Dry Hop Aroma in Beer – a review

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Barth Haas Group

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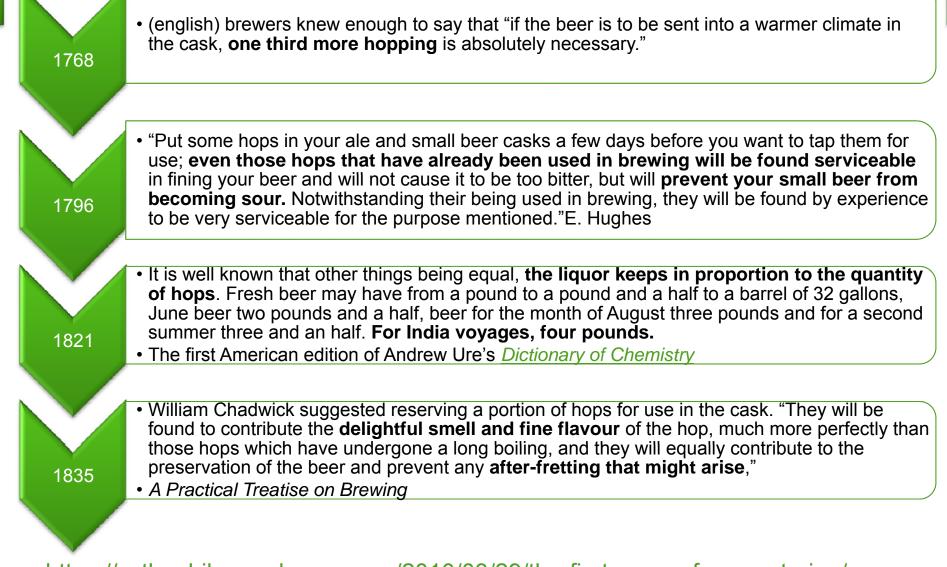
2015 ASBC Annual Meeting June 14–17 La Quinta, California

Agenda

- 1. A look into the past of dry hopping
- 2. Basics of hop aroma and dry hopping
- 3. A background on flavour perception and odor activity
- 4. Why do dry hopped beers smell and taste the way they do?

Since when do we dry hop?

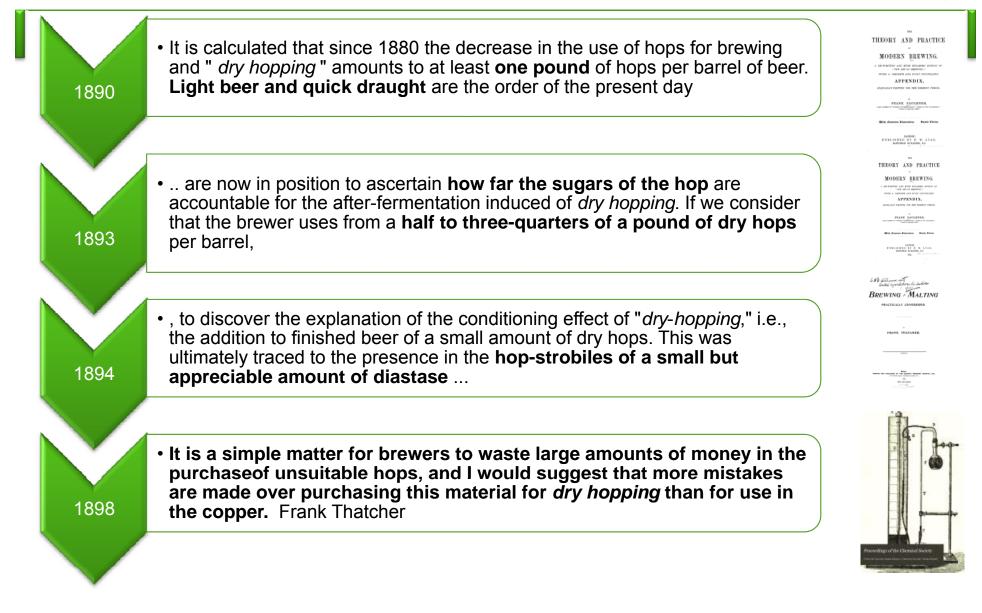




https://zythophile.wordpress.com/2010/03/29/the-first-ever-reference-to-ipa/

Since when do we dry hop?

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The Germans and Dry hopping

- In China the way of adding the hops is rather close to what is done in Middle Europe, especially in the United Kingdom and what is called "Hopfenstopfen" (dry hopping)" 1901, Dry hopped beers of the "Tarasuns" in Manchuria 2000 years ago, 1914
- Higher amounts of essiential oils added in the lager tank can cause irritation of the nerves and the digestive system. This might be in context with some headache or restlessness experienced after extensive beer consumption, 1901
- "Hopfenstopfen" is time consuming end expensive and needs a strict control to avoid overdosing, therefore the use of hop oil should be the preferred option, 1901



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Hop Oil Components



Substance groups and their concentrations in hop oil

(Hopfen- vom Anbau bis zum Einsatz in Bier, Hans Carl Verlag)

Substance Group	Concentration		
Monoterpenes	approx. 40 %		
Sesquiterpenes	approx. 40 %		
Carbonacid-esters	approx. 15 %		
Carbonacids	approx. 1 %		
Monoterpenoxides	approx. 1 %		
Sesquiterpenoxides	approx. 1 %		
Aldehydes, Ketones	approx.1 %		
Aliphatic hydrocarbons	< 1 %		
Sulfur containing compounds	< 0,1 %		
Glycosidically bound aroma compounds	?		

Sensory relevant hop aroma compounds

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Compound	Aroma description	Threshold µg/l
4-Mercapto-4-methyl-pentane-2-one		
	muscat grape, blackcurrant	0.002
b-Damascenone	apple, peach, fruity	0.02
3-Mercapto-4-methylpentan-2-ol	rhubarb, grapefruit	0.07
(E,Z)-2,6-Nonadienal	cucumber, green	0.5
b-lonone	floral, violet, berries	0.6
Ethyl-4-methylpentanoate	citrus, pineapple	1 – 18
Ethyl-2-methylbutanoate	citrus, apple	1.1 – 45
Linalool	lavender, floral	2 – 80
Ethyl-3-methylbutanoate	citrus, apple	2
Geraniol	floral, rose	4 – 300
Ethyl-2-methylpropanoate	citrus, pineapple	6.3 – 164
b-Citronellol	lime, lychee	9 – 40
Myrcene	herbal, resinous, green	9 – 1000
Humulene epoxide I	hay	10*
(Z)-3-Hexenal	green, leaves	20
4-(4-Hydroxyphenyl)-2-butanone	citrus, raspberry	21.2
Nerol	floral, lime, citrus	80 – 500
Humulenol II	pineapple, mugwort	150 – 2500
b-Caryophyllene	cedar, spicy, cloves	160 – 420
a-Terpineol	lilac, resinous, rose	330
1-Hexanal	green, leaves	350
Limonene	citrus, green	1493
Humulene epoxide II	cedar, lime	450
Humulene	floral, grassy	747
Humuladienone	-	100
Geranyl isobutyrate	-	450
Farnesene	-	550
Eudesmol	-	10000

