



Formation of Humulinones in Hops & Hop Pellets and Its Implication for Dry Hopped Beers

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What Are Humulinones

How Humulinones Form & Their Concentrations In Hops and Hop Pellets and Dry Hopped Beers

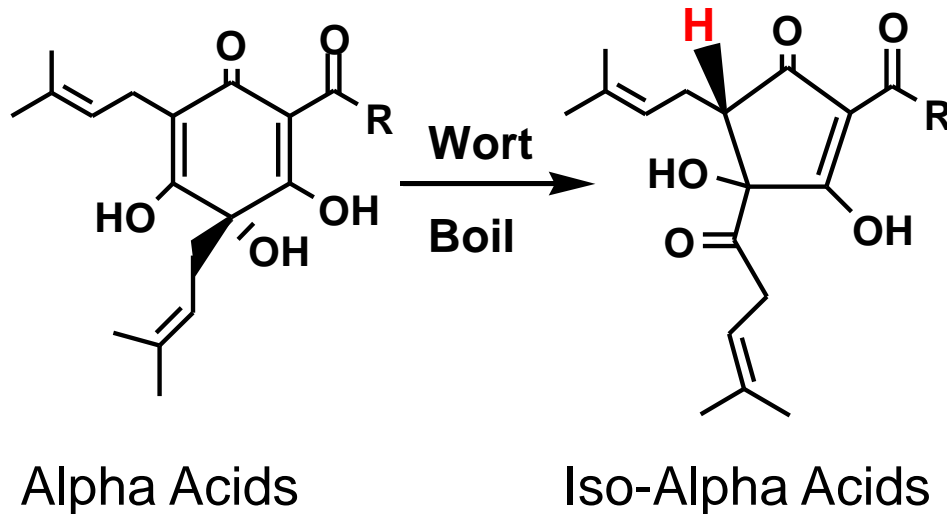
Dry Hopping Experiments

Humulinones and Other Non-Volatile Hop Compounds That Dissolve in Dry Hopped Beers

