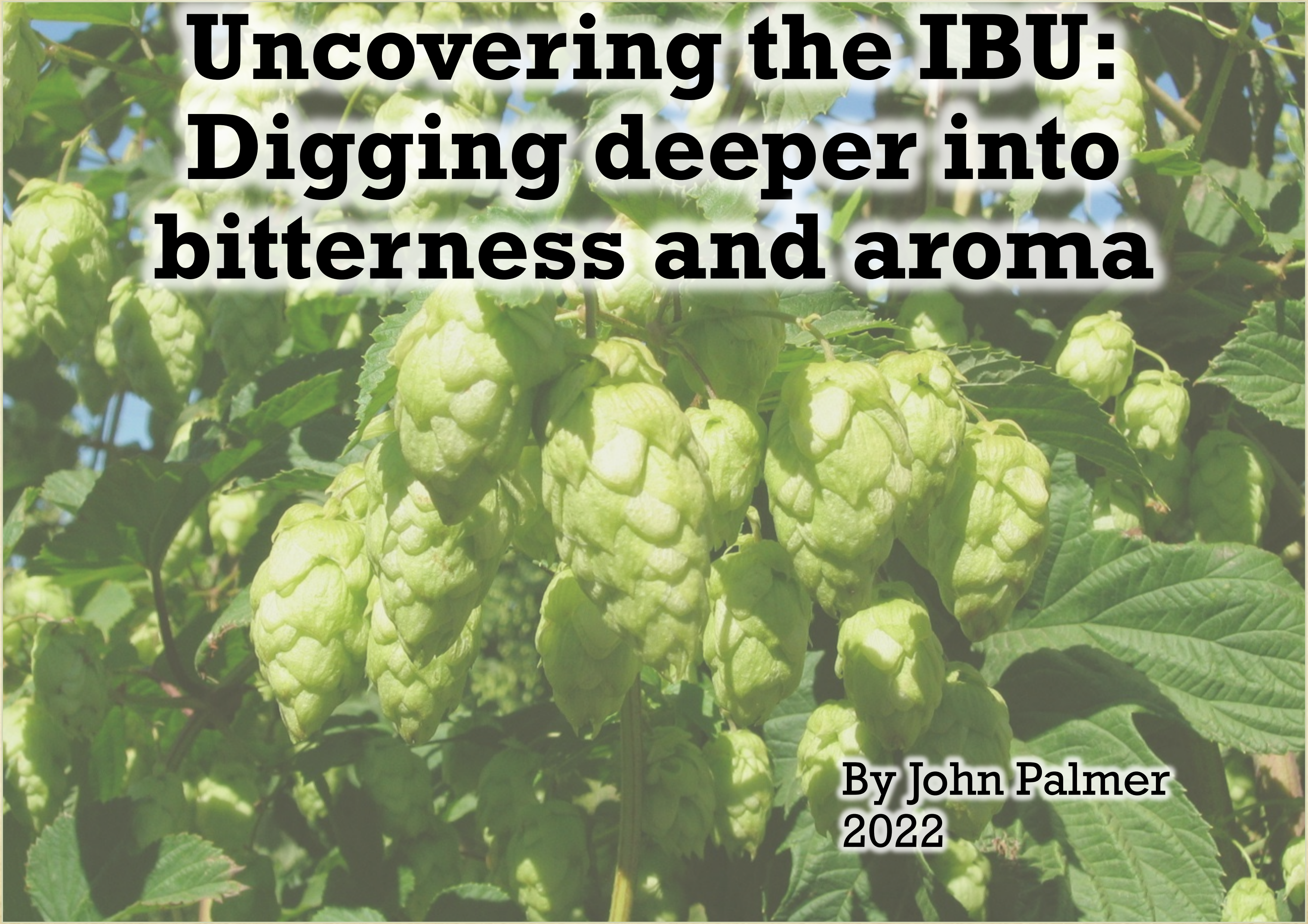
Uncovering the IBU: Digging deeper into bitterness and aroma



By John Palmer
2022

Syllabus

- Hop Components
- Bitterness and the IBU Test
- Utilization
- Hop Aroma and Flavor Development during the Brewing Process

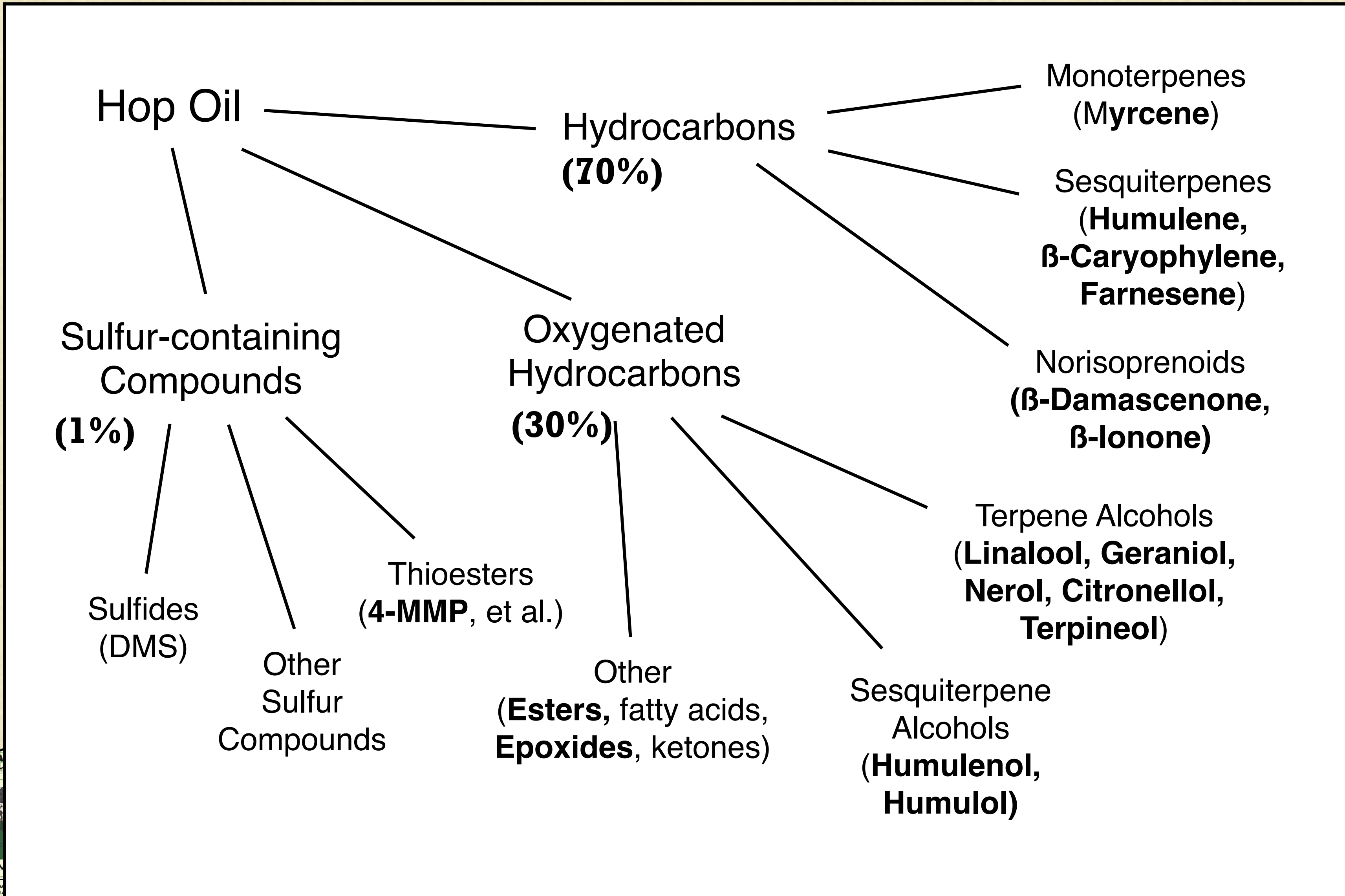
What are Hops?