Threshold Interaction



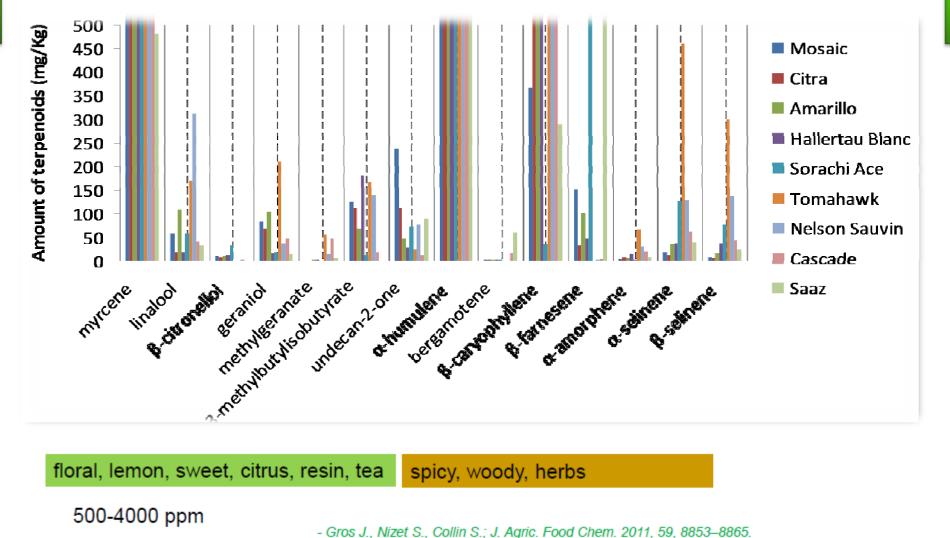
Geraniol Humulen Caryo. Terp. Far. µg/l Linalool Nerol Myr. 27 104ª: 493° Linalool 133^b 104ª: 90 2304 Geraniol 133^b d Humulene 3483 4346e 1843^f 5668 Single components g Synergism Beta-4346e 239 147^h 1297ⁱ additive Caryophyllene masking 1843^f 147^h 1206 2699^j Nerol 56689 1297ⁱ 2699^j 1076 Alpha-Terpineol Myrcene 119 493° 2304^d 2020 Famesene

Hanke 2009

Hop oil composition of different hops

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unlocking the potential of hops



- Kankolongo C. M-L., Gros J., Nizet S., Collin S., J. Agric. Food Chem. 2015, 63, 3022–3030.

Kankolongo Cibaka, EBC 2015

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Monoterpene composition of hops

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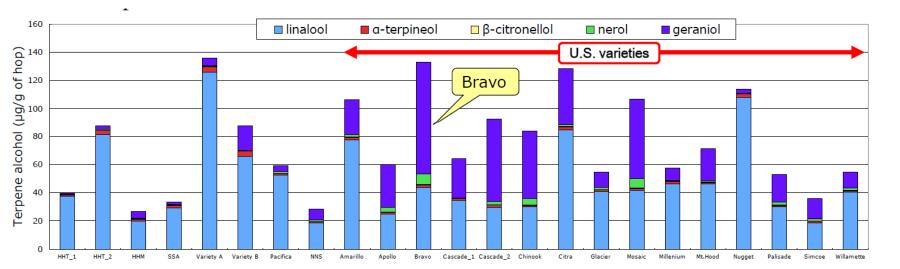


Figure 3. Comparison of monoterpene alcohol compositions in various hops: 2007 crop (HHT_1, HHM, Variety A, Variety B, Pacifica, NNS, Cascade_1, Citra, Millennium and Nugget); 2008 crop (Amarillo, Apollo, Bravo, Cascade_2, Chinook, HBC369, Glacier, Mt. Hood, Palisade, Simcoe and Willamette); 2009 crop (HHT_2 and SSA).

Takoi, 2012 WBC

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Descriptors	More detailled attributes		
Menthol	Peppermint, melissa, sage, metallic, camphor		
Теа	Green tea, camomile, black tea		
Green Fruits	Pear, quince, apple, gooseberry, enteric, cognac oil		
Citrus	Grapefruit, orange, lime, lemon, bergamot, lemongrass, ginger		
Green	Green grass, tomato leaf, bell pepper		
Vegetable	Selerie, leek, onion, artichoke, garlic		
Cream/Caramel	Butter, chocolate, yoghurt, gingerbread, honey, cream, caramel, toffee, coffee		
Woody/ Aromatic	Tobacco, cognac, woody barique, leather, tonka bean, sweet woodruff, resinous, incense, myrrh, resinous		
Spicy/Herbal	Maggie, black pepper, chillies, curry, juniper berry, marjoram, estragon, dill, lavender, anis, liquorice, fennel		
Red Berries	Cassis, blueberry, raspberry, blackberry, strawberry		
Sweet Fruits	Banana, water melon, honeydew melon, peach, apricot, passion fruit, leeches, dried fruits, plum, pineapple, white jelly baby		
Floral	Elder, camomile flower, muguet, jasmine, apple blossom, rose, geranium		

Parameters important for dry hopping

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- Variety (s); crop year; growing region, post harvest handling, processing (pellet type)
- Presence of yeast, yeast strain, contact time
- Movement in tank, tank geometry
- Cones or pellets (or extracts)
- Composition and temp. of medium (beer; water etc.)