Conclusion

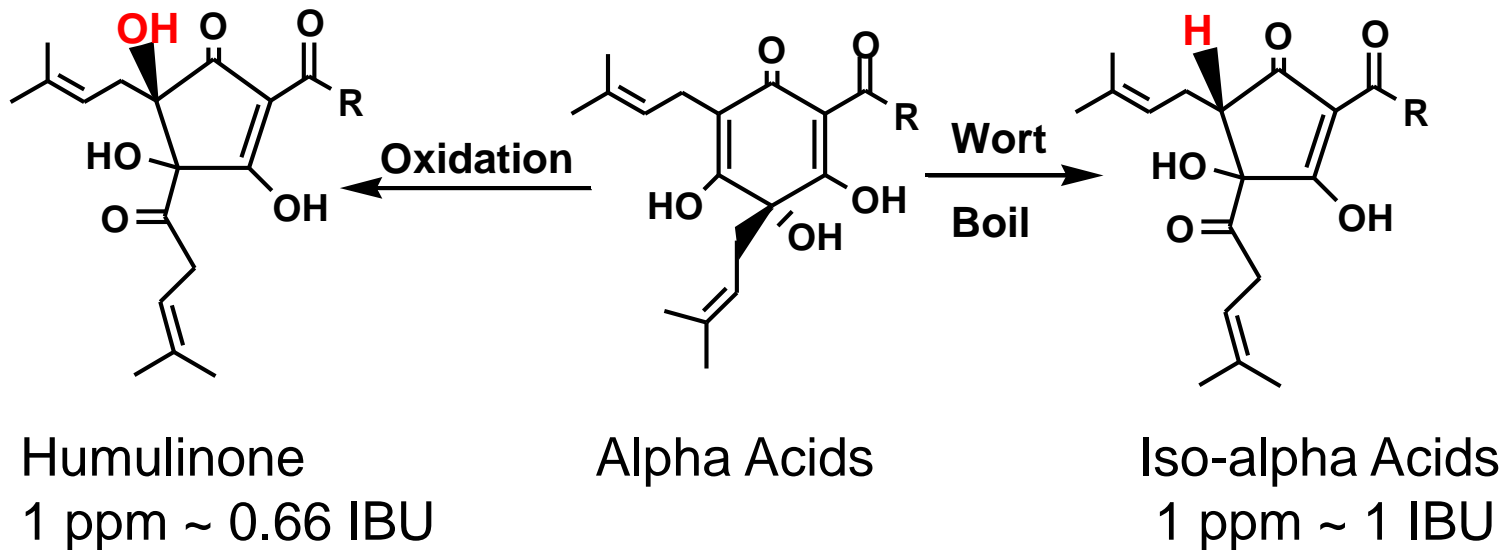


The Best Way to Appreciate Humulinones is to Recall Iso-Alpha Acids

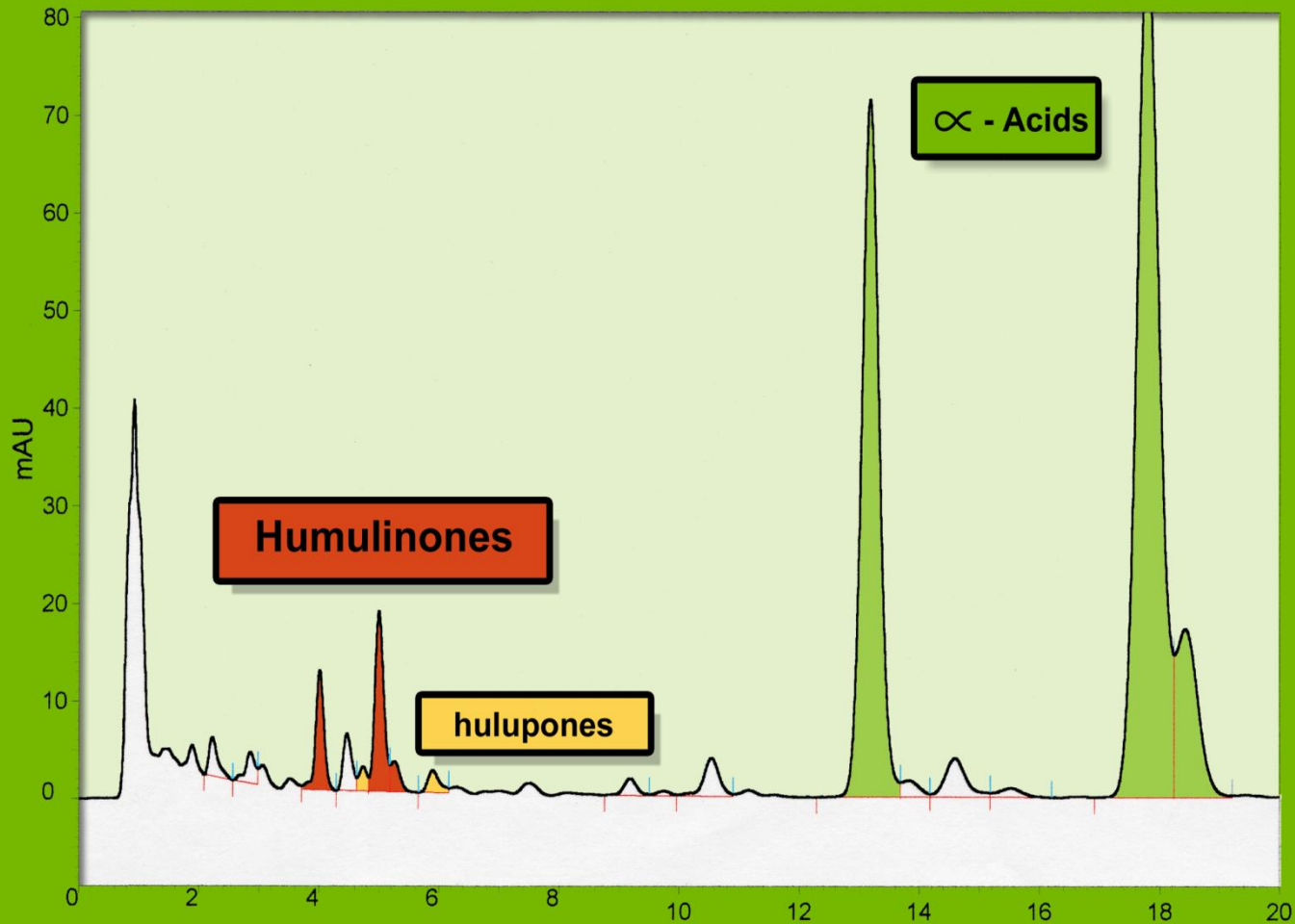




Humulinones Are Extremely Similar In Molecular Structure to Iso-Alpha