavors

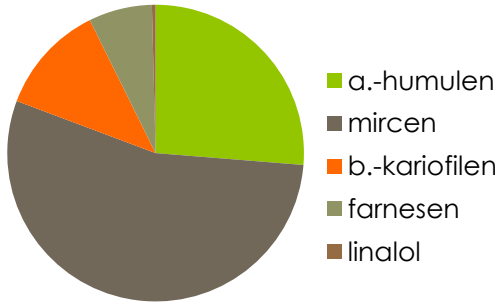
Esters

Contribute to fruity and floral notes

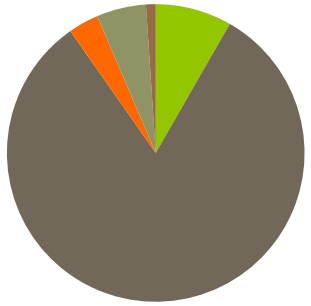
- Understanding the role of hop essential oils is crucial for brewers to create beers with desired flavor profiles.
- Most of them can be lost during boiling process, because of the low boiling point.
- Stability: degradation products – oxidation, reduction and reactions between volatiles.
- Oxidation process during aging→ hop oil becomes richer in oxygenated compounds (fruity, flovery aromas)
- Over 40 compounds can be produced from myrcene auto oxidation.
- Not every hop variety is suitable for every beer

In different hop varieties, essential oil components are present in different proportions