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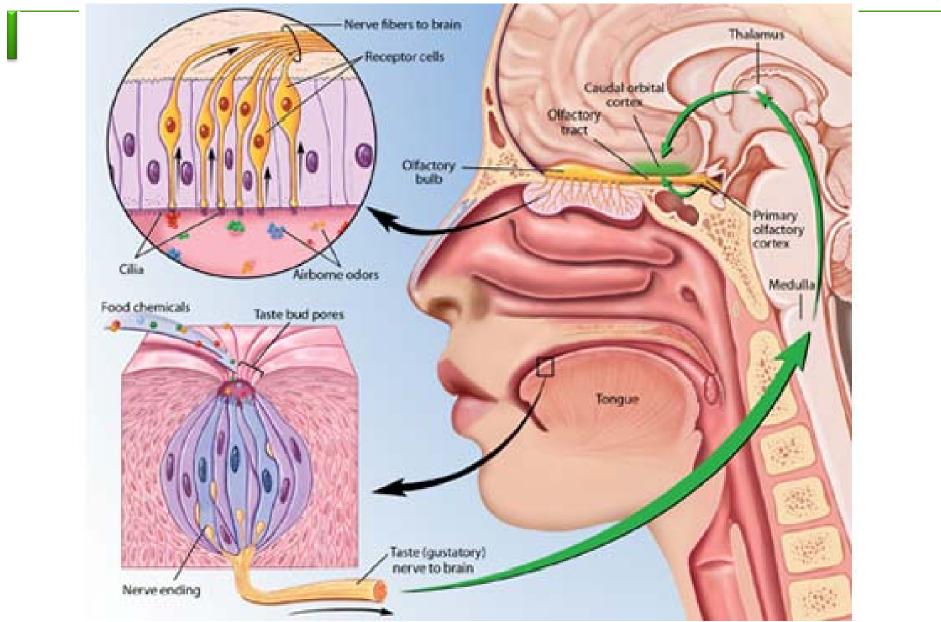


- Removing the hops (centrifuge; filtration; sedimentation)
- Pasteurization
- Bottling (oxygen pick up, crown compound material)
- Temperature of storage

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Polarity

- Osmophore groups \geq
- \geq Mucosa solubility

Mol. Weight

 \geq

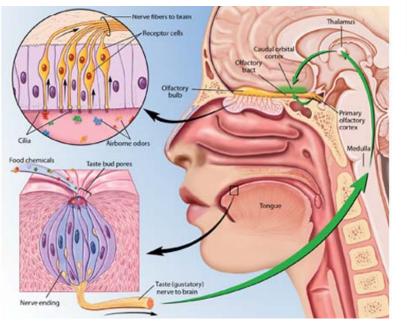
Lipid solubility

Olfactory System :

- 400 types of odorant receptors (OR)
- translate external chemical stimuli into internal information that can be processed by neural \geq circuits
- relationship between the number of odorants that we can discriminate and the number of \geq receptors that we have is unclear
- Smell and emotion are just one synapse apart \geq
- We breath (and smell) 15-30 000 times a day \geq
- \geq Olfaction is in context with objects (tough verbalisation) and emotions

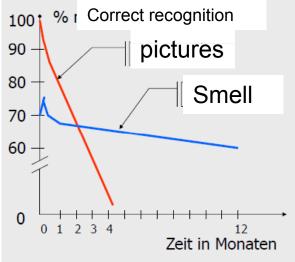
Retronasal System plus Trigeminale System

How do we smell and taste?



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- Olfactation and Memory
- Odors can relax, decrease/increase concentration etc.
- Est. 1 trillion of odors that can be discriminated (Nature 2014)
- A mixture of 2 components is only correctly identified by 12 % of tasters
- A mixture of 5 components is only correctly identified by 0,5 % of tasters
 (80% can identify prevailing component)



Aroma activity value = <u>concentration of compound</u>

threshold value

- Threshold values of volatiles have a high standard deviation
- There is no linear context for aroma activity
- Every threshold is influenced by another –don't believe in thresholds
- Additive, masking, synergistic, adaption, saturation effects change perception
- Quality of aroma changes according to configuration, concentration, individual perception, and matrix of the food...and emotions
- In mixtures with more than four components, odorants lose individuality and produce a new odor percept conveying a unique odor quality not elicited by the single components.
- > Only few labs are in the position to measure relevant hop oil compenents in beer

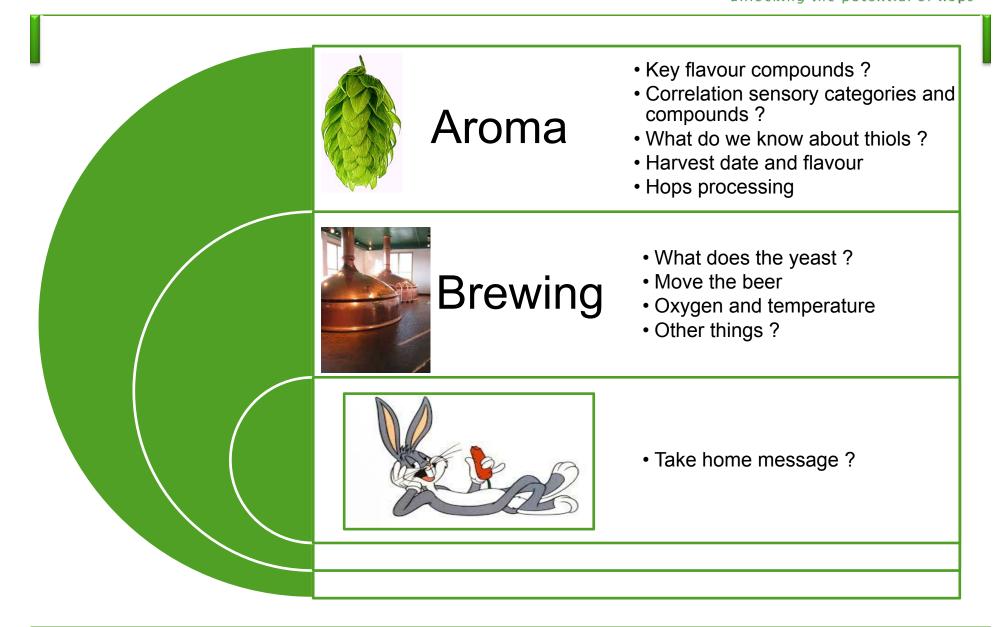


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Questions about dry hopping

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Possible Key Odorants in dry hopped beers

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Key odorants in dh beers ? Myrcene
Linalool
Geraniol
Citronellol
alpha-Terpineol
Limonene
Linalool oxide
Geranyl acetate
Methylgeranate
ß-Damascenone, beta-Ionone 2- Undecanone
3 Methylbutyl-2-methylproanoate
2-Methylbutyl-2-Methylproanoate
2-Methylbutyl-2-Methylbutanoate
2-Methylbutyl-3-Methylbutanoate
Ethylbutanoate, -hexanoate etc.
ЗМН
ЗМНА
3M4MP
4MMP
3MOal

Key odorants from other beverages	
Phenylethyl Acetat	spirits
Methylbutyl Acetat	spirits
Delta-nonalactone	spirits
cis-rose oxide (from geranyl-diol)	wine
4MMP	wine
Limonene	orange/grapefruit juice
Linalool	orange/grapefruit juice
Myrcene	orange/grapefruit juice
Pinene	orange/grapefruit juice/apple
3-Hexenal	orange/grapefruit juice
1-p-mentene-8-thiol	orange/grapefruit juice
ethyl 2- and 3 methylbuatonate	apple
ß-damascenone	apple
2,5-dimethy-4-hydroxy-	
3(2H)furanone	strawberry
1,3,5-undecatriene	pineapple
2-methyl-3-mercaptopropanoate	pineapple