Acids But Are Formed By Alpha Acid Oxidation

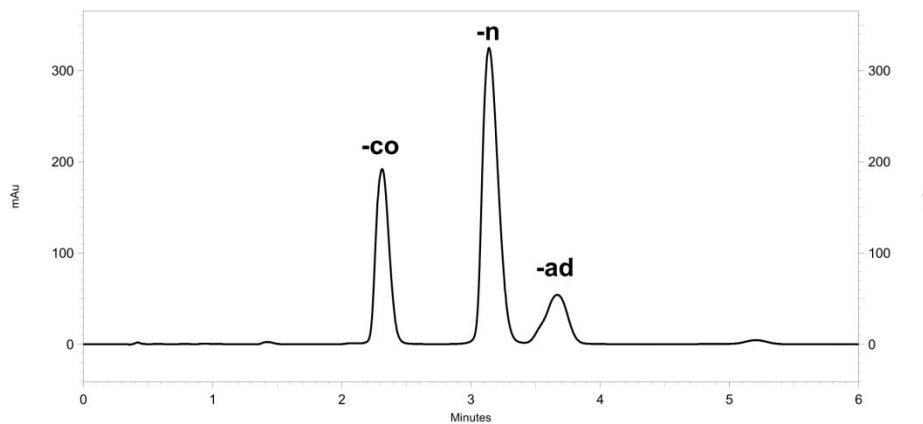
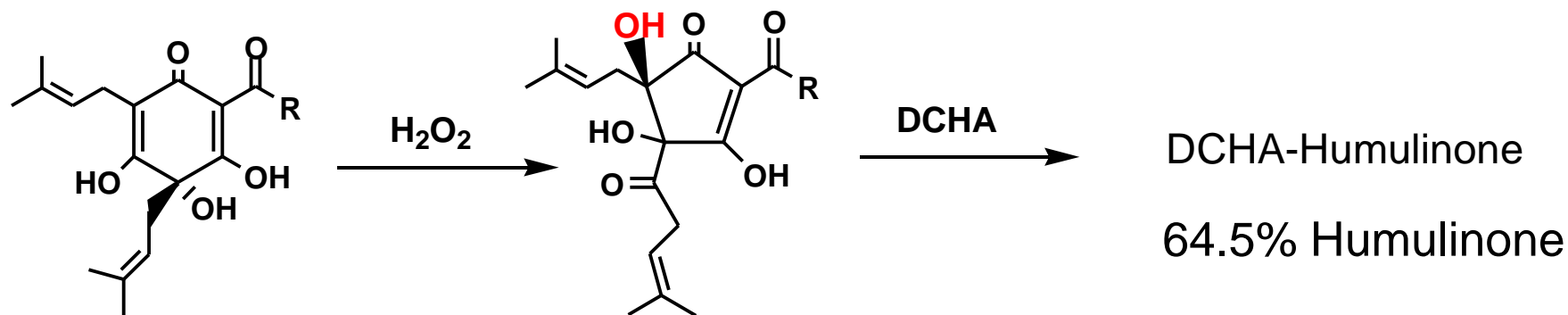


Humulinones are more polar than isoalpha acids and reported to be 66% as bitter as isoalpha acids.