Styrian Gold

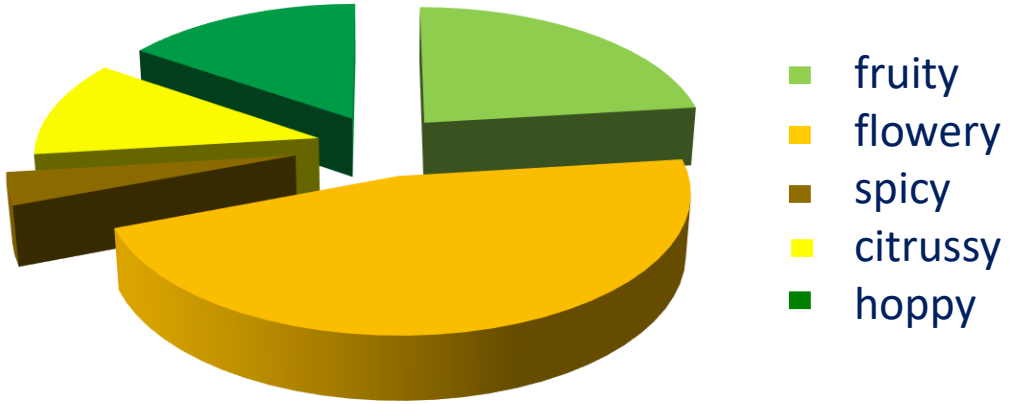


Styrian Wolf

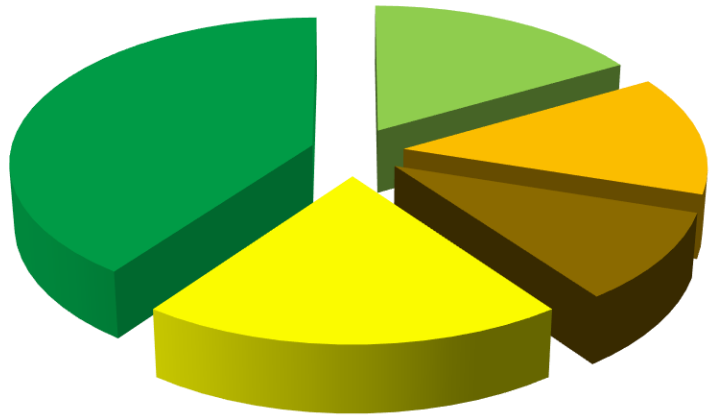


Aroma expression upon different hopping used

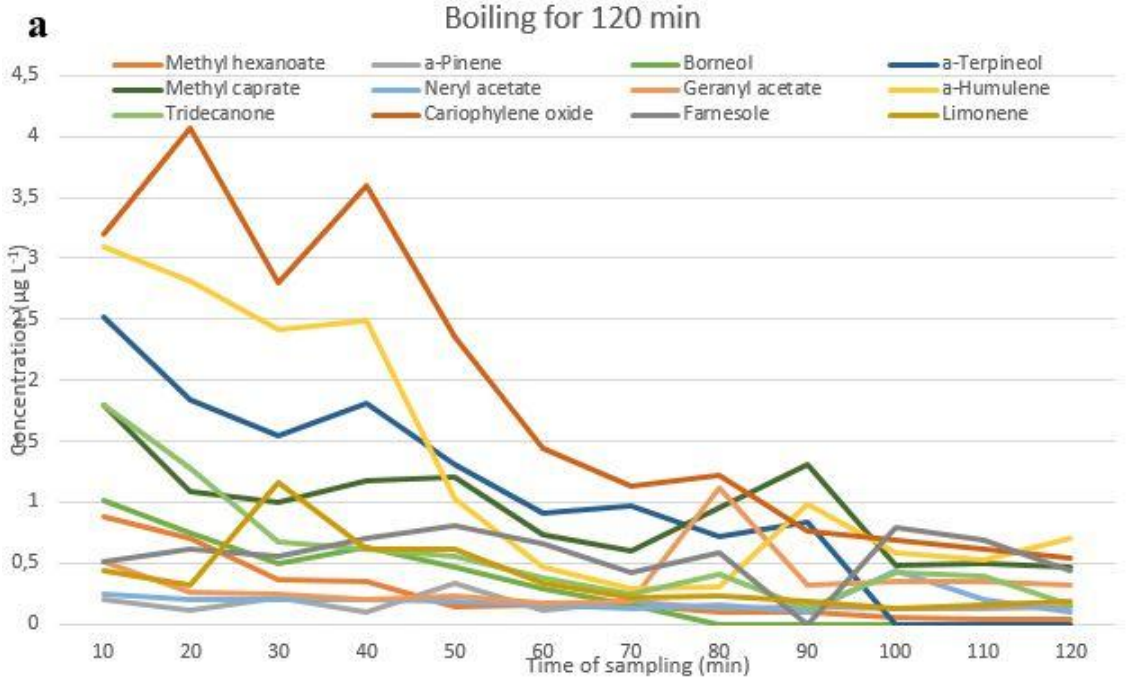
Styrian Dragon

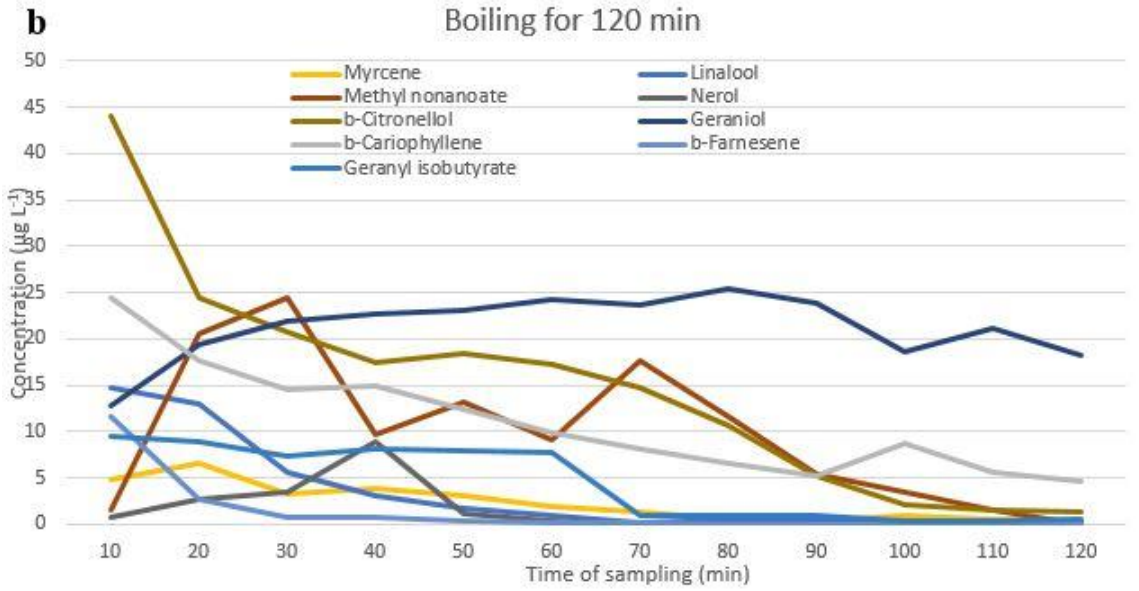


Dry hopping with Styrian Dragon



Hydrocarbons are among the most evaporative compounds of hop essential oil. They are usually found only in dry hopped beers. For example, 50% of myrcene evaporates within 10 minutes of boiling, and it evaporates completely within the typical 60 minutes' boil