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And how they fit into sensory description

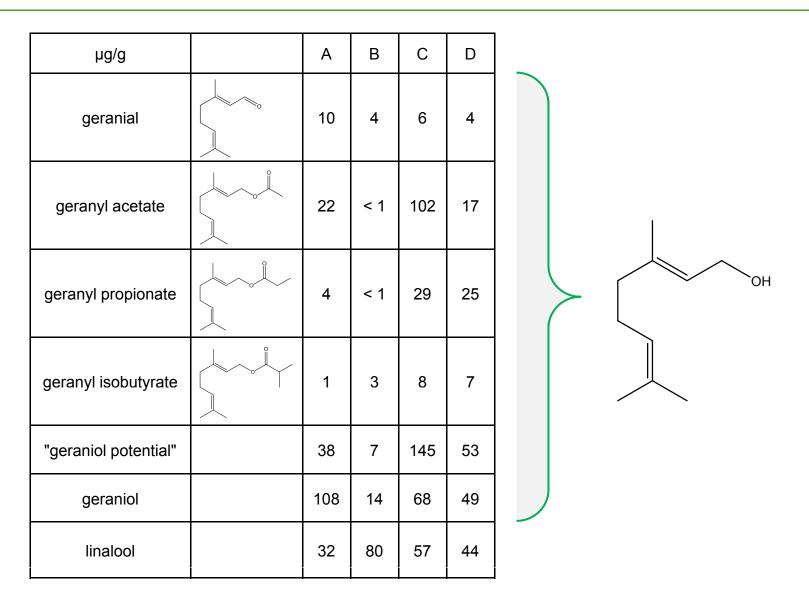
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Descriptors		
Descriptors	Possible key compounds of dry hopped beers	
Menthol		
Теа	Linalool	
Green Fruits	Beta-damascenone, esters	
Citrus	Limonene, linalool, myrcene, ethyl-2-methylbutanoate, α-pinene 3M4MP, 3MHA	
Green	Cystein conjugates	
Vegetable	Polyfunctional thios	
Cream/Caramel	Lactones, vanillin	
Woody/ Aromatic	Oxygenated sesquiterpenoids	
Spicy/Herbal	Oxygenated sesquiterpenoids – aldehydes, ketones	
Red Berries	4MMP	
Sweet Fruits	3MH, 3MOal, esters	
Floral	Geraniol, Citronellol	



Geraniol – the underestimated aroma compound?barth!nnovations

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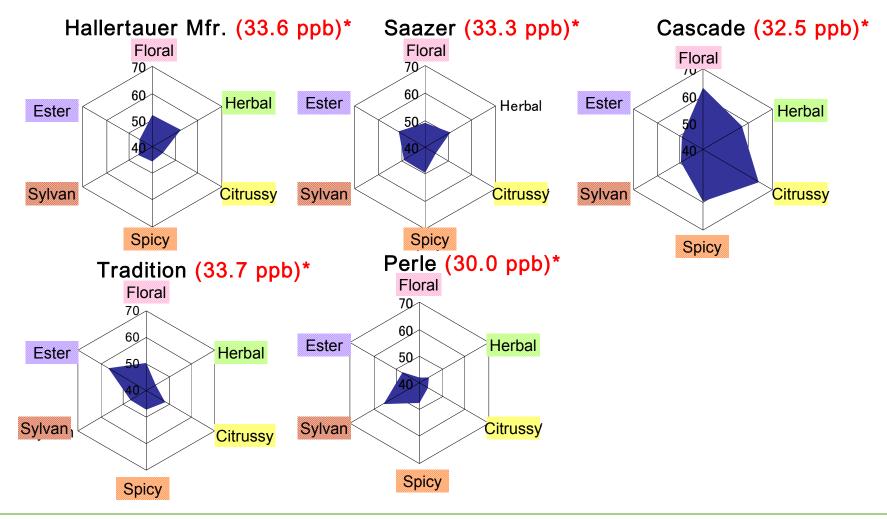


data Rettberg 2014, further reading: Takoi et al, J. Inst. Brew. 116(3), 251–260, 2010

Linalool

- Is a good marker compound in kettle/late hopped beer
- contributes to the aroma of late hopped beers
- Linalool conc. are rather stable in final beer
- ➢ R/S linalool
- > Not a key aroma compound in dry hopped beer
- Importance overrated (Peacock, MBAA 2010)

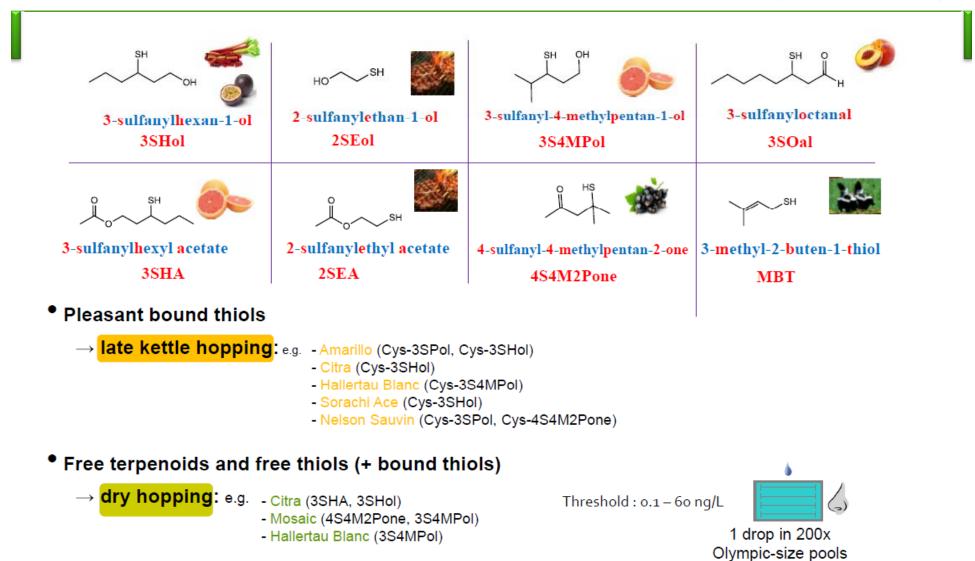
*The concentration of Linalool in beer



Thiols -the good, the bad and the ugly...

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Team of Prof. Collin, EBC 2015 and EBC 2013

Thiols-the good, the bad and the ugly...