- A vine native to northern (40-60°) latitudes and 14-18 hours of summer daylight.
- The lupulin glands contain the resins and oils that add bitterness, flavor, and aroma to our beer.
- We know that boiling hops makes beer bitter, and contributes hop flavor and aroma.
- But what do we really know…?

Hop Components

	Weight %
Alpha Acids – Humulones	2-23%
○ Humulinone (oxi-alpha)	0.1-0.5%
Beta Acids – Lupulones	2-10%
○ Hulupones (oxi-beta)	~0.05%
Polyphenols	3-6%
Essential Oils	0.5-4%
○ Hydrocarbons	(70-80%)
○ Oxygenated Hydrocarbons	(15-30%)
○ Sulfur Compounds (Thiols)	(<1%)

Hop Oils


Hop Oil
Hydrocarbons (70%)
Monoterpenes (Myrcene)
Sesquiterpenes (Humulene, ß-Caryophylene, Farnesene)
Norisoprenoids (ß-Damascenone, ß-Ionone)
Sulfur-containing Compounds (1%)
Sulfides (DMS)
Other Sulfur Compounds
Thioesters (4-MMP, et al.)
Oxygenated Hydrocarbons (30%)
Other (Esters, fatty acids, Epoxides, ketones)
Sesquiterpene Alcohols (Humulenol, Humulol)
Terpene Alcohols (Linalool, Geraniol, Nerol, Citronellol, Terpineol)

Essential Oil Aromas

Hydrocarbons:	
myrcene	Green, resinous, piney
caryophyllene	Woody
humulene	Woody, piney
farnesene	Floral
Oxygenated Hydrocarbons:	
linalool	Orange, fruit loops
geraniol	Floral, rose, geranium
cis-rose oxide	Fruity, herbal
citronellol	Citrusy, fruity
limonene	Citrusy, orange
nerol	Rose, citrusy
pinene	Spicy, piney
Sulfur Compounds:	
3-mercaptohexanol (3MH)	Grapefruit, passion fruit
3-sulfanylhexanol (3SH)	Black currant, muscat
4-mercapto-4-methylpentanone (4MMP)	Box tree, broom
4-methyl-4-sulfanylpentanone (4MSP)	Black currant, tropical

From Stan Hieronymus, 2019

Hop Oil Variability

- Alpha Acid content and Oil content vary year to year, but generally within a characteristic range for the variety.
- %AA and Total Oil do not vary proportionally.
  - % Oil $\neq f$(%AA)
- Total Hop Oil content is a varietal characteristic, but it varies due to length of time on the bine. Longer = More.

Bitterness and the IBU

Quantifying Bitterness

- 1 IBU is defined as 1 mg/L of isomerized alpha acids.

WRONG!!

- 1 unit of Sensory Bitterness may be defined as 1 mg/L of isomerized alpha acids, but that is different than the IBU test method.

What is Bitterness?

- Bitterness is defined by the number from the ASBC IBU light absorption test.
- Brewers needed a fast, repeatable test that could measure "bitter stuff".
- The test measured "bitter stuff" that is extracted by iso-octane solvent.
- We assumed that "bitter stuff" was the isomerized alpha acids and other bitter hop compounds, and that they are all equally bitter.

The Standard BU Test

- Many, many beers were measured for both absorption and iso-alpha and the standard equation became:

$$IBU = 50 \times abs@275nm$$

- Thus an IBU is a correlation to *perceived bitterness,* as measured by *the absorption of light by extract of "bitter stuff",* circa 1955*.*

Beer Bitterness Then

- Iso-alpha acids were known to be bitter.
- Oxidized beta acids were known to be bitter.
- All hop varieties in the 1950s typically had an Alpha: Beta ratio of 1-to-1, and were basically low % Alpha.
- Formation of oxidized beta acids and oxidized alpha acids doesn't appear to be time dependent.(3)
- Therefore, more hops per barrel were used to hit target BU, and likely a higher percentage of oxi-alpha and oxi-beta comprising the total bitter character than today.

Beer Bitterness Now

- Today's bittering hops are typically high alpha varieties, with higher oil content.
- Hops are well-stored, ie., less oxidation and alpha loss, and less green matter.
- Therefore, today's bitterness is sharper; predominately Iso-Alpha, with more aroma/oil.
- Whirlpool hopping and Dry hopping add lots of "other stuff" to the IBU measurement.

IBUs and IAA as Hops Age

Storage Temp.	Alpha Acid in Hops	Iso-Alpha (HPLC)	IBUs (Std Method)
-15°F (-26°C)	3.2%	19.8 ppm	13.5
25°F (-4°C)	2.9%	18.1 ppm	12.0
45°F (7°C)	1.7%	14.4 ppm	13.5
70°F (21°C)	0.4%	2.9 ppm	11.0

- Willamette hop aged for 18 months at noted temperatures.
- Beers brewed with same weight of hops.

Peacock, V., The IBU Method, its Creation and What it Measures, MBAA Annual Meeting Proceedings, 2014.

What is actually Bitter?

- Bitter:
  - Iso-alpha acids are bitter
  - Oxidized alpha acids (humulinones) are bitter
  - Oxidized beta acids (hulupones) are bitter
  - Hop polyphenols are bitter
- Not Bitter
  - Raw beta acids are not bitter
  - Raw alpha acids are not bitter
    - J. Am. Soc. Brew. Chem. 65(1):26-28, 2007.
  - Decomposition products of alpha and beta acids.

Light Absorption of Compounds

- Different hop compounds absorb light differently:
  - Humulones at about 62% (raw alpha)
  - Isohumulone at about 70% (iso-alpha)
  - Humulinones at about 54% (oxi-alpha)
  - No number given for hulupones (oxi-beta)
  - Hop Oils are not absorb at 275 nm and do not affect the measurement.
    - Dry Hopping and its Effects on the International Bitterness Unit Test and Beer Bitterness, J.P. Maye, R. Smith, MBAA TQ Vol. 53, No. 3, 2016
- Note: these numbers only affect the measured IBU number, not perception of bitterness.

But that's not all…!

- However, the test picks up anything that is soluble in iso-octane and absorbs at 275 nm. This includes ALL hop bitter compounds and oxidation products, some ***malt color***, and some ***fermentation by-products***, like 2-phenylethanol.
  - V. Peacock, 5/21/19.