Aroma from Yeast and Fermentation

Lager vs. Ale

Categorized based on the yeast strain used. Lagers, fermented with *Saccharomyces pastorianus* or *Saccharomyces carlsbergensis* at lower temperatures (around 12°C), typically have a clean, crisp flavor.

Ales, fermented with *Saccharomyces cerev*isiae at warmer temperatures (around 22°C), often exhibit more complex and fruity aromas.

Biochemical Activities

Yeast cells convert sugars into alcohol and carbon dioxide, but they also produce a range of volatile compounds that contribute to aroma. Different strains produce different flavors and aromas, ranging from fruity and estery to spicy and phenolic.

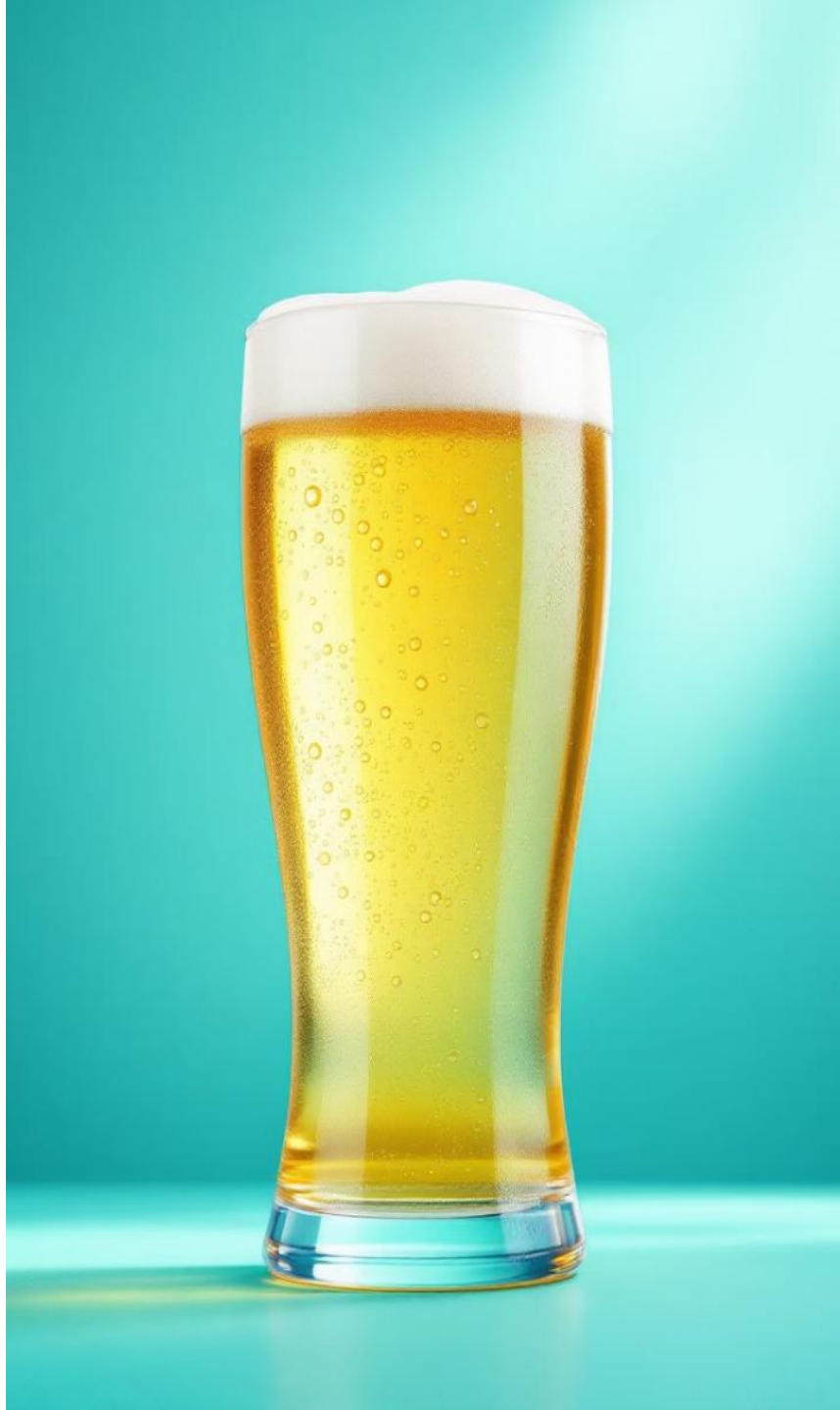
Higher Alcohols and Esters

Higher Alcohols (Fusel Alcohols)

These compounds are produced from amino acids (leucine, isoleucine and valine) through two mechanisms: the Ehrlich mechanism, where amino acids are absorbed by yeast and converted into higher alcohols, and the biosynthetic mechanism, where they are formed during sugar metabolism.

Esters

Esters are formed by the reactions of organic acids and alcohols during fermentation. Esters are responsible for the fruity and solvent-like aromas in beer. Some esters increase in concentration during beer storage.



Factors Influencing Yeast Byproducts formation

Cereal Type

The type of cereal used in brewing significantly impacts the concentration of higher alcohols and esters.

Barley beers tend to have higher levels of 1-propanol compared to beers made with other grains.

Amino Acid Concentration

High concentrations of amino acids in wort lead to increased production of higher alcohols. This is because yeast utilizes amino acids for growth and metabolism, producing higher alcohols as byproducts.

Yeast strain

pH

Reduced pH→ decrease of esters

Fermentation Temperature

Fermentation temperature is a crucial factor in the synthesis of higher alcohols and esters. Higher temperatures generally result in higher concentrations of these compounds.

Variable	Possible Result
Higher fermentation temperatures	Increased esters and alcohols
Trub present in the fermenter	Reduced esters and increased alcohols
