Hop Quality – A Brewer's Perspective

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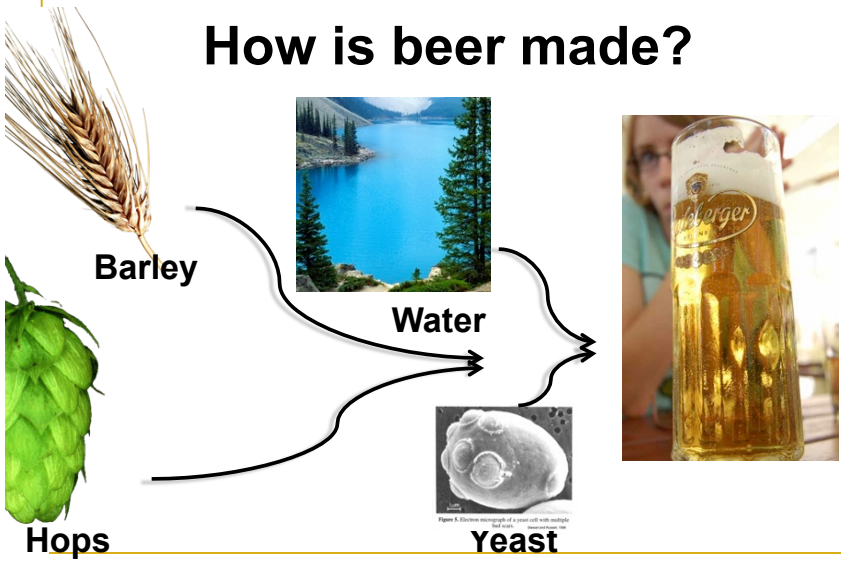
How is beer made?



Barley Malting

- Steeping - grain hydration

- Germination – kernel modification
  - Enzymes produced that will be used by brewers

- Kilning – color & aroma

Inside the brewery

Mashing ➔ Boiling ➔ Fermenting ➔ Finishing ➔ Packaging

Mashing

From M. Jackson. 1993. Beer Companion

Boiling

From Krones Inc, 2001. The Way to Good Beer

Large copper kettle

Hops
humulus lupulus

Lupulin glands

Fermentation

From M. Jackson. 1993. Beer Companion

Finishing

- Maturation
- Carbonation
- Filtration
- Packaging

Where are hops added?

On the hot side

- To boiling wort
  - At the beginning (primarily for bitterness)
  - At the end (primarily for aroma)
  - After boiling but right before cooling (just aroma)

On the cold side – dry hopping

- To beer
  - Solely for aroma

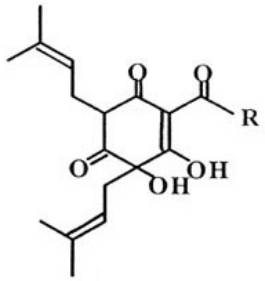
Lupulin glands

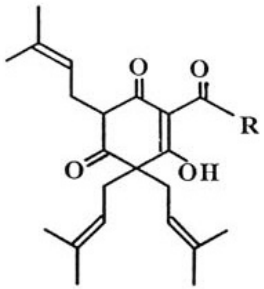
Hops composition

Principle Components	Concentration (%w/w)
Cellulose + lignin	40.0 - 50.0
Protein	15.0
Alpha acids	2.0 - 17.0
Beta acids	2.0 - 10.0
Water	8.0 - 12.0
Minerals	8.0
Polyphenols and tannins	3.0 - 6.0
Lipids and fatty acids	1.0 - 5.0
Hop oil	0.5 - 3.0
Monosaccharides	2.0
Pectin	2.0

European Brewery Convention *Hops and Hop Products, Manual of Good Practice*; Getranke - Fachverlag Hans Carl: Nurnberg, Germany, 1997.

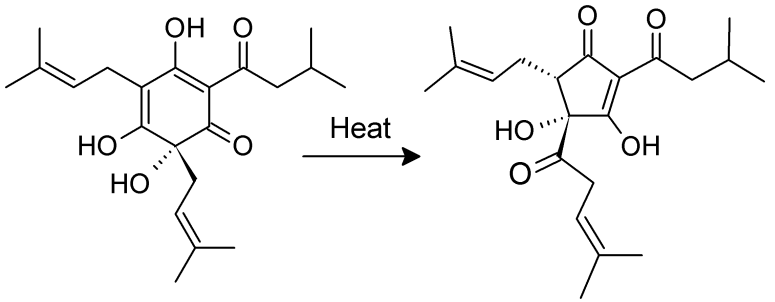
Hop Acids – α & β Acids





α-Acids	R	β-acids
Humulone	$-CH_2CH(CH_3)_2$	Lupulone
Cohumulone	$-CH(CH_3)_2$	Colupulone
Adhumulone	$-CH(CH_3)CH_2CH_3$	Adlupulone

The most important reaction in hop chemistry?