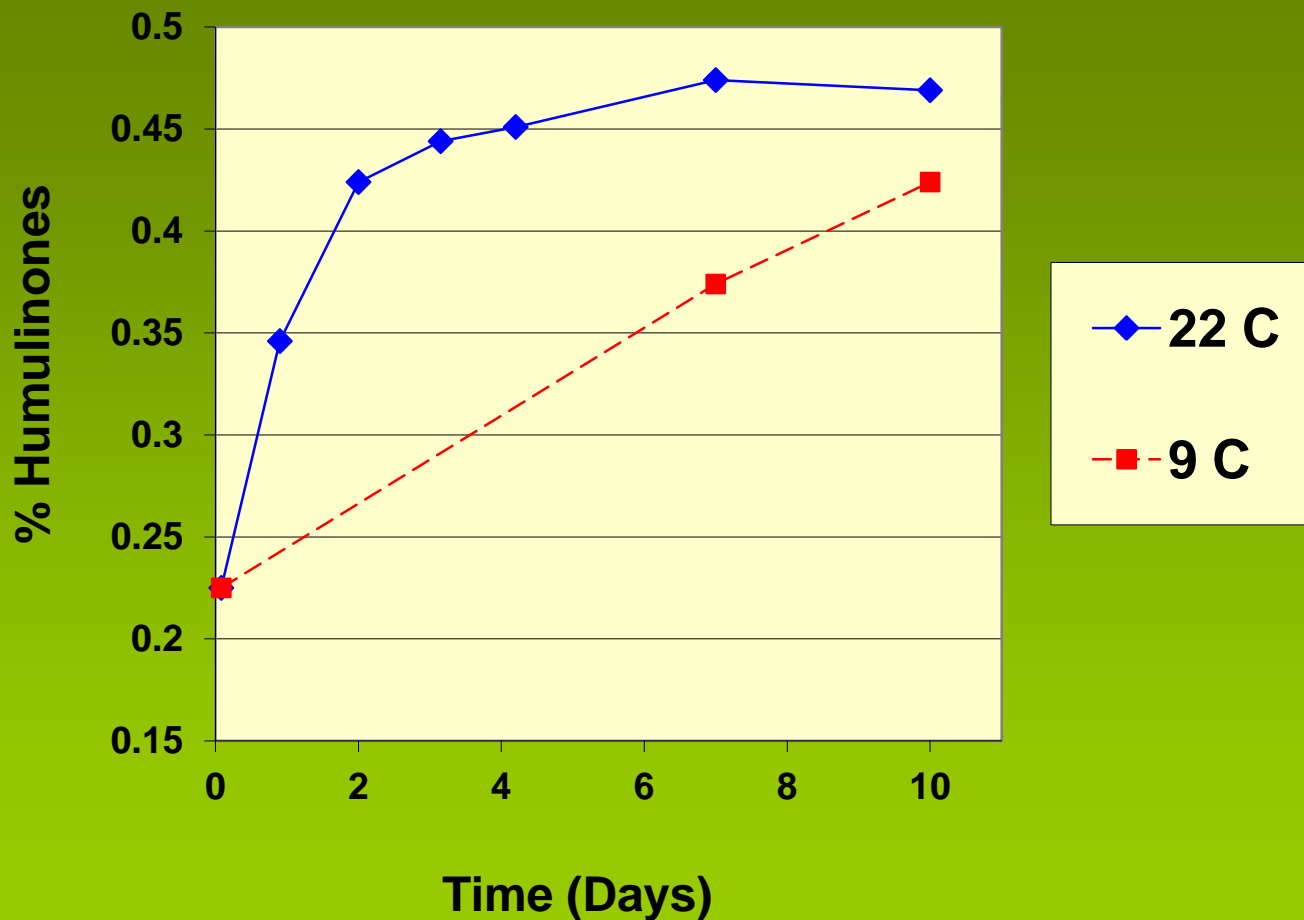


Preparation of Dicyclohexylamine Humulinone An HPLC Calibration Standard



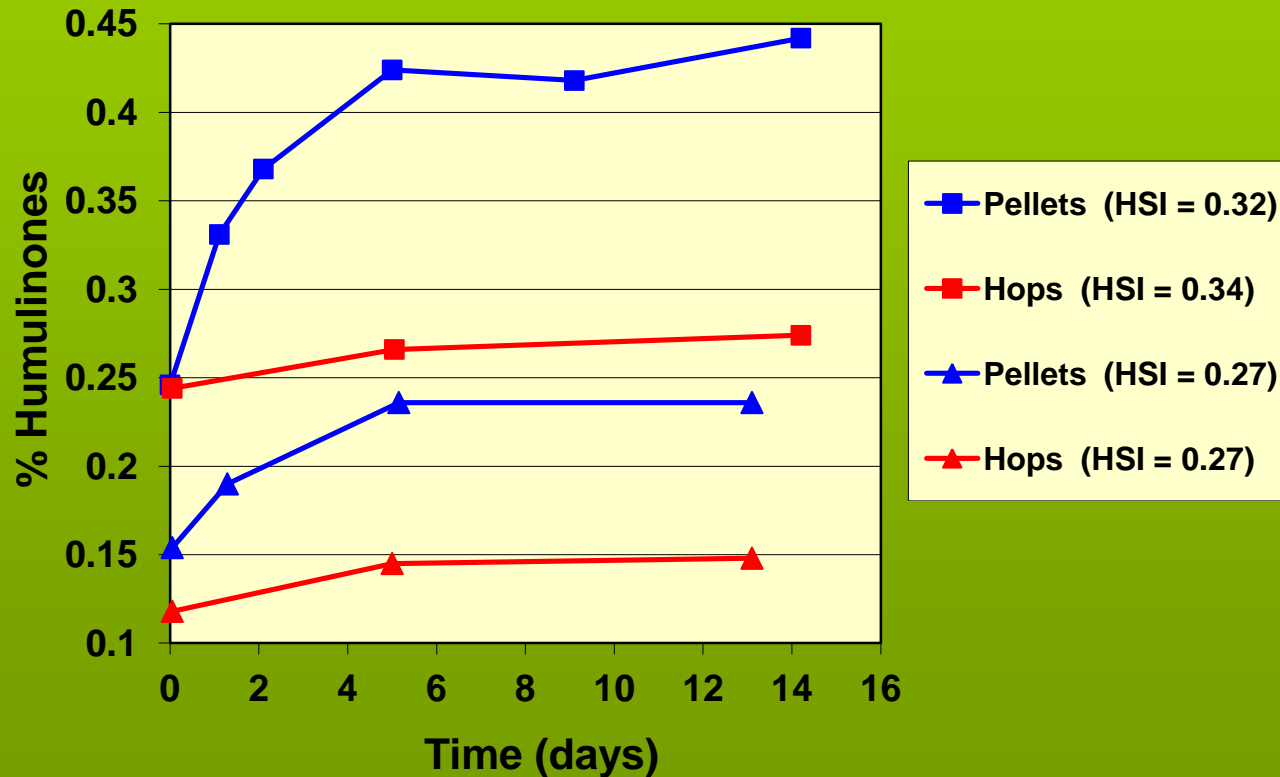


Humulinone Formation in Zeus Hop Pellets vs Temp