Adding yeast nutrient to fermenter	Increased esters and alcohols
Increased oxygen during fermentation	Reduced esters
Top pressure (dissolved C02 or capped ferment)	Reduced esters and alcohols
Increased yeast pitching rate	Increased esters (only when heavily overpitched)
Reduced wort pH (3.0)	Decreased esters
Increasing fermentation temperature at climax of fermentation	Decreased esters (lower than keeping constant temperature)
Decreasing fermentation temperature at climax of fermentation	Increased esters
Higher gravity fermentations	Increased esters and alcohols
Increasing wort gravity with maltose syrup	Decreased esters (compared to other syrups)
Increased wort lipids (like oats)	Decreased esters
Beer aging	Decreased esters

Impact of Higher Alcohols on Aroma

- General term for high-boiling alcohols containing more than two carbon atoms.
- An appropriate amount of higher alcohols contributes to the mellow taste, delicate aroma and imparting a warm mouthfeel
- Imbalanced or excessive amount will generate undesirable flavours and easily cause hangover symptoms such as thirst, dizziness and headaches after consumption
- The primary higher alcohols found in beer are isoamyl alcohol, isobutyl alcohol, phenylethyl alcohol,2 and 3 methylbutanol
- Some of them contribute to the both desirable and undesirable aroma
- e.g.: High conc. of 3methyl butanol can impart heavy aroma that affect drinkability
- Normal conc. of 3methyl butanol: 30 -70 ppm in classic lager beers with 11-13 % extract.

Esters: The Source of Fruity and Solvent Aromas

Iso-amyl Acetate

This ester contributes a banana-like flavor to beer. 0,5-3 ppm

Ethyl Hexanoate

This ester imparts a red apple aroma to beer.

0,1-3 ppm

Phenyl Ethyl Acetate

This ester contributes to a rose-like aroma to beer.

0,1-2 ppm

Ethyl acetate

Ethanol + acetic acid solvent like aromas

10-40 ppm

2 ways of changing ester profile in beer:

- Refermentation by yeast
- Condensation of organic acids with ethanol.

e.g.: Winy aroma in aged beer is a result of esterification of methyl butyric acid.
In aged beers, fruity notes of aroma are loose and sweeter notes prevail.