Perceived Bitterness and Testing

Compound	Perceived Bitterness	Perception Threshold	275nm Absorption Factor
Humulone (raw alpha)	(not bitter)	(unknown)	62%
Isohumulone (iso-alpha)	100%	5-6 ppm	70%
Humulinone (oxi-alpha)	66%	~7-8 ppm	54%
Hulupones (oxi-beta)	84%	7-8 ppm	(unknown)

i.e., 50ppm iso + 10ppm oxi-α = 40 IBU (test)

i.e., 50ppm iso + 10ppm oxi-α = 56.6 IBU (taste)

Note: It is not clear if bitterness is additive or synergistic.[1]

Isomerization boils down to Heat

- Isomerization rate only varies with temperature.
  - Utilization = Rate x Time - Loss
- Therefore whirlpool isomerization is a function of temperature (and time).
- According to Malowicki and Shellhammer[5], the Isomerization Rate:
  - at 90C/195F is 40% of that of the boil
  - at 80C/175F is 15% of that of the boil

Isomerization and Altitude

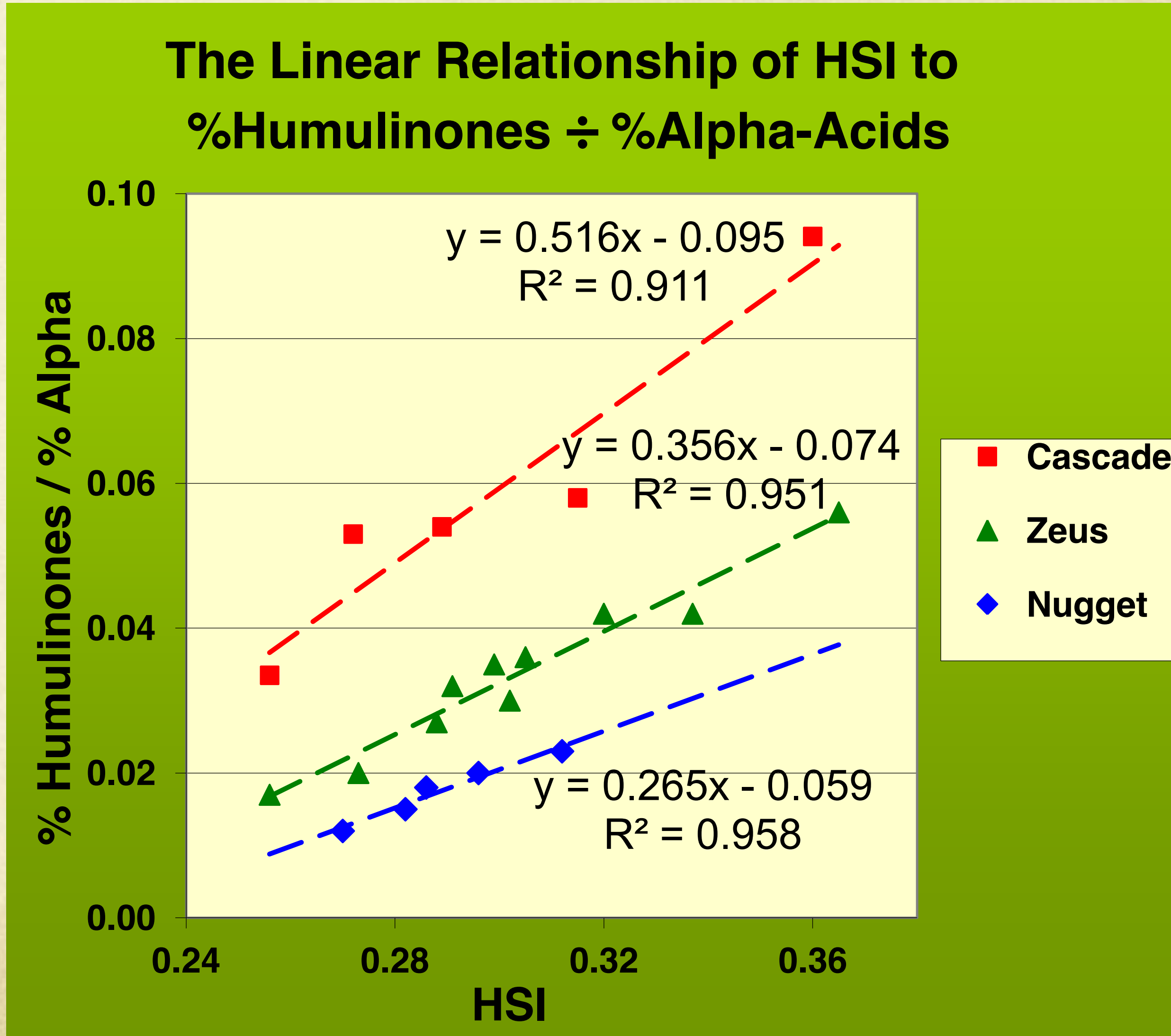
Altitude (m)	Altitude (ft)	Boiling °C	Boiling °F	% Rate
0	0	100.0	212.0	100%
500	1,640	98.4	209.1	87%
1,000	3,281	96.8	206.2	76%
1,500	4,921	95.1	203.3	67%
2,000	6,562	93.5	200.3	58%
2,500	8,202	91.9	197.4	50%
3,000	9,843	90.3	194.5	44%
3,500	11,483	88.7	191.6	38%
4,000	13,123	87.0	188.7	33%
4,500	14,764	85.4	185.8	28%
5,000	16,404	83.8	182.8	25%

Two Words about Humulinones
(oxi-alpha)

- Leaf hops typically contain less than 0.3% w/w humulinone, however, following pelleting that concentration can increase up to 0.5% w/w.
- The higher the HSI is in hops or hop pellets the higher the humulinone concentration and this relationship is variety dependent.
- Humulinones are more polar than isoalpha acids and over 87% dissolved in dry hopped beer.
- CO_2 Hop Extracts contain low humulinones.

Humulinones (oxi-alpha)

- There seems to be a linear relationship between %Humulinone, %AA and Hop Storage Index that is variety specific.[3]



Hulupones (oxi-beta)

- Beta acids are typically 2-6% by weight.
- The hulupones (oxi-beta) are typically 0.05% by weight.
- A sampling of well-known Belgian beers, brewed with Aged Hops, contained less than 3 ppm (below threshold).
  - (in fact, all the bitterness in the beers came from oxi-alpha)
  - Ferreira et. al., Why Humulinones are Key Bitter Constituents Only After Dry Hopping: Comparison With Other Belgian Styles, J.ASBC, 76(4), 2018.
- Therefore, hulupones are probably not significant bittering factors for whirlpool and dry-hopped beers.