Alpha acid: Humulone

Iso-alpha acid: isohumulone

Analysis of hop resins – in hops

- Conductometric
- Spectrophotometric
- HPLC

Lead conductance value for measuring alpha acids in hops

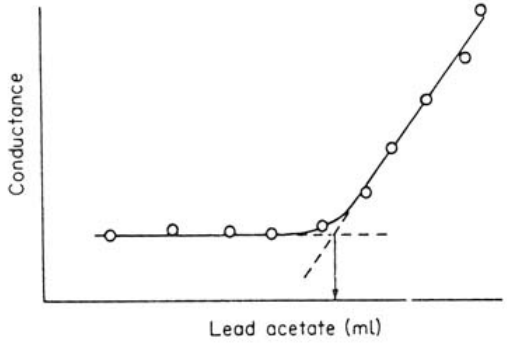


Fig. 2.4 Conductometric titration of α-acids.

Stevens, 1987

UV spectra for methanol extracts of hops

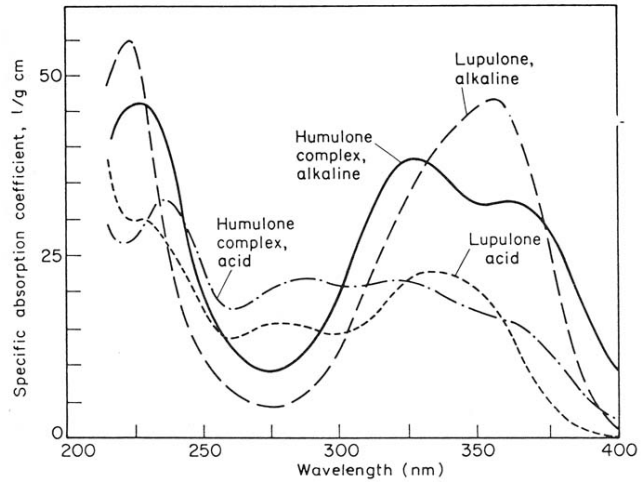


Fig. 2.5. Absorption spectra of lupulone and humulone complex in acidic (0·002 N) and alkaline (0·002 N) methanol.

Stevens, 1987

The Hop Storage Index (HSI)

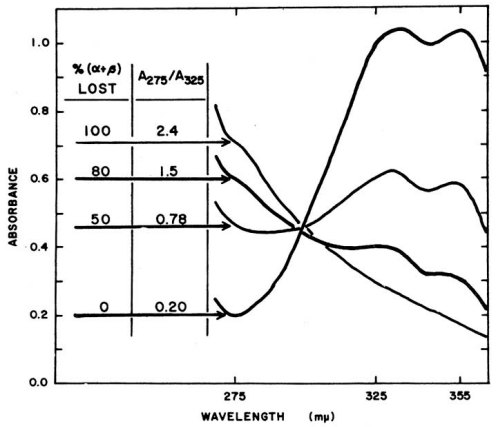


Figure 1. Typical spectra of alkaline methanol solutions obtained from hops in various stages of deterioration. A_{325} decreases as hop acids are oxidized and A_{275} increases as oxidation products accumulate, resulting in proportional increases in A_{275}/A_{325}.

Lickens, et al., 1970

(HSI) = A_{275}/A_{325}

HSI data 1970

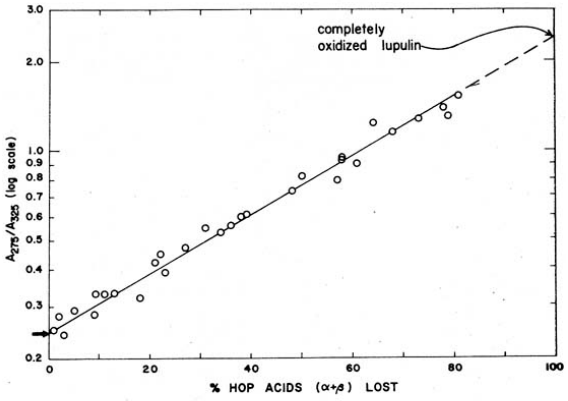
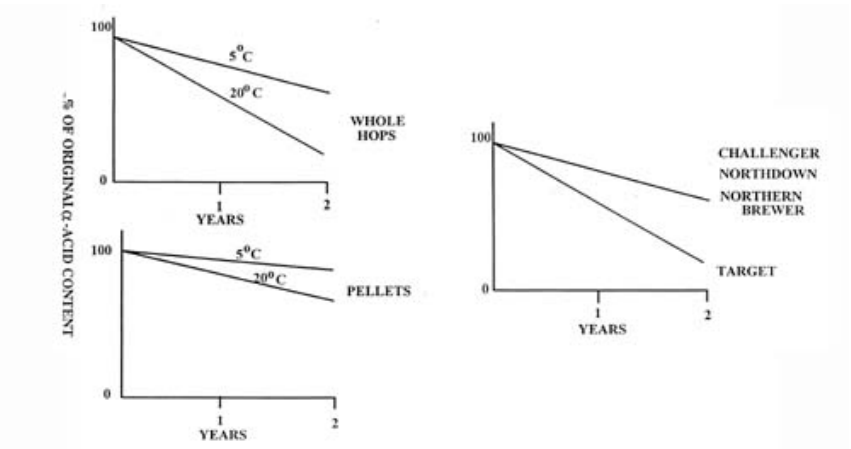


Figure 2. Relationship of deterioration of hop acids to increase of A_{275}/A_{325}. Nine varieties stored 3, 6, and 10 months are represented. The arrow at A_{275}/A_{325} = 0.24 is the average initial value for all varieties. Lupulin was held at elevated temperatures until no further change took place in its absorbtion spectrum: A_{275}/A_{325} = 2.5 and represents 100% loss.