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substance		
Name	Acronym	Odor (GC-O)
2-sulfanylethan-1-ol	2SEol	grilled
3-methyl-2-buten-1-thiol	MBT	coffee, skunky
3-sulfanylpropan-1-ol	3SProl	pop corn
2-sulfanylethyl acetate	2SEA	toasted, grilled
4-sulfanyl-4-methylpentan-2-one	4S4M2Pone	catty, blackcurrant
3-sulfanyl-3-methylbutan-1-ol	3S3MBol	sulfur, soup
1-sulfanyl-3-pentan-1-ol*	1S3Pol	nettle
3-sulfanylhexylacetate	3SHA	Passion, grapefruit
3-sulfanylpropyl acetate	3SPrA	grilled
3-sulfanylhexan-1-ol	3SHol	grapefruit/rhubarb
3-sulfanylheptanal*	3SHptal	lemon, candy
3-sulfanyl-2-ethylpropylacetate*	3S2EPrA	floral, vinegar
3-sulfanyl-4-methylpentan-1-ol*	3S4MPol	grapefruit
3-sulfanylheptan-1-ol*	3SHptol	lemon, hoppy
3-sulfanyloctanal*	3SOal	citrus, peach
3-sulfanyloctan-1-ol*	3SOol	catty, grapefruit
Total		

Onion, burnt, rubber, cat urine



grapefruit, rhubarb, black currant, muscat, ribes, grapes

0000

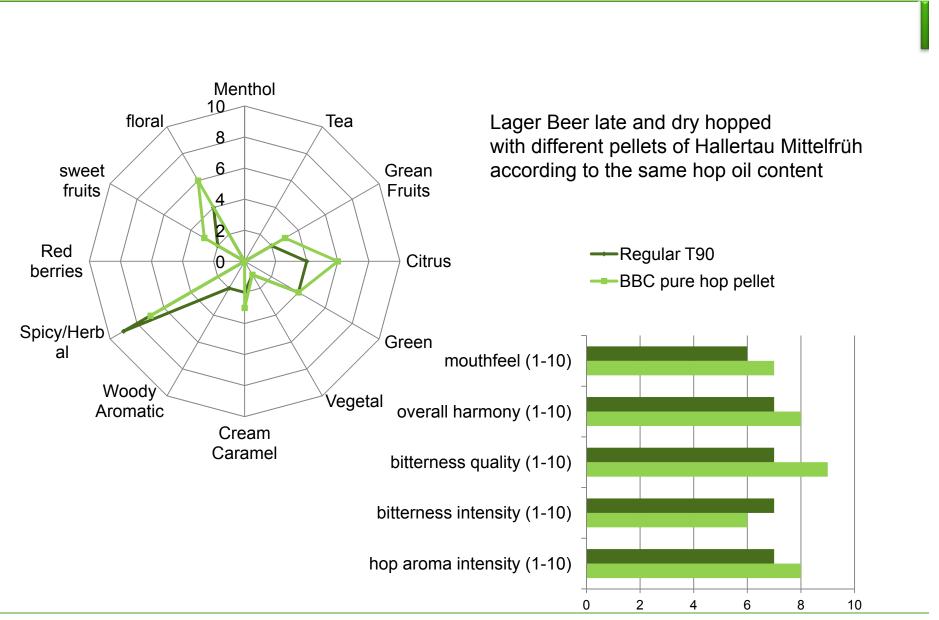
depending on configuration, concentration, interaction and perception

bad

29

- Increases in oil quantity correlate with a-pinene, b-pinene, myrcene, limonene, methyl-heptonoate, and linalool (Shellhammer et al 2013).
- Beers brewed with typical harvested Cascade hops were significantly distinguishable in sensory analysis and preferred by consumers over late harvested hops (Shellhammer et al, 2013)
- Beers dry hopped with Mittelfrüh harvested late were preferred over beers with normal Mittelfrüh (Bailey et al, 2009)
- Beers hopped with same variety from different hop garden were significantly different (Bailey et al, 2009)
- Dry hopping with pelletized more rapid extraction higher concentration of hop aroma compounds compared to dry hopping with cones (higher polyphenol content) (Wolfe, 2011, Mitter 2012)

Sensory impact of pelletization..



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Extraction time

<u>32</u>

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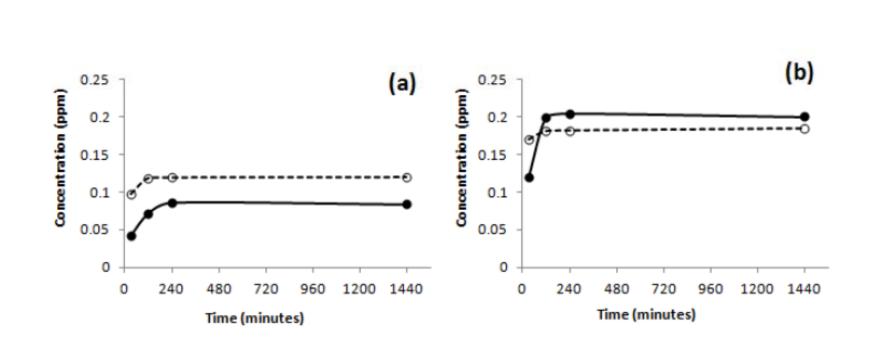


Figure 7. Myrcene (a) and humulene (b) concentrations during a 24 hour dry hop treatment with pellets (--0--) or whole cone hops (---).