Utilization

Utilization

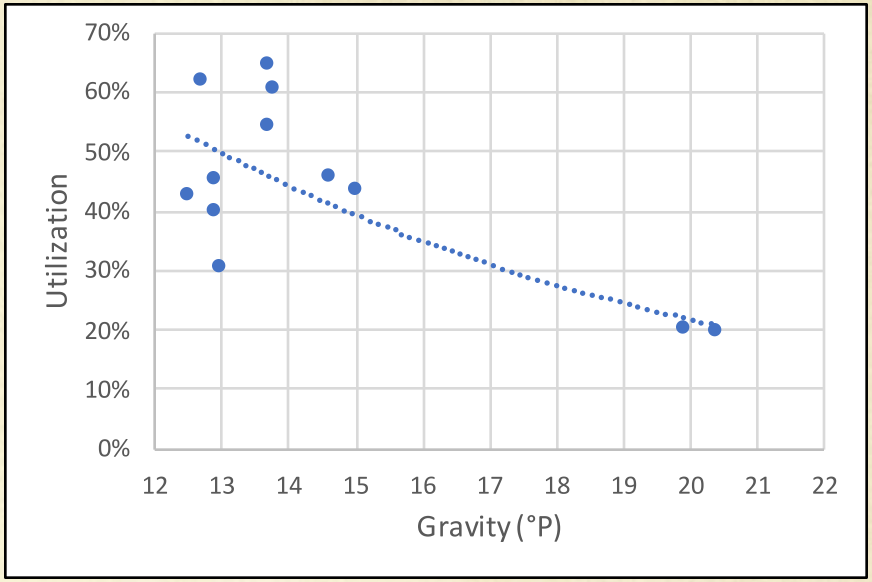
- Utilization = Bitter Stuff - Losses
- Losses are generally related to saturation/insolubility:
  - Bitter stuff sticks to:
    - Equipment
    - Hot and Cold Break (proteins)
    - Yeast
    - Hop material

Output / Input

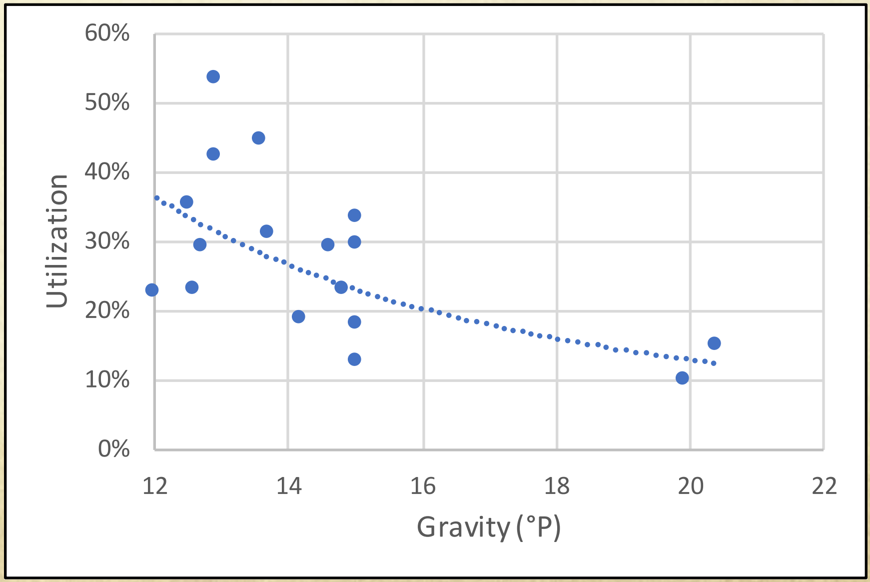
- Utilization is the measured IBU versus the amount of alpha acid that was added.
  - $\%Util = IBU/(Ounces \times \%AA \times 75/V_{Gallons})$
  - $\%Util = IBU/(Grams \times \%AA \times 10/V_{Liters})$
  - $\%Util = IBU/(pounds \times \%AA \times 38.7/V_{Barrels})$
- Bitterness = IBU = 50 x abs@275nm
- Bitter Stuff = Iso-Alpha + Oxi-Alpha
  - Oxi-beta is typically insignificant (by weight)[7].
  - Hop polyphenols are typically insignificant (by weight)[7].

Ballast Point Utilization vs. OG[4]

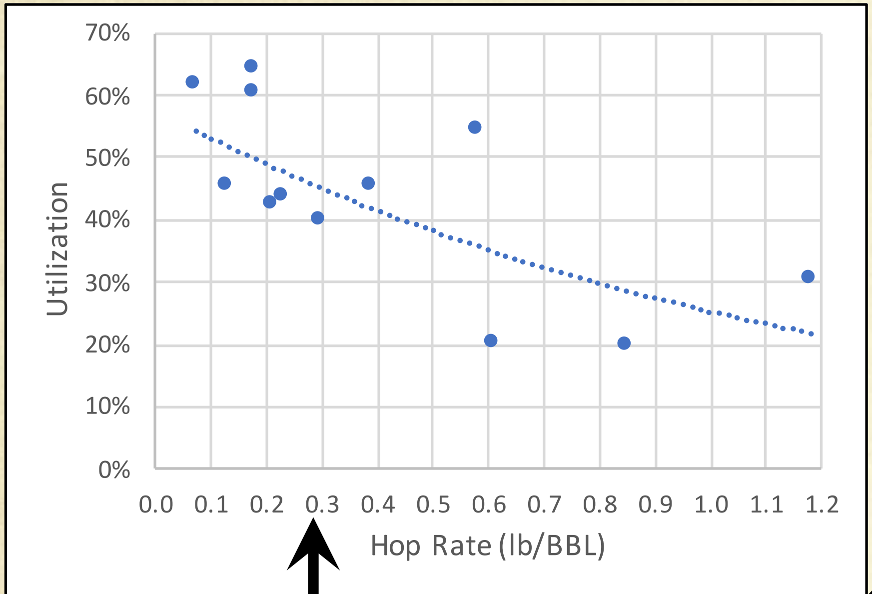
60 minute – Various Beers
1.050-1.080

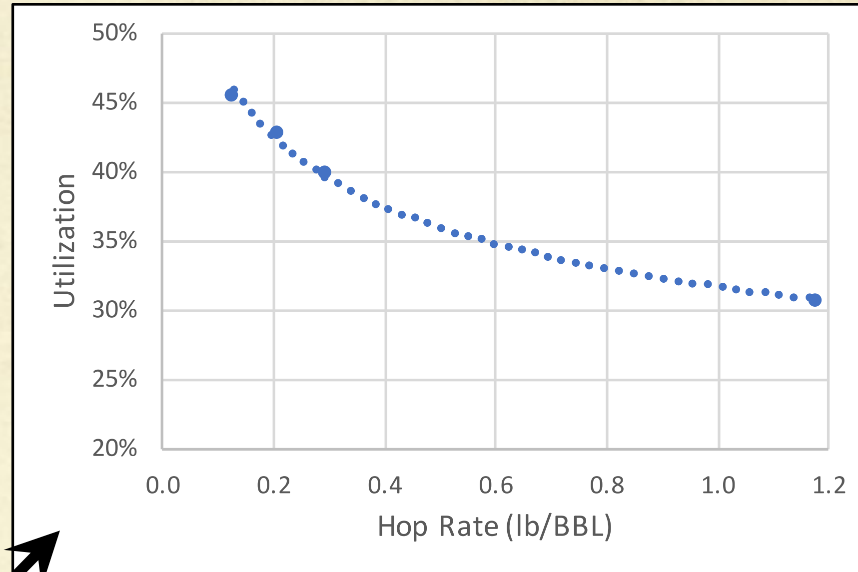


Whirlpool– Various Beers
1.048-1.080



Utilization vs. Hopping Rate[4]