Lickens, et al., 1970

Hop Deterioration During Storage



Bittering can stay constant during storage

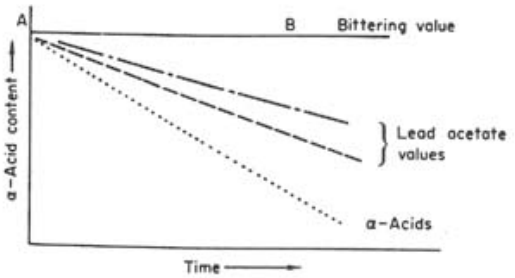


Fig. 2.6. Schematic diagram of changes in resin content and bittering value of hops during storage. .-.-.-, Conductometric analysis using chloroform as extractant;--- Conductometric analysis using toluene as extractant; . . . . Polarimetric analysis.

Stevens, 1987

Abused hops still produce bitter beer

Brews made with an identical amount of cone hops stored 18 months at different temperatures

STORAGE TEMPERATURE	ALPHA ACIDS IN HOPS	ISO-ALPHA ACIDS IN BEER	BEER IBUs
-20F	3.22%	19.8 ppm	13.5
25°F	2.91%	18.1 ppm	12.0
45°F	1.71%	14.4 ppm	13.5
70°F	0.41%	2.9 ppm	11.0

Peacock, 1998

The IBU analysis

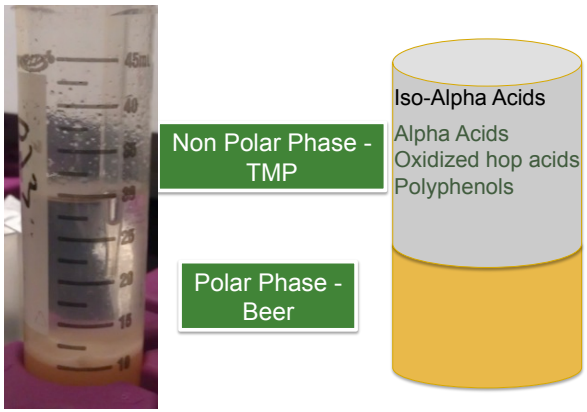
Liquid-Liquid extraction of bitter compounds from beer

Strong Acid		Non-Polar Solvent		Beer
Adds excess hydrogen ions to solution – protonating all carboxylic acid functional groups	+	When functional groups are charged at a lower pH they are more non-polar	+	**Bitter compounds** Iso alpha acids Oxidized hop acids Polyphenols **Non-bitter compounds** Alpha acids
3 N Hydrochloric Acid		**2,2,4 trimethylpentane**		

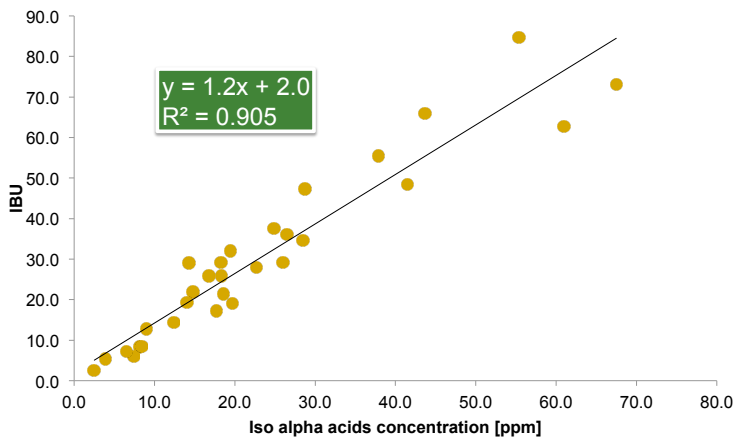
Measure the absorbance at 275 nm
Absorbance @275 x 50 = *Bittering Units*