Diacetyl: The Buttery Off-Flavor

2,3 butanedione is produced outside of the yeast cell when the compound alpha-acetolactate is oxidized by metal ions or dissolved oxygen

1

Formation

Diacetyl is a vicinal diketone (VDK) produced during fermentation. It contributes a buttery-like flavor to beer, which is generally considered undesirable.

2

Control

Brewers use a technique called a "diacetyl rest" to control and reduce diacetyl concentrations. This involves holding the beer at a slightly elevated temperature to allow yeast to metabolize diacetyl.

Odour threshold: cca 150 ppb, up to 400 ppb in ale

Concentration range in lager beers: 30 ppb -1000 ppm

3

Other Sources

High diacetyl levels can also result from infection by *Pediococcus* or *Lactobacillus* bacteria, or from excess oxygen during fermentation.

Phenols: Contributing to Smoky and Medicinal Aromas

in most cases, phenols are not desirable, but there are some exceptions for certain beer styles

1

Origin

primarily malt (70-80%) and hops (20-30%), which are perceived more through taste then smell. The most dominant phenolic acids are ferulic acid and p-coumaric acid. Volatile phenols originates from yeasts or bacteria.

2

Conversion

These phenolic acids can be converted (decarboxylation) into vinyl and ethyl derivatives by aging or MO, which have much lower flavor thresholds and can significantly contribute to the final aroma of beer.

3

Off-Flavors

The most dominant volatile phenols in beer, 4-vinylguaicol (4VG) and 4-ethylguaicol are responsible for clove-like, horsey, leathery, smoky, stable, and medicinal aromas, which are generally considered off-flavors, but 4VG is a signature characteristic of Bavarian wheat beer.

Biotransformations in Beer Aroma

Biotransformation is the fascinating biochemical process that sculpts the aromatic profile of beer. They become more and more popular in recent years.

Knowledge of this process may allow more precise control over the final sensory characteristics of the beverage.

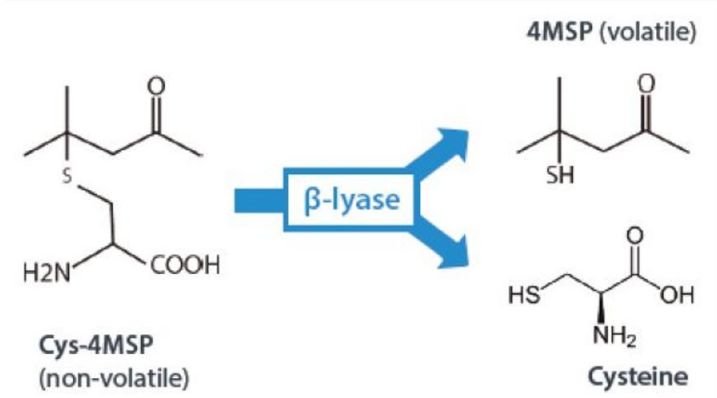
Enzymatic reactions during fermentation release additional aromatic compounds. These are especially prevalent when brewers use a technique called "dry hopping".

Microorganisms, primarily yeast and bacteria, work their magic during brewing and fermentation. They interact with compounds, transforming them into „new volatiles“ ≠ microorganism contamination (normally have negative impact on beer aroma.

Biotransformations enhance beer aroma complexity and richness. It can help enhance hop character or complement malt flavors.