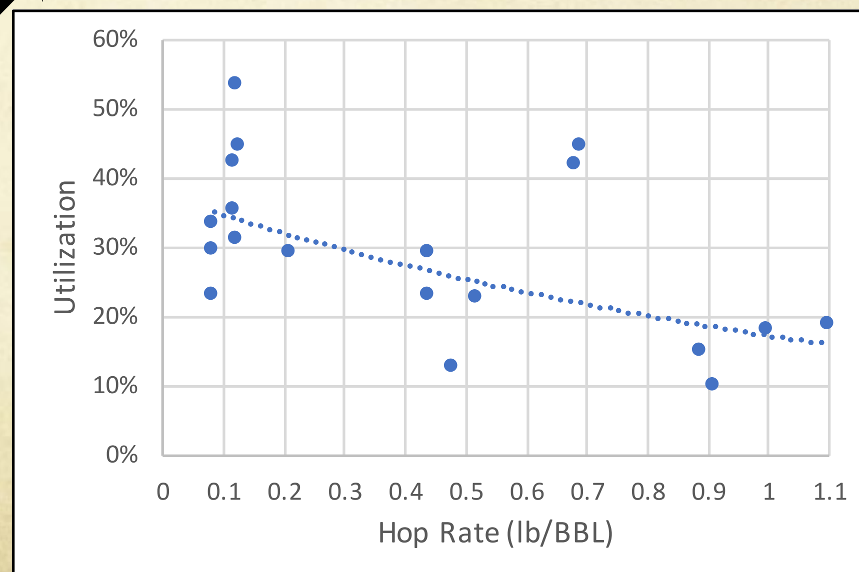




60 Minute – Various

60 Minute – 1 Beer

Whirlpool - Various



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Mash Hopping

- Utilization = rate x time – losses
- Losses are due to poorly soluble oils and resins sticking to the kettle, proteins, trub, etc., and not staying in the wort.
- Mash Hopping: Resins stick to grain, etc.
  - Justus[4] reported that mash hopping gave an average utilization of <u>9%</u>.
  - Curtis[8] reported that mash hopping had utilization of 1/3 of 60 minute addition (i.e., about 9%).
  - Thus, Mash Hopping is a waste of money.

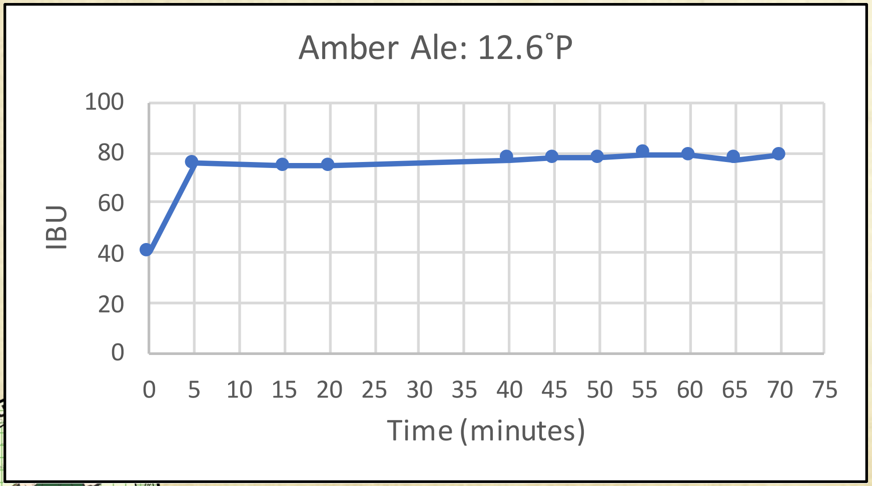
First Wort Hopping

- Essentially a longer boil.
- More potential for hop compounds to be absorbed into the hot break.
- Minimal aroma and flavor contribution compared to Late and Whirlpool hopping.
- Experiments (FWH vs 60 min) have not demonstrated a statistical difference in perception, although IBU Test showed a ~10% IBU increase for FWH.

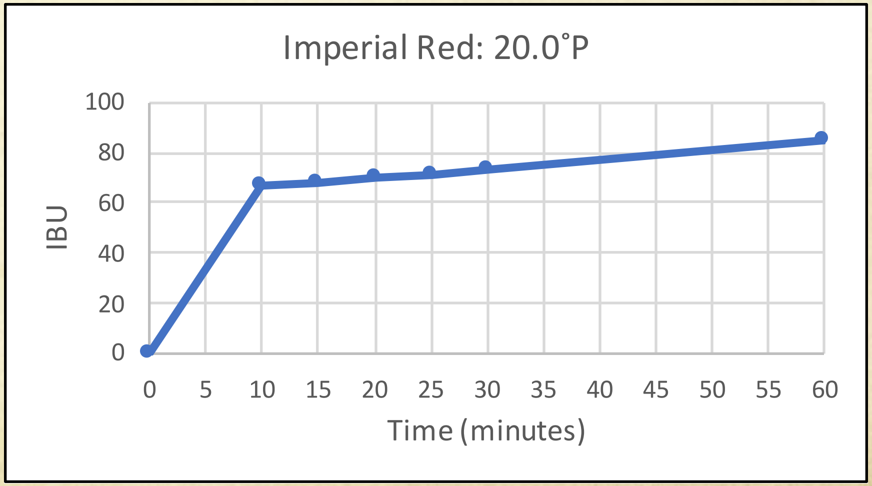
Whirlpool Hopping

*Photometric method !

- Justus[4] noted that most of the IBUs* where realized in the first 10 minutes of the typical 60-70 minute whirlpool.
- Same behavior as 60 minute addition!



whirlpool



60 minute

What does this mean?

- It means most of the "bitter stuff" solubilizes in the first 10 minutes at high temperatures.
  - Raw Alpha acids are much more soluble at high temperatures, and are therefore captured and measured in the IBU test.
- However! These high-temperature-soluble alpha acids still take <u>Time</u> to isomerize and thus be soluble in beer at room temperature.
  - (we know this).
  - "These are not the IBUs you are looking for."

Loss of Iso-Alpha During Fermentation

- Where does it go?
- Their results corresponded to the rise and fall of the krausen.
- When the yeast activity leveled off and the krausen fell, the level of iso-alpha acids in the beer stablized.

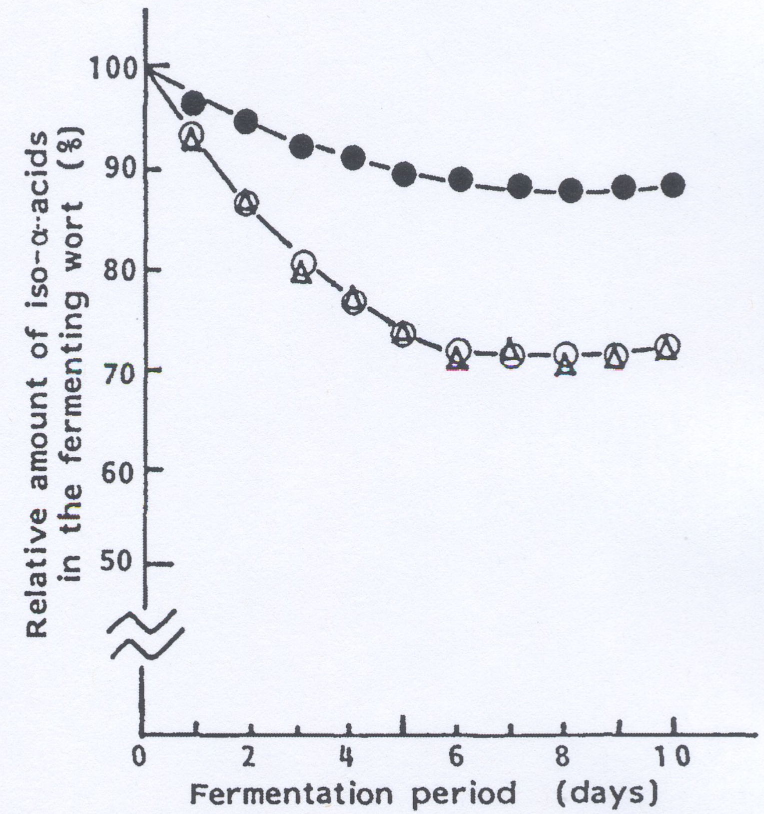


Fig. 8. Changes in concentrations of iso-α-acids during fermentation. ● = isocohumulone, ○ = isohumulone, and Δ = isoadhumulone. Relative amounts calculated as percent of each iso-α-acid in the starting wort.