1 BU ≠ 1 ppm iso-alpha acid

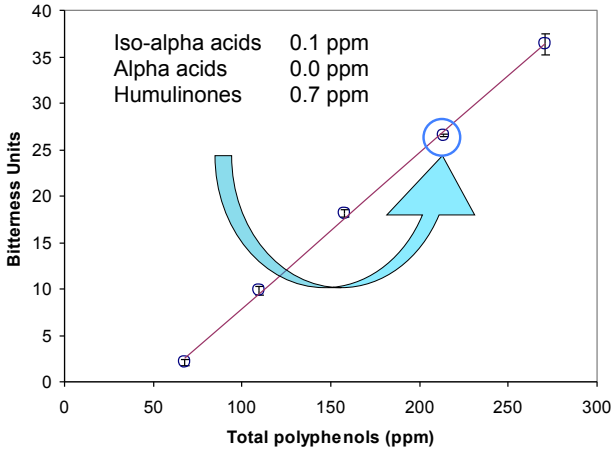
Extraction removes more than just Isos



Correlation between total IAA & IBU



BU increase due to hop polyphenols



Alpha and Iso-Alpha Acids by HPLC

Terminology

Chromatography

The **method** of separation

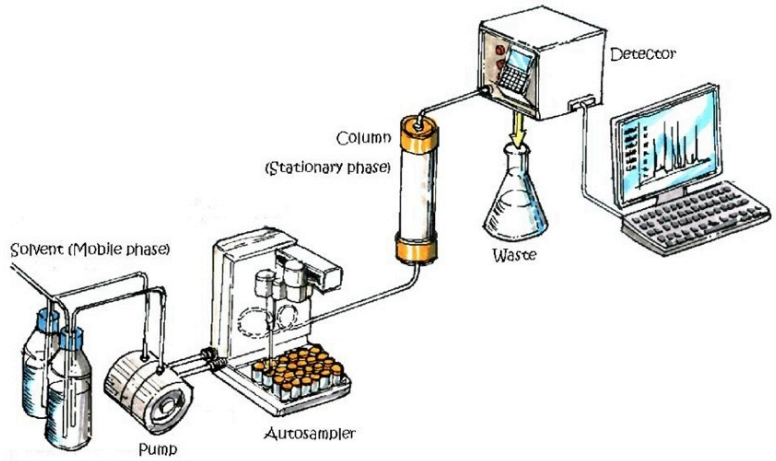
Chromatograph

The **instrument** of separation

Chromatogram

The **visual output** of the separation

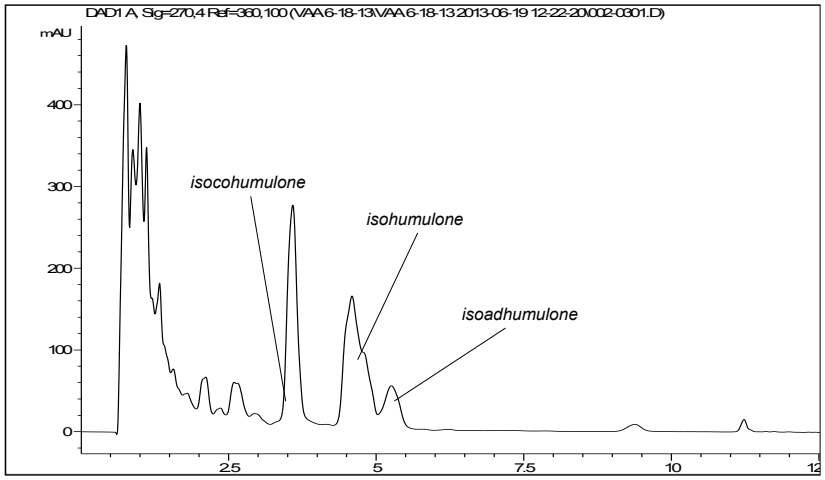
HPLC Process Flow



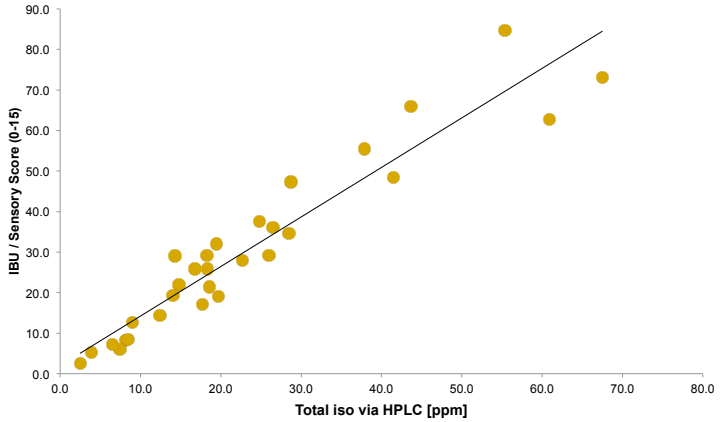
High Performance Liquid Chromatography

- Atmospheric pressure Separation
- Separation variables can be manipulated based on target analyte
- non-volatile analysis