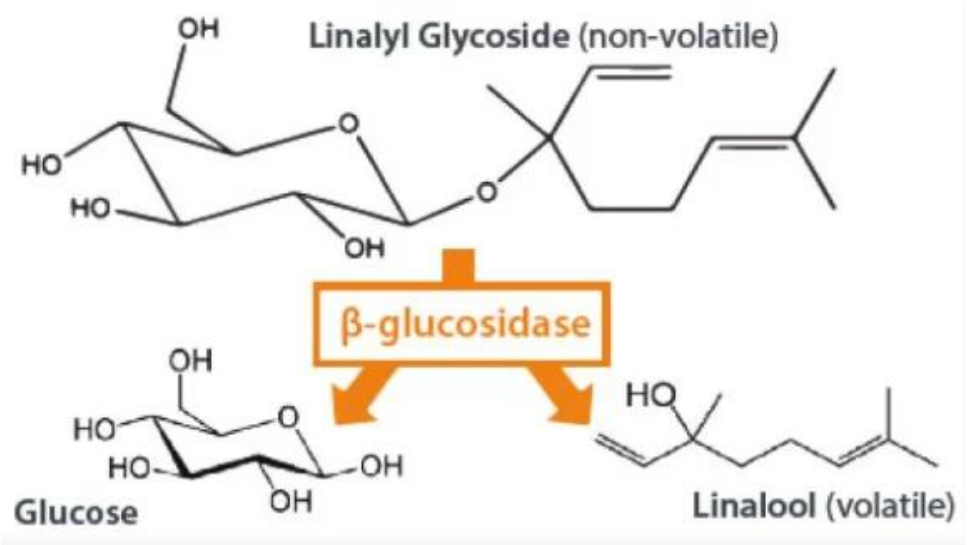
The role of β-lyase

- β-lyase is an enzyme responsible for the release of volatile sulfur compounds called thiols or mercaptans
- The enzyme has the ability to convert non-aromatic forms of thiols into active aromatic forms.
- In addition, hop also contain thiol precursors which does not impart any flavor, but through β-lyase activity these highly aromatic compounds can be released and therefore, perceived by the consumer.
- Normally, they have a very low detection threshold and can contribute in both negative (like onion, ferret) and pleasant aromas (like black currant, tropical fruit). The most important are *3-mercaptohexan-1-ol* (3MH), *4-mercapto-4-methylpentan-2-one* (4MMP) and *4-Methyl-4-sulfanylpentan-2-one* (4MSP) .



The role of β-glucosidase

- Terpenoids can be present in the form of glycosides. Glycosides are water-soluble and non-volatile due to the presence of sugar and can be found in hops
- β-glucosidase is an enzyme (fermentation) able to break glycosides, as a result of that, the glycoside molecule is broken via hydrolysis into two parts: a monoterpene alcohol and a glucose.
- Glycosides break down can lead to the release of free terpenoids in beer, further contributing to the challenge of identifying the origin of aroma in beer.