Quantitative Analysis of Hop Bittering Components and its Application to Hop Evaluation, M. Ono et. al., Journal of ASBC 42-04, pp. 167-172, 1984.

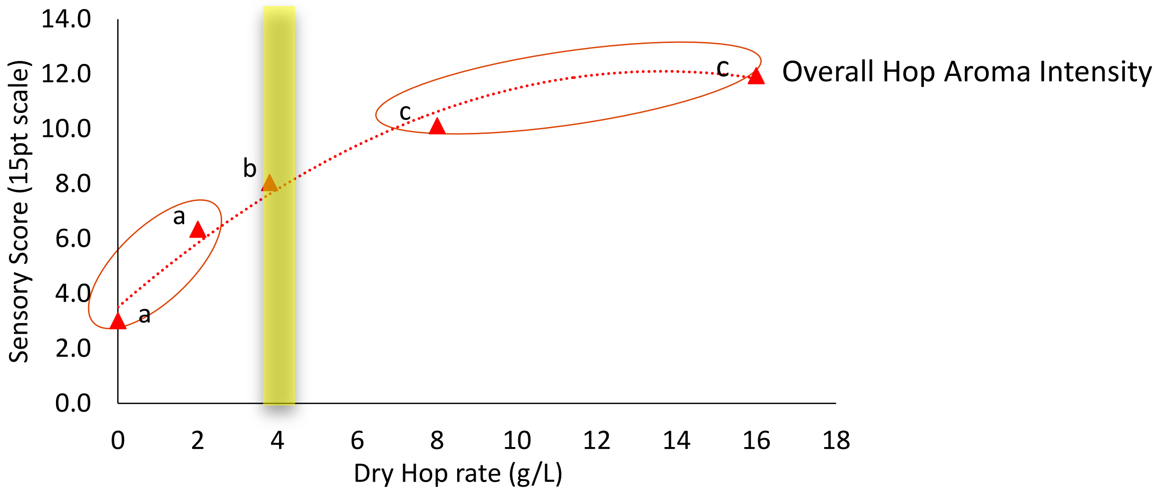
Losses During Fermentation

- The average IBU loss for 14 different beers during fermentation and clarification was 33.7%, std dev 7.9%.[4]
- "All else being equal:"[4]
  - More Whirlpool IBUs are lost in fermentation.
    - Are isohumulones more stable than humulinones?
  - Low flocculent yeast lose more IBUs than High flocculent yeast during fermentation.
  - Large IBU loss due to excessive blow-off.

Dry Hopping

- Raw alpha acids are almost insoluble at room temperature.
- Therefore the soluble stuff is humulinones, hulupones, and “other”.
- Common benchmark for dry hopping:
  - = <u>1 pound per barrel</u>
  - = 4 gram per liter
  - = 0.5 oz per gallon

Diminishing Returns – Hop Rate



- **Panelists could discriminate the different dry hop rate samples (ie 0, 2, 3.8, 8, & 16)**

DH Dosing Rates and Extraction Efficiencies, Scott Lafontaine, 2018 Craft Brewers Conference, Nashville, TN.

What Happens when you Dry Hop?

- About 33% of the dry weight of the hop is soluble and will raise the beer gravity by 0.1-0.3°P (~1.001) per lb per barrel.[9]
- About 75% of the initial alpha acids are retained in the spent hops.[9]
  - The higher the %AA, the lower the % retained.
- About 50% of the initial oil is retained.[9]
  - The higher the wt% Oil, the more retained.
- Therefore, the less green matter, the better utilization. (IOW, use cryo.)

Other Results of Dry Hopping[3]

- The higher the IBU, the greater the loss of Iso-alpha Acids, due to green matter.
- Humulinone utilization is nearly 100% at low dry hopping dosages and greater than 89% at high dry hopping dosages.
- ~ 26 IBU's (from Kettle) seems to be the sweet-spot or cut-off line. Dry hopping beers above 26 IBU's decreases total bitterness, and dry hopping below this level increases a beers total bitterness.
- Dry hopping increases a beer's pH linearly by about 0.14 pH units per 1 lbs. hops/barrel and is independent of starting IBU.

Hop Aroma and Flavor Development During the Brewing Process

What is Hop Aroma in Beer?

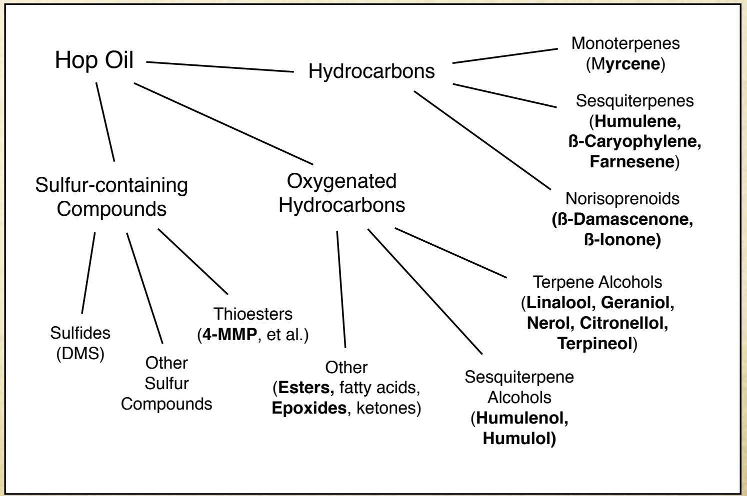
- Hop Compounds identified in beer include:
  - **Fresh Hop Aroma: Linalool, Geraniol, Limonene, Terpineol, Myrcene**
  - **Noble Hop Aroma: Oxides/Epoxides of Humulene, Caryophyllene, Farnesene**
  - **Hop Derived Ethyl Esters**
  - **Converted compounds (4 of the most prevalent)**
    - **Herbaceous/floral note**
    - ***cis* Rose Oxide (floral)**
    - **Cedarwood note (noble)**
    - **Intense Grapefruit/Tomato plant**

What is Hop Flavor?

- Flavor is a combination of the Bitterness & Aroma
  - Alpha acids and compounds
  - Beta acids and compounds (minor but synergistic??)
  - Heavier hop oils: the Sesquiterpenoids: Humulene, Caryophyllene, Humulene epoxides
  - Hop Esters formed from short chain fatty acids (the cheesy character).
- All of these compounds are modified by the boil and fermentation to produce compounds not present in raw hops.