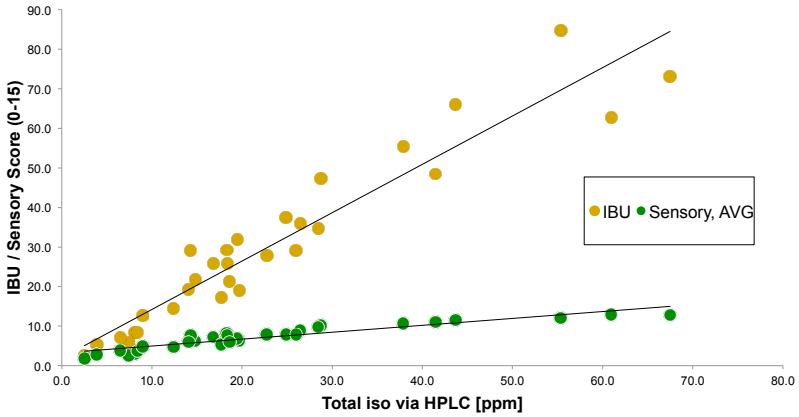
Beer Sample



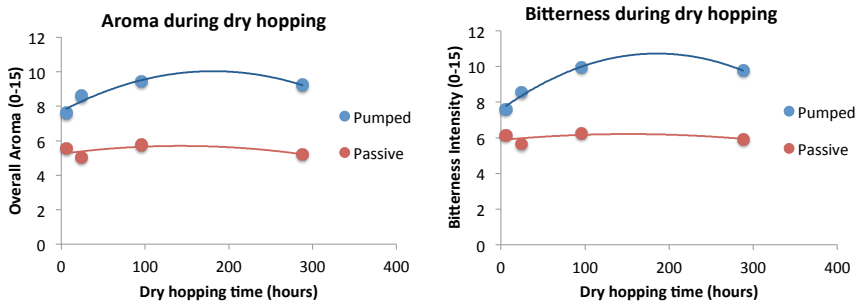
Correlation between total IAA & IBU



Correlation between IAA & IBU & Sensory



Dry hopping study with Cascade pellets



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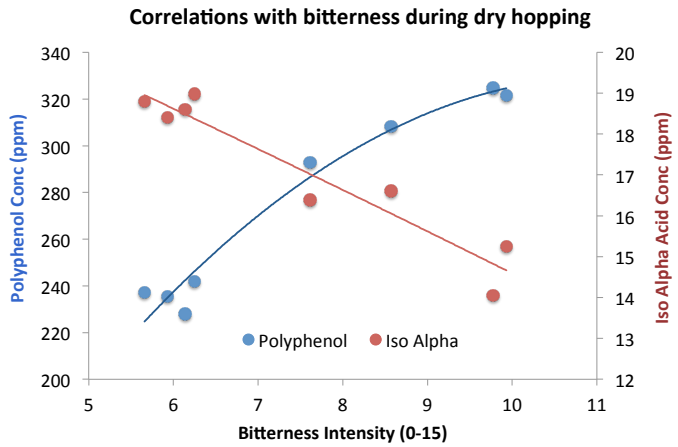

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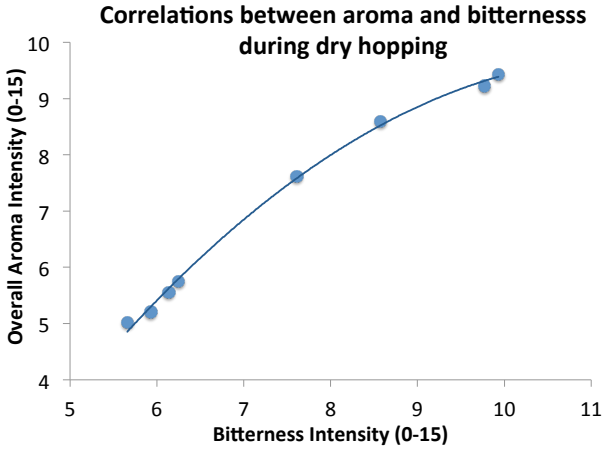

Hop acids quality

- Total alpha acids are important
- HSI is important
- Cohumulone – not important
  - Shellhammer's opinion
- The IBU measures more than Isos
  - 1 BU ≠ 1 ppm Iso alpha acids