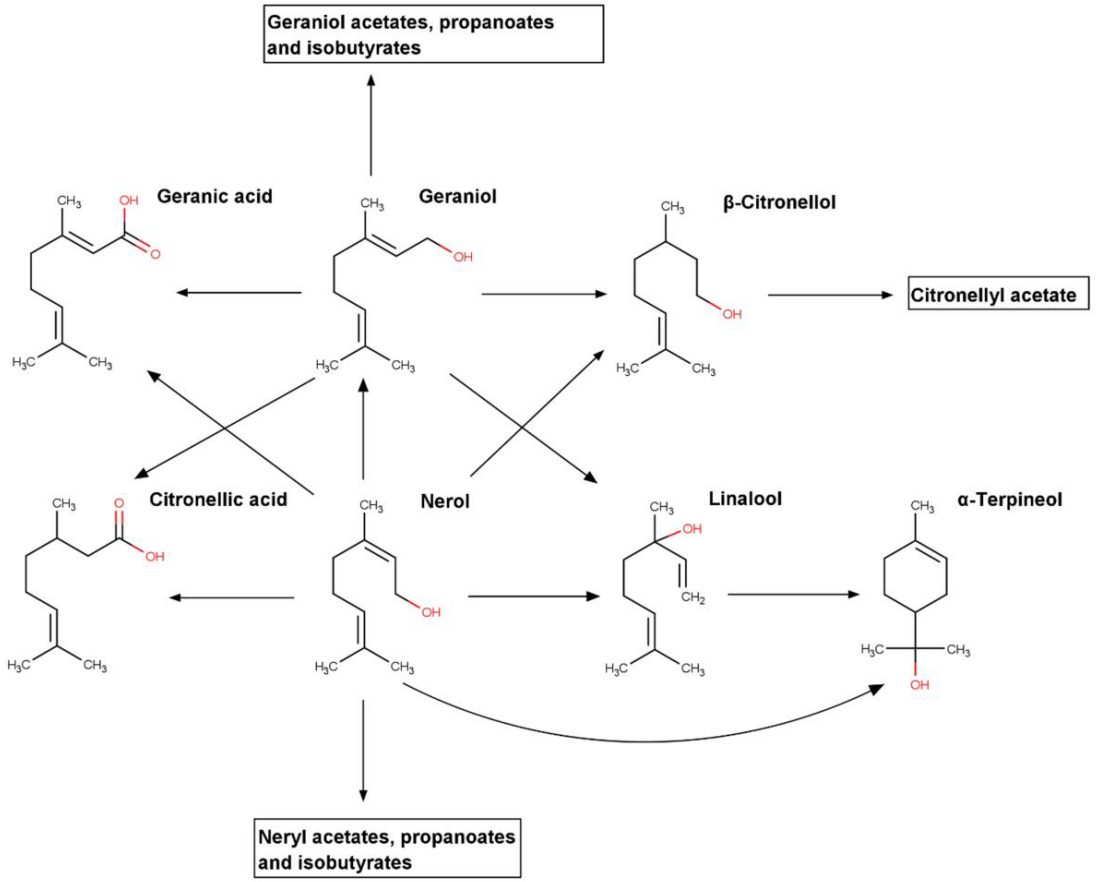


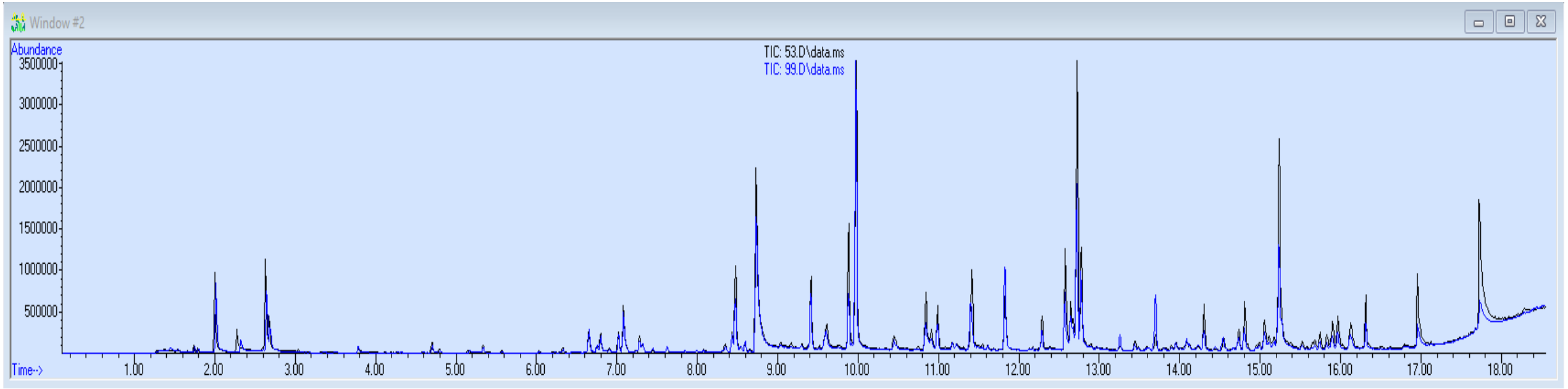
a non-volatile terpenyl glycoside is hydrolyzed through the β-glucosidase activity resulting in the release of a monoterpene alcohol (linalool) and a glucose molecule.

Further conversion of terpene alcohols

The levels of terpene alcohols in beer cannot be increased only by adding hops.

It is necessary to consider numerous biotransformations and reactions, in which terpene alcohols are involved, and where they are transformed from one form to another.





Enzyme preparation with high glycosidase activity (pure β-glucosidase enzyme) - developed to increase the complexity of the hop aroma and flavor profile in beer.

Key Takeaways

The aroma of beer is a complex interplay of volatile and non-volatile compounds, originating from raw materials, fermentation byproducts, and maturation processes.

While these compounds are present in very low concentrations, their low odor thresholds give them a significant impact on the overall flavor profile.

Various yeast strains may exhibit different enzymatic activities towards hop-derived compounds, resulting in different sensory attributes of the beverage.

Understanding the factors that influence the production of these compounds is crucial for brewers to create beers with desirable aromas and flavors.

Synergy between volatiles – volatiles in some conc. level