Bio/Transformation

- The assumption is that it always happens.
- More likely that it sometimes happens, depending on hop variety and yeast strain.
- Four groups of transformations (so far)
  - Hydrocarbons (Chemical during boil)
    - Humulene epoxides, caryophyllene oxide
  - Oxygenated Hydrocarbons
    - Geraniol, Linalool, nerol
  - Thiol transformation
    - 4MMP, 3MHA, 3MH
  - Transesterification
    - E.g. 2-Methylbutyl Isobutyrate to Ethyl Isobutyrate (green apple/apricot)



Free Geraniol and G-Precursors[12]

- Free Geraniol
  - Motueka
  - Cascade
  - Citra
  - Chinook
  - Mosaic
  - Bravo
- Geraniol Precursors
  - Vic Secret
  - Comet
  - Hallertau Blanc
  - Polaris
  - Amarillo
  - Summit
  - Galaxy

Hop Harvest Time and Usage

- Late Harvest Cascade had:
  - Higher total oil
  - More intense hop aroma
  - More citrus, less herbal aroma
  - Higher Geraniol concentration
  - Higher Free Thiols

- Early Harvest:
  - More Precursors
  - Use for Kettle

- Late Harvest:
  - More Free volatiles
  - Use for WP, DH

Sharp, Townsend, Qian, Shellhammer, *Effect of Harvest Maturity on the Chemical Composition of Cascade and Willamette Hops,* JASBC 72(4), 2014.

Monoterpene Alcohol Transformation

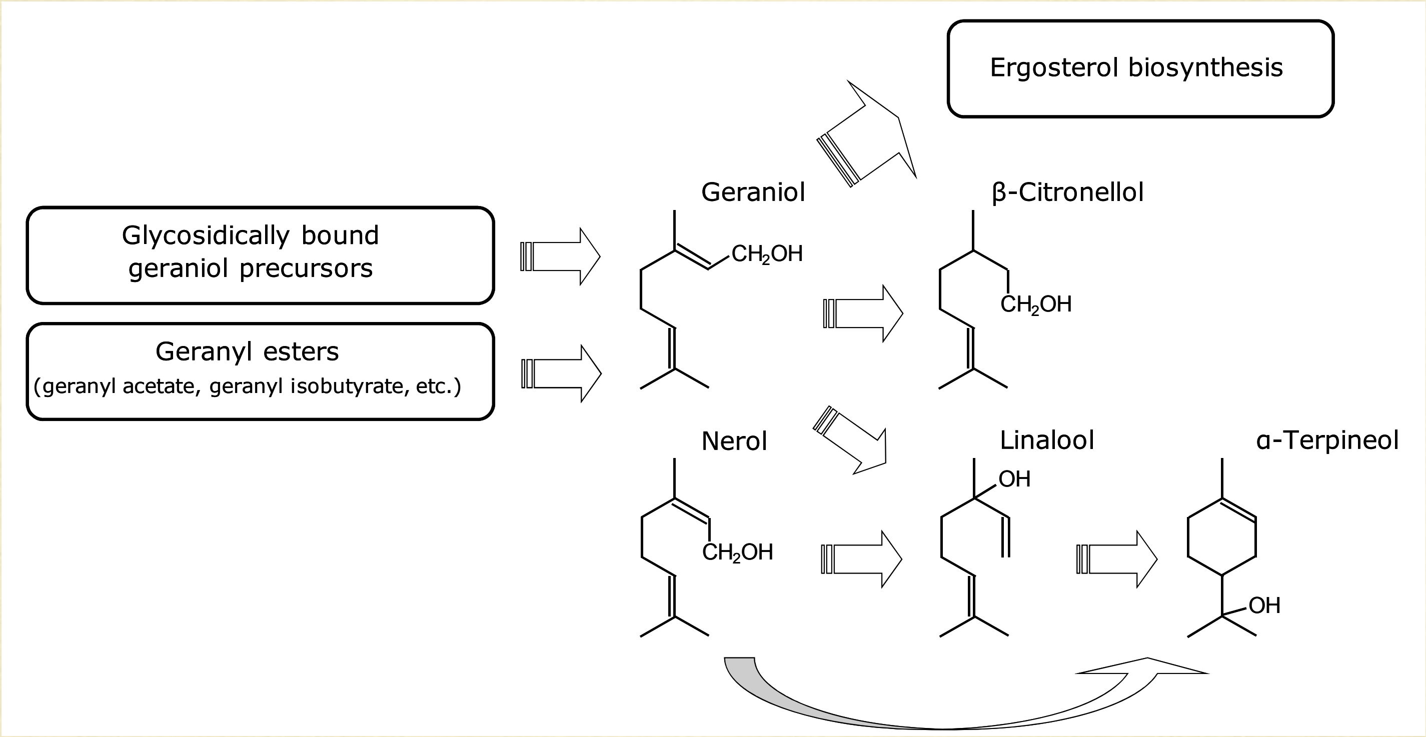


Fig. 4 **Biotransformation pathway of monoterpene alcohols by brewing yeast (On the basis of ref. 3, 4, 6, 8, 15, 17, 38–40)**

Tokai et. al., (12)