Hops composition

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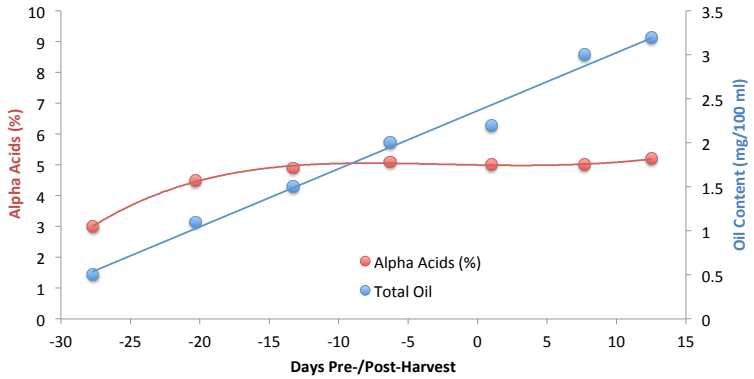
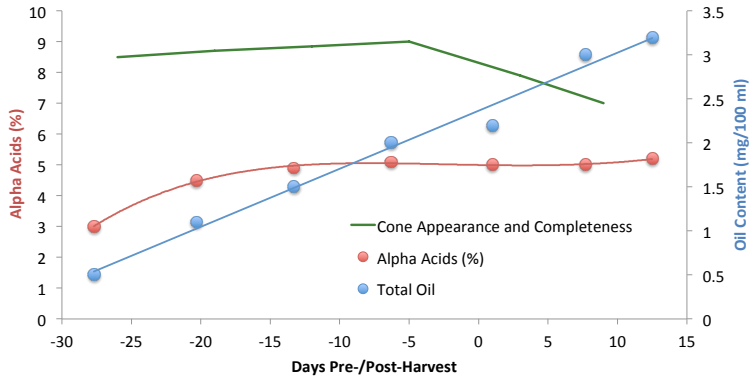
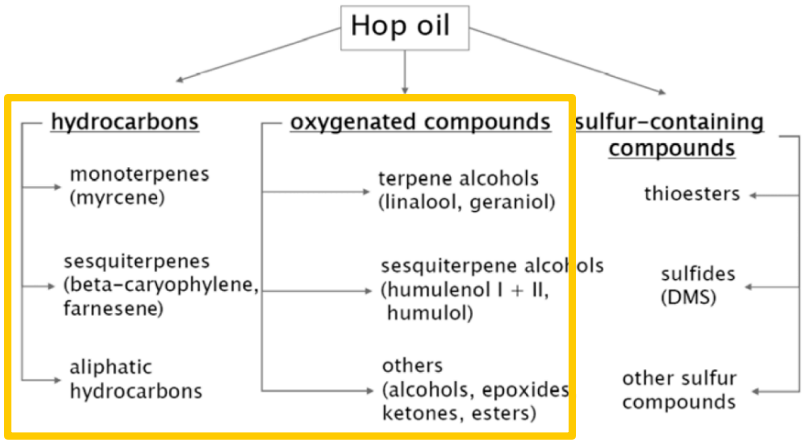
Mt. Hood Maturity Study (Probasco)



Mt. Hood Maturity Study (Probasco)



Hop Oil Composition



Schönberger, C.; Kostelecky, T. 125th Anniversary Review: The Role of Hops in Brewing. *J. Inst. Brew* **2011**, *117*, 259–267.

Hop Oil Compounds by Flavor Grouping

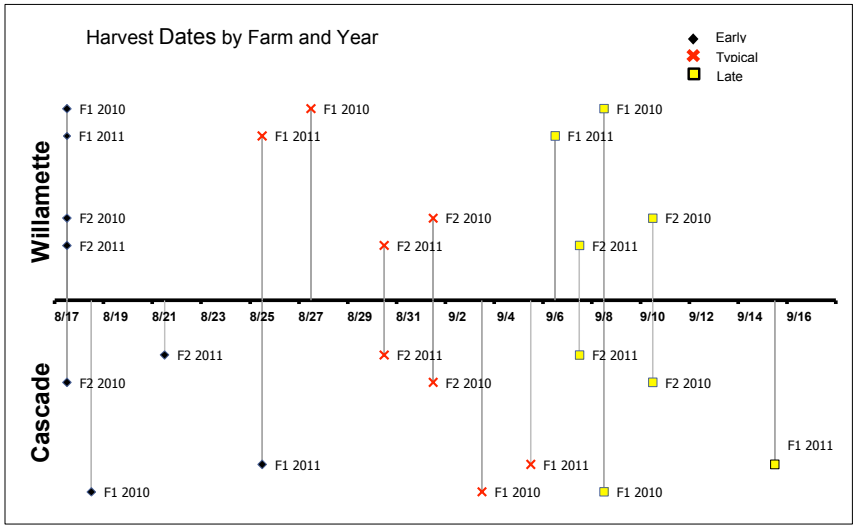
Major Hydrocarbons	Oxidation Products	Floral Compounds	Citrus Compounds
β-Pinene	Caryophyllene epoxide	Geranyl acetate	Limonene
Myrcene	Caryolan-1-ol	Geranyl isobutyrate	Citral
β-Caryophyllene	Humulene monoepoxide I	Geraniol	Cadinene
Farnesene	Humulene monoepoxide II	Linalool	Nerol
α-Humulene	Humulene monoepoxide III		Limonen-10-ol
	Humulene diepoxide A		
	Humulene diepoxide B		
	Humulene diepoxide C		
	Humulenol II		
	Nerolidol		

Note: The major hydrocarbons group of compounds do not survive brewkettle boil nor fermentation and are therefore unimportant to beer flavor. The oxidation products group of compounds are thought to be the "noble aroma," herbal, and spicy beer flavor contributions. The floral and citrus groups contribute similar flavors to finished beer.