Wolfe, Shellhammer 2011

Extraction time

<u>3</u>33



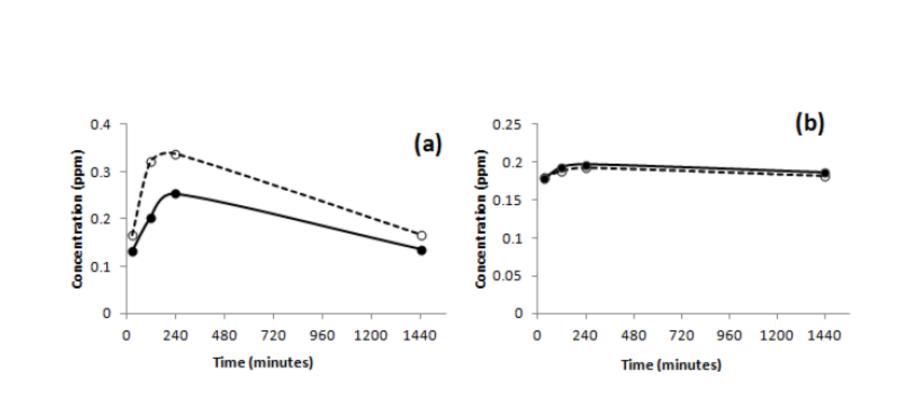
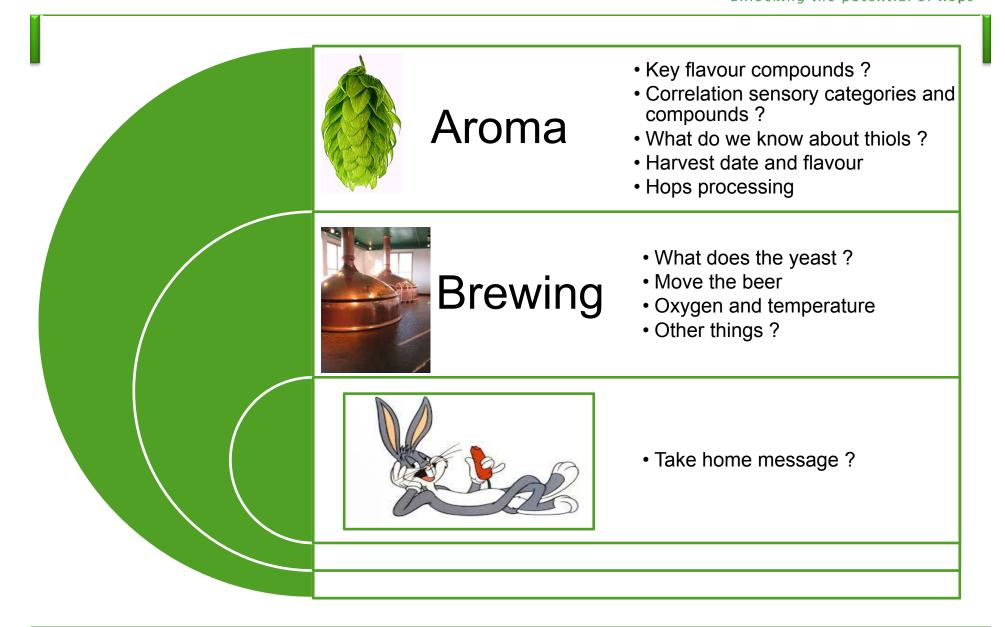


Figure 8. Linalool (a) and geraniol (b) concentrations during a 24 hour dry hop treatment with pellets (--O--) or whole cone hops (----).

Wolfe, Shellhammer 2011

Questions about dry hopping

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What do we know about the yeast ?



biotransformation by yeast or reactions triggered by beer pH

- glycosidically bound aroma precursors are released
- acids are converted into (ethyl) esters
- esters are trans-esterified or hydrolysed
- monoterpene alcohols isomerize
- carbonyl compounds, epoxides, and ethers are reduced to alcohols / diols

some odorants are efficiently removed (during fermentation)

- binding / adsorption of on biomass (hydrocarbons > terpenoids)
- stripping of volatiles

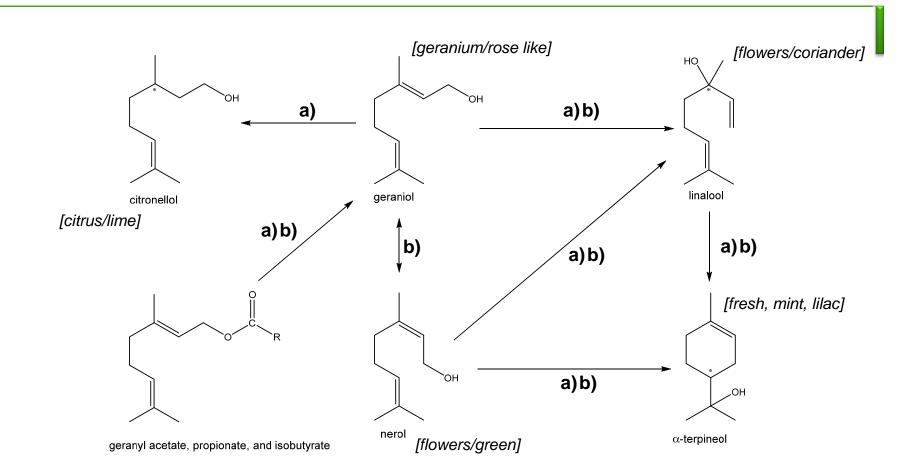
(Rettberg, personal conversation)

- The presence of yeast decreased the aroma and flavour intensities of floral, citrus and fruity characters, also decrease in concentration of measured aroma components (Schönberger)
- Decrease of myrcene, geraniol and citronellol with yeast (Ruehle, YSS 2014)
- Influence of yeast strains (same hops) from minor (Sharp 2013) to very destinct (Schönberger, EBC 2015)
- > Yeast influences the ester concentration, hop variety dependency (Dresel 2015)
- Except if spicy notes are the target, dry hopping in presence of yeast is damagable for the delicate and noble hoppy touches (peach, apricot, pineapple) (Derdelinckx 2013, ASBC)
- > Temperature profile of fermentation effects intensities of hop fruity flavours
- Negative correlation between 1-heptanol and fruity hop flavours (masking effect) (Takemura 2012, WBC)

What is the role of the yeast?

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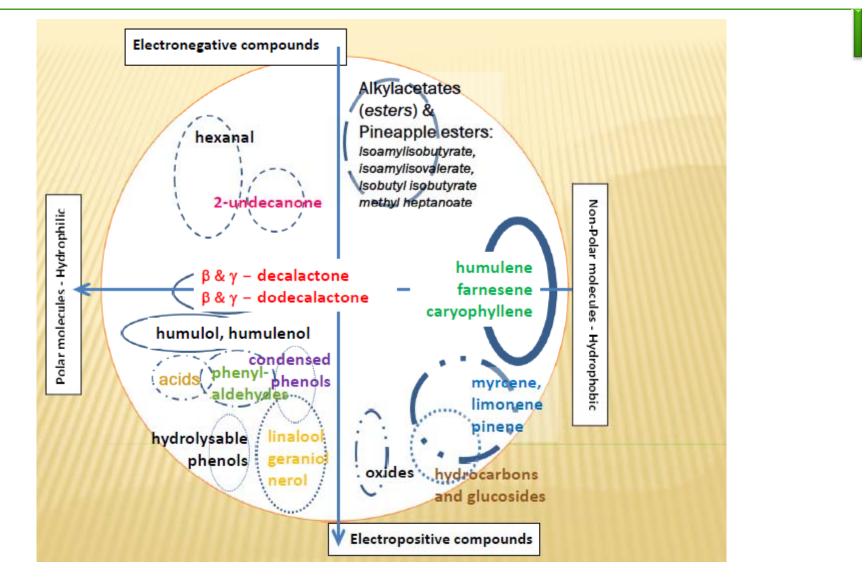