Biotransformation of Oxygenated Hydrocarbons

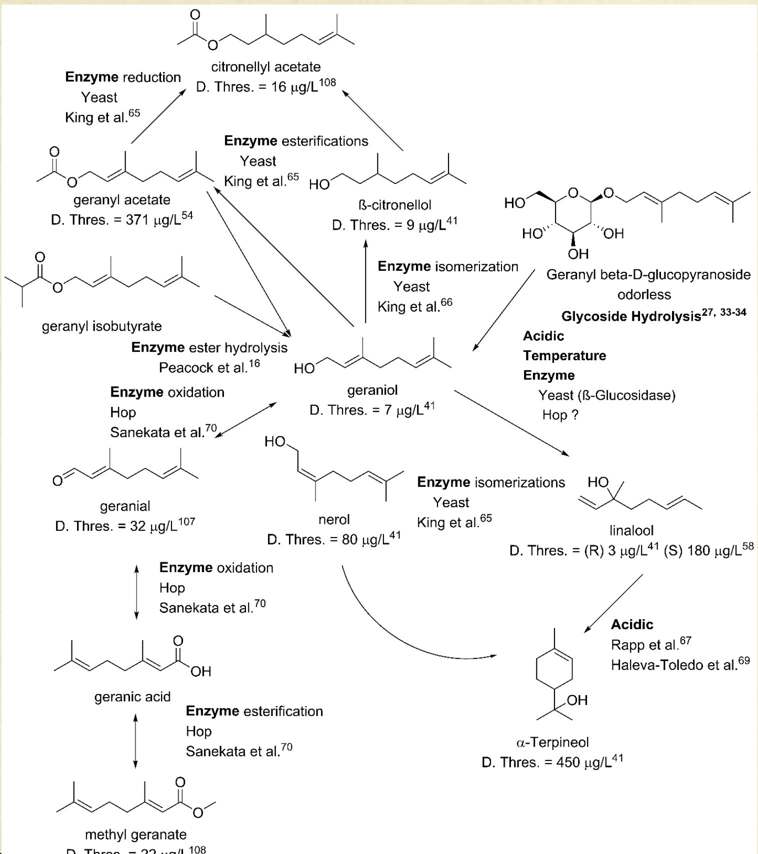
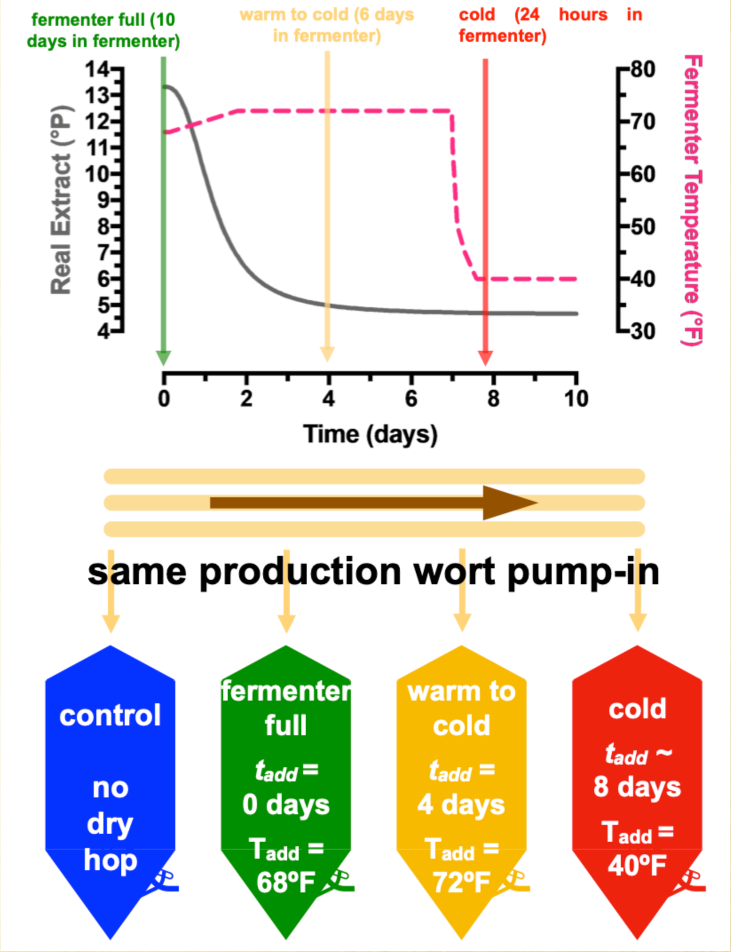


Figure 3. Reactions associated with geraniol biosynthesis in hops, associated with yeast enzymatic activity during fermentation, or influenced by environmental conditions (e.g., temperature and pH). Detection thresholds (D. Thres.) of individual compounds in water and beer are listed when available. References regarding thresholds and pathways are indicated in the figure.

From Mike Brennan, 2019

Biotransformation and Timing[10]

- One wort, split four ways.
- Sierra Nevada Yeast
- 3 Hop timings:
  - Beginning (T=0)
  - Middle (T=4)
  - End (T=8)
- 3 Replicates

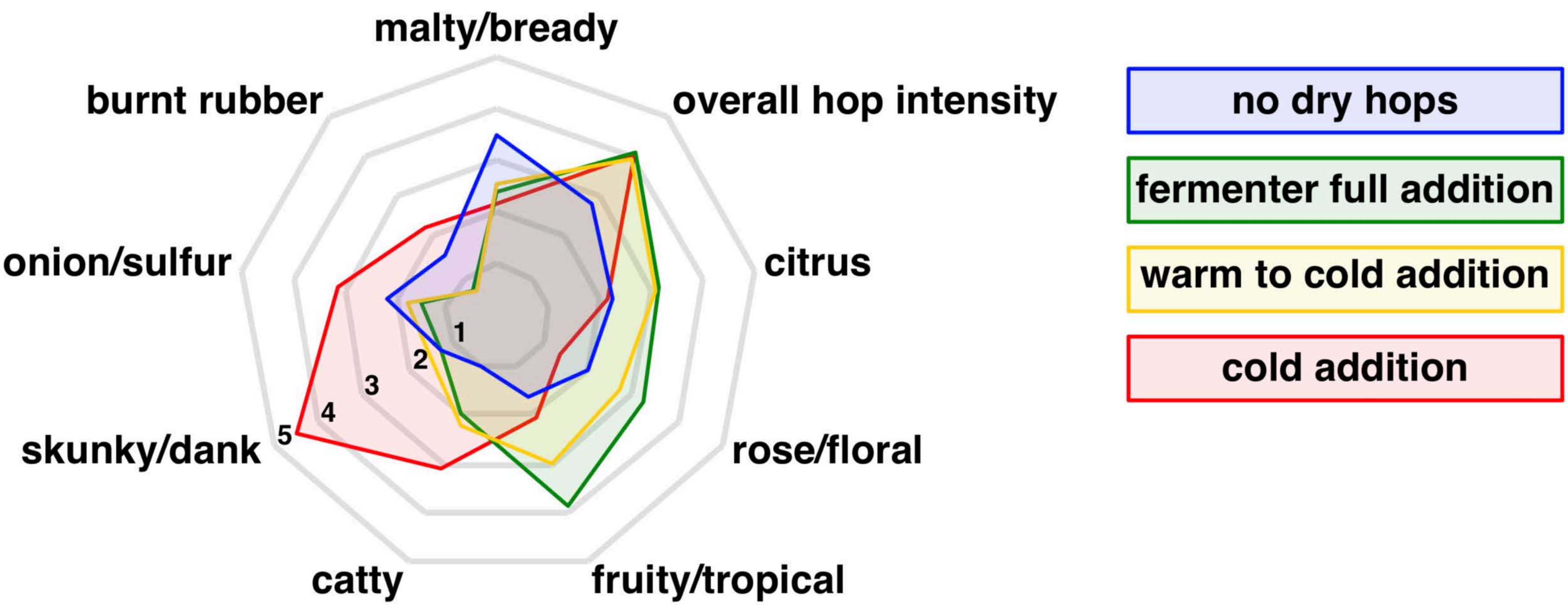


DH Timing Affected Character[10]

significant organoleptic qualities

quantitative descriptive panel assessment:
n ~ 8 trained panelists per screening

rated intensity from 0 to 8 (8 = most intense)



average of intensity ratings
from *n* = 3 panels
α = 0.05

Extract! Extract!

- Biggest Utilization Losses are due to hop rate, i.e., hop mass in the kettle.
- Biggest Beer Losses are due to hop mass in whirlpool and fermenter. (1 kg => 10 L)
- Hop Creep is due to enzymes in hop mass in fermenter.
- What if you didn't have the hop mass?
  - New Belgium/Haas found improved aromas with CO_2 extracts compared to pellets in whirpool – more fruit, less catty, onion/garlic.[11]

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Bitterness Summary

- The IBU is still relevant, you just have to know what it means.
- Hopping Rate has a <u>huge</u> impact on hop utilization.
- Total IBUs has a <u>big</u> impact on hop utilization. (~100 IBU max)
- Temperature has a <u>big</u> impact on isomerization rate and utilization.

Aroma Summary

- Harvest Time affects best hop usage.
- Boil hopping causes chemical transformation of hydrocarbons to noble hop character.
- Whirlpool hopping and dry hopping adds humulinones and essential oils.
  - Limited isomerization, f(temperature).
  - Raw materials for biotransformation.
  - Dry hopping at beginning of fermentation seems to reduce cattiness and onion/garlic.

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