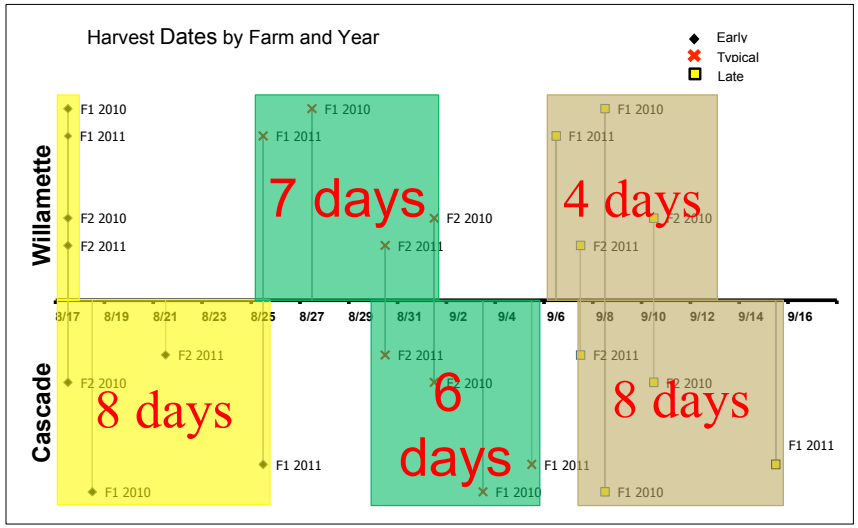
Hop Oil Compounds of Interest

Compound Name	Classification	Description
α-pinene	Hydrocarbon, Monoterpene	Pine
β-pinene	Hydrocarbon, Monoterpne	Confierous Pine, woody
β-Myrcene	Hydrocarbon, Monoterpene	Green, balsam, slightly metallic
Limonene	Hydrocarbon, Monoterpene	Citrus, Orange
ρ-cymene	Hydrocarbon, Monoterpene like	Orange, Woody, Spicy
Caryophyllene	Hydrocarbon, Sesquiterpene	Woody, Carrot
E, β -Farnesene	Hydrocarbon, Sesquiterpene	Green, woody, weedy, herbal, pine and gin
Humulene	Hydrocarbon, Sesquiterpene	Woody
Methyl heptonoate	Oxygenated, Ester	Sweet, fruity, peach, apricot, green, berry
Geraniol	Oxygenated, Monoterpene Alcohol	Sweet floral, perfumy
Linalool	Oxygenated, Monoterpene Alcohol	Floral, Orange
Citronellol	Oxygenated, Monoterpene	Floral, Rose Citrus
Farnesol	Oxygenated, Sesquiterpene Alcohol	Spicy
Citral	Oxygenated, other	Sweet Citrus
Geranyl Acetate	Oxygenated, Monoterpene or ester	Floral, Sweet Citrus
Humulene Epoxide I	Oxygenated, Epoxide	Hay-like
Humulene Epoxide 2	Oxygenated, Epoxide	Cedar, Lime