(isomeric) alcohols differ in aroma impression and flavor thresholds

- a) enzymatic
- b) acid catalysis

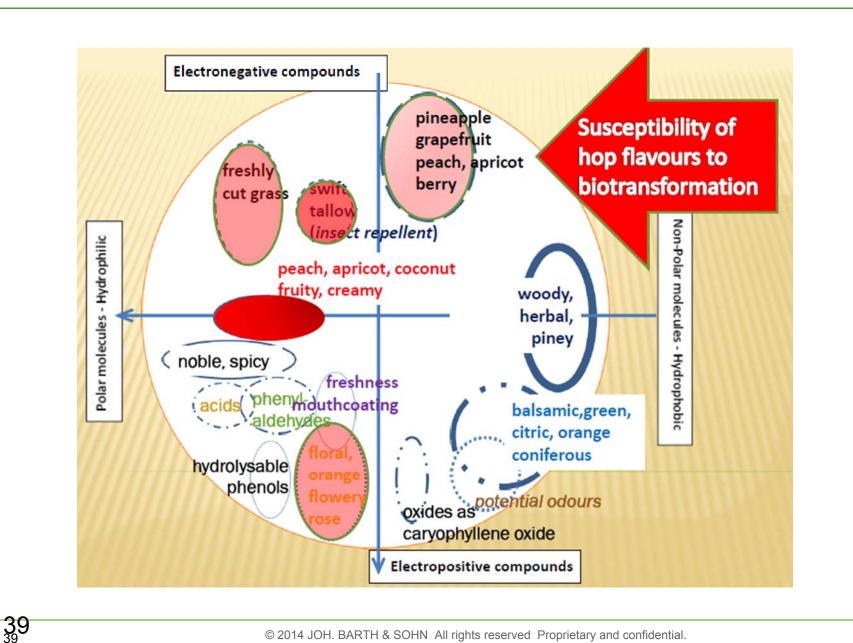
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Derdelinckx, 2013

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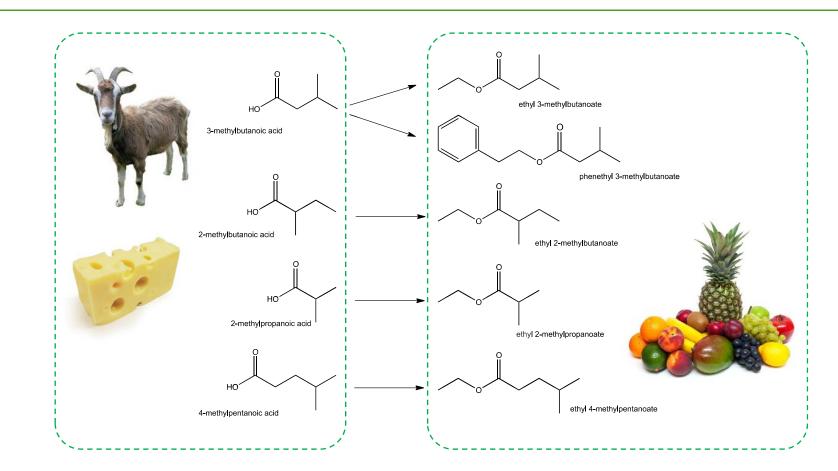


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Esterification

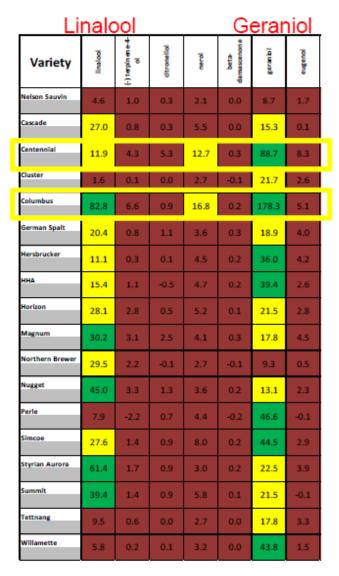
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- flavor threshold of acids by factor 100 higher than those of corresponding ester
- Increase in ester concentration with yeast "stress"
- Increase of acids in old hops
- chemical esterification is slow (beer staling)

Hydrolysis of bound aroma compounds with enzymes



Instrumental Results



- = Treatment Control
- Averages of duplicate injections using SBSE
- Centennial & Columbus
- Geraniol & linalool driving instrumental changes

Greater than 30 ppb Between 10 – 30 ppb Less than 10 ppb

Shellhammer, 2014, ASBC

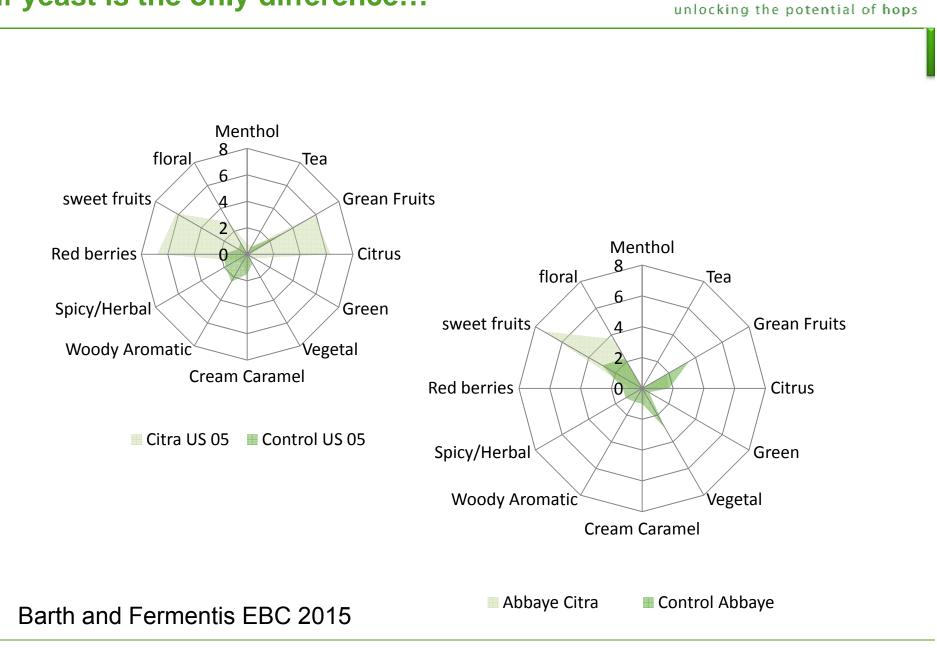


Hop derived glycosides found in Cascade and Mt. Hood (Shellhammer)

- 3-methyl butanol glucose (fruity, banana, ethereal)
- Benzyl alcohol glucose
- 2-phenyl ethanol glucose (floral, rose)
- > 1-octanol glucose (waxy, green, citrus, orange)
- Vanillin glucose (vanilla)
- Linalool glucose (citrus, orange, floral)
- > alpha-terpineol glucose (pine, lilac, citrus, woody, floral)

Murakami et al, 2006, Use of hop glycosides extracted from hop plant parts to flavor malt beverages. US Patent 7,001,638 B2

If yeast is the only difference...