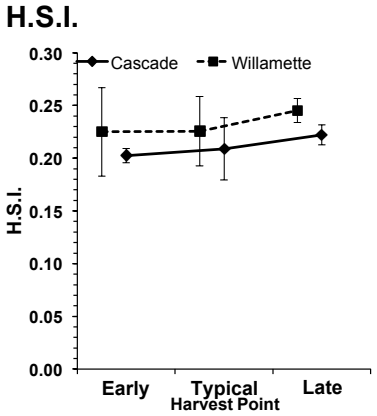
Harvest Timeline

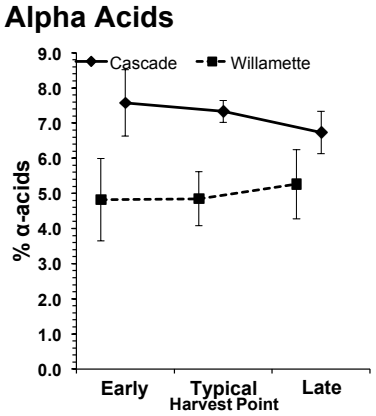


Harvest Timeline

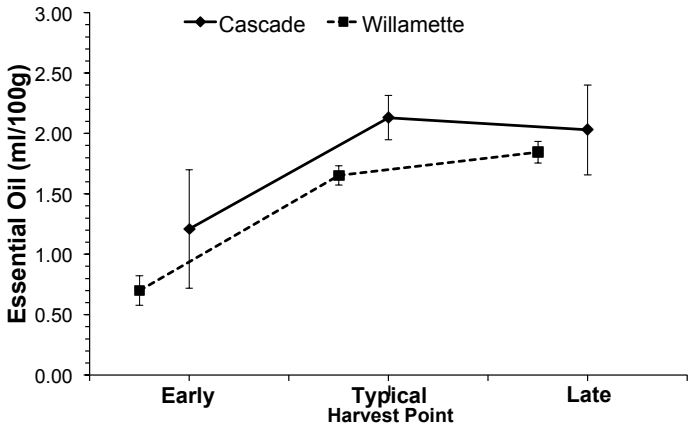


Traditional Brewing Quality Parameters

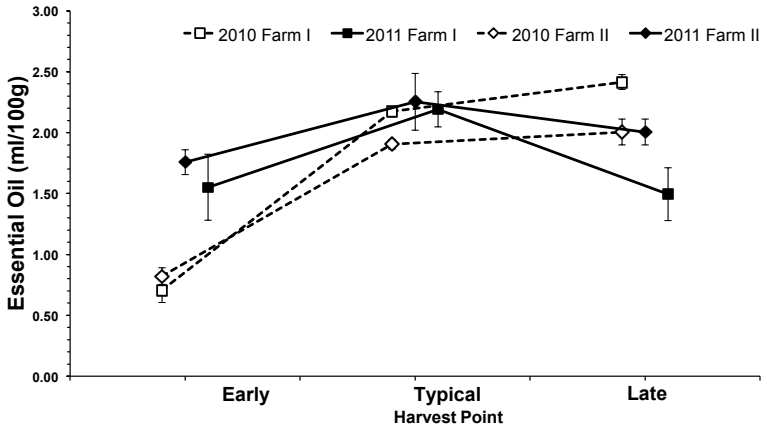




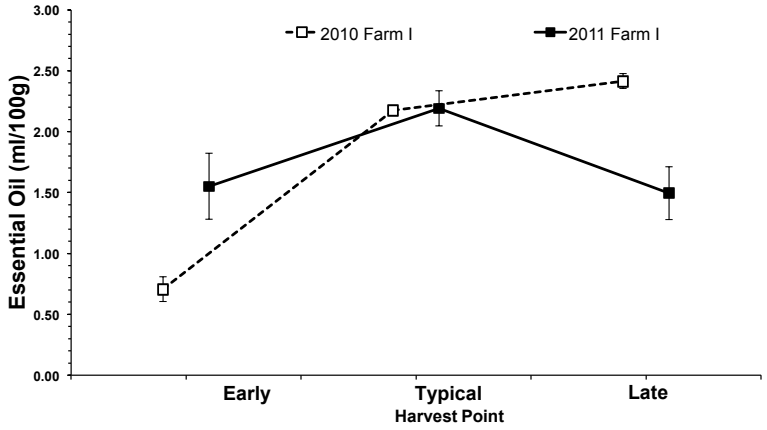
Total Essential Oil



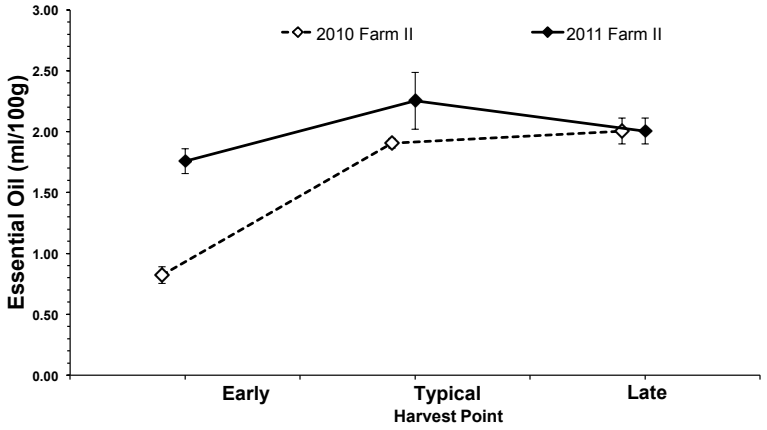
Cascade Essential Oil



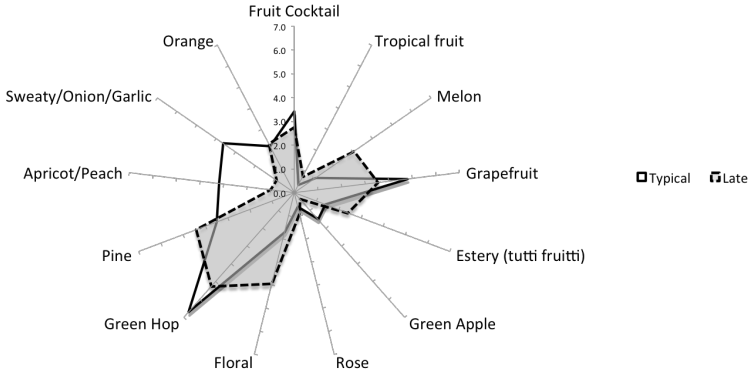
Cascade Essential Oil



Cascade Essential Oil



Preliminary brewing: Cascade



- Typical harvest hops = apple, apricot/peach, and sweaty/onion/garlic notes.
- Late harvest hops = higher melon and floral notes.

Timing of hop addition and flavor impact

- Bitterness a function of alpha and boil time
- Aromatic level is a function of volatilization

	Floral	Citrus	Spicy	Resinous
Kettle hop	+	+		
Late hop	++	++	++	
Dry hop	+++	+++	+++	+

Oil quantity and quality

- Maturity influences both
- Hop processing influences both
  - Drying
  - Pelletizing
  - Storage conditions
- Hop aroma is tied to hop oil