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- Dynamic dry hopping better aroma extraction (even in comparison to very long static contact time) (Wolfe, 2012)
- Dynamic dry hopping positively correlates with medium size polyphenols (procyanidines, polydatine,polyphenolglycosides)
- A negative correlation for dynamic dry hopping was shown for foam values, decanoic acid (indicates yeast quality) and low molecular carbonic acids (Schönberger, 2015)
- > All systems with circular extraction show good efficiency (e.g. Hopgun)

Temperature

- Higher temperature (8°C vs 0°C) higher concentration of hop aroma components (10-30%) (Schüll, Tech. Seminar 2014)
- Higher temperature (20°C vs 4°C) no influence on linalool extraction efficiency (Mitter et al 2012)
- Not much scientific material
- Higher temperatures, faster extraction, consequences for aroma and flavour stability?



Oxygen; thermal treatment and flavour stability barth!nnovations

- Moderate oxidation possibly benifitial for dry hop aroma (more intense)
- Oxidation produces fruity flavours in hops (Kishimoto, Vollmer 2014)
- > Oxygen pick up with cone hops can be x 20 compared with pellets !
- Oxygen impact on polyfunctional thiols ageing flavours (Tran, EBC 2013)
- Pasteurization decreased the aroma and flavour intensities of floral, citrus and fruity characters (more aroma than flavour)
- > Typically hop aroma decreases strongly within 3 months, after that stable
- Decrease of floral and fruit flavour correlates with decrease of geraniol
- Decrease of esters; mono- and sesquiterpenes rel. stable (Forster, EBC)
- Linalool content is very stable

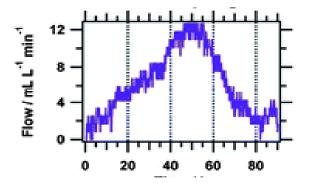
Other facts...

- Increase of amino acid spectrum by dry hopping (especially L-Asparagine and L-Arginine, (turbidity and bitterness) (Foehr, 2014)
- Increase of polyphenols with dry hopping (turbidity and bitterness) (Foehr, 2014)
- Epicatechin and oligomers B2 and C1 improve shelf-life of beers versus Maillard reactions (ale beers), (Derdelinckx, 2013)
- > Any kind of filtration reduces hop aroma
- Influence of crown material
- > The more hops you use, the less efficient is the aroma extraction

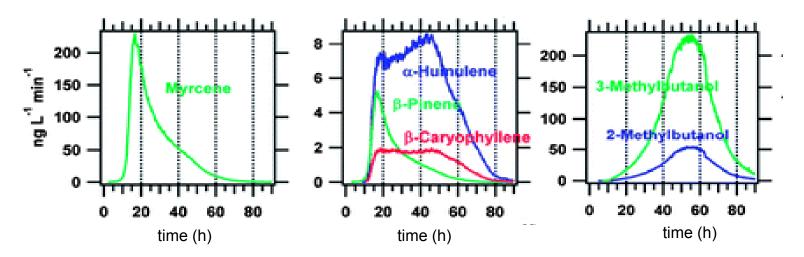
Stripping

volatile + hydrophobic compounds are lost by stripping

carbon dioxide evolution rate

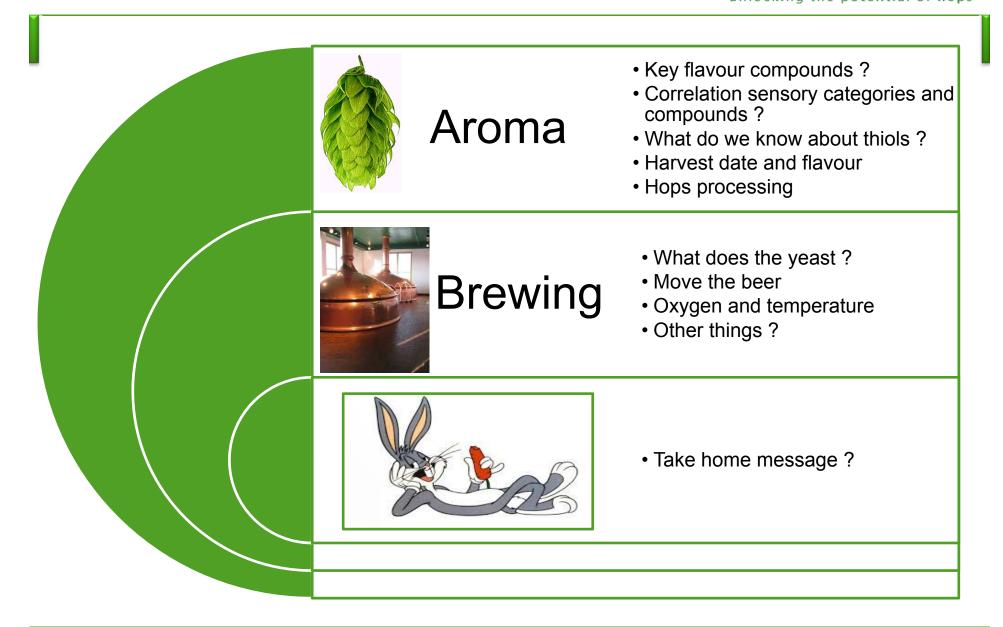


release curves of aroma compounds



Questions about dry hopping

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- High hopping rates and the need for more efficient dry hopping was a topic already more than 100 years ago
- > Also German beers were dry hopped
- Our olfactory/gustatory system is made to discriminate aromas but not to identify them, Dry hop aroma is emotional
- Looking into aroma research it is likely that the aroma of varieties and in dry hopped beers is determined by the individual combination of key hop aroma compounds (most of them we already know)
- > The contribution of thiols is being discovered (powerful thresholds!)
- Calculating the sensory importance using thresholds is not helping
- Need for marker components in dry hop aroma that correlate with sensory descriptors

Summary and take home messages

- Everything outside of the brewery has sensory influence, harvest time, location, drying, storage, pellet processing, product form and can be tasted in a dry hopped beer
- Everything inside of the brewery has sensory influence, time of dry hopping, number of dry hopping, method of dry hopping, presence of yeast, possibilities for oxygen pick up, centrifugation, filtration, bottling, crown material
- > Why calculating transfer rates from hops to beer ?
- > Myrcene is up in the air, linalool is the base, geraniol is underestimated
- Dry hopping does only good things for your flavour stability but characteristic aroma is fragile
- Stable dry hop aroma is an illusion

Thank you for our attention

Thanks to

The teams of Guy Derdelinckx, Filip v. Opstaele (KU Leuven), Tom Shellhammer (OSU), Nils Rettberg (VLB) and Martina Gastl (TUM) Andreas Gahr (Research brewery St. Johann) All passionate brewers

www.HopsAcademy.com

www.BarthHaasGroup.com