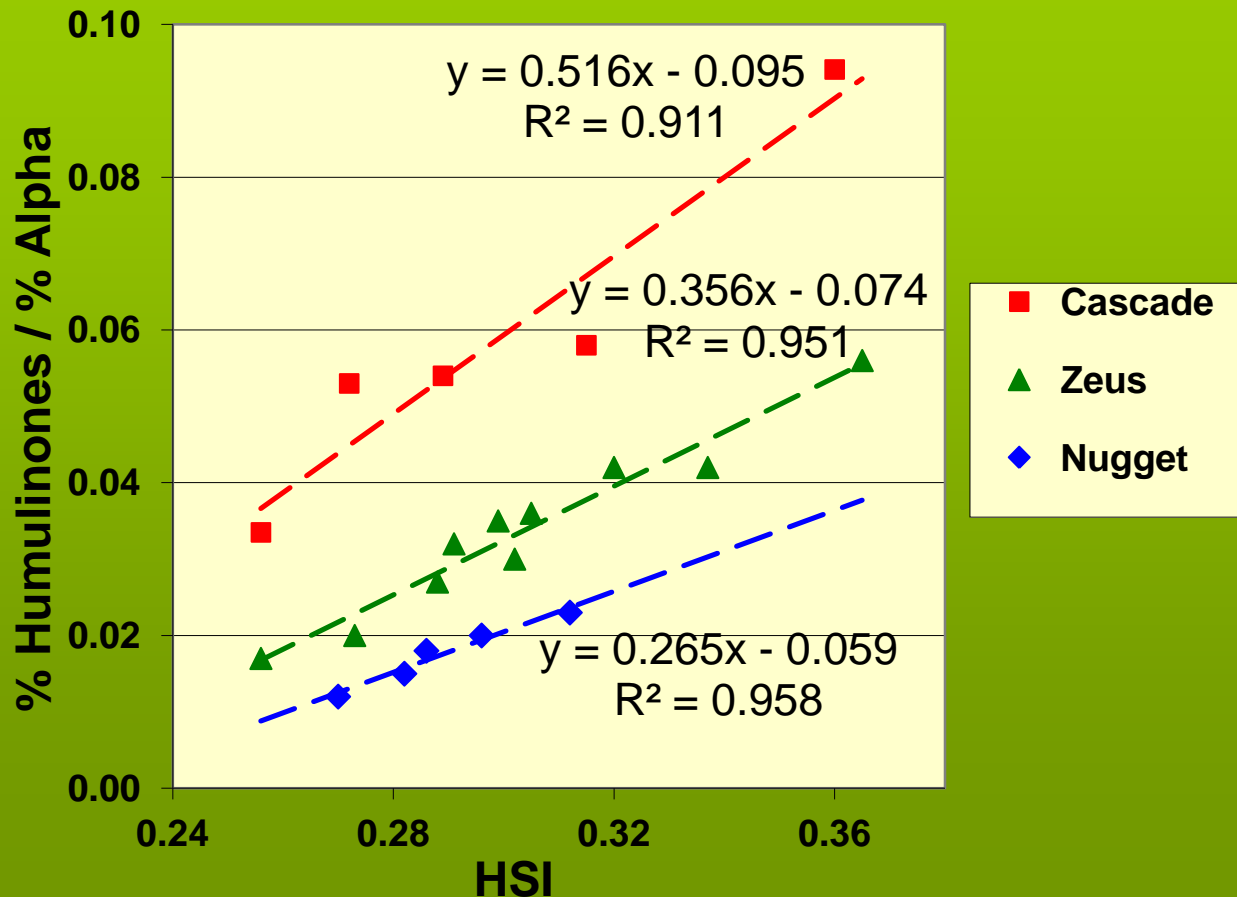


Humulinone Formation is Greater in High HSI Hops and Hop Pellets vs Low HSI





The Linear Relationship of HSI to %Humulinones ÷ %Alpha-Acids



Using this data one can estimate the amount of humulinones in hop pellets if one knows the HSI and Alpha Acid concentration !

This is variety dependent.



What Causes Alpha Acids to Oxidize to Form Humulinones? And Why do Humulinones Increase After Pelleting?

Oxygen

Oxidized Fatty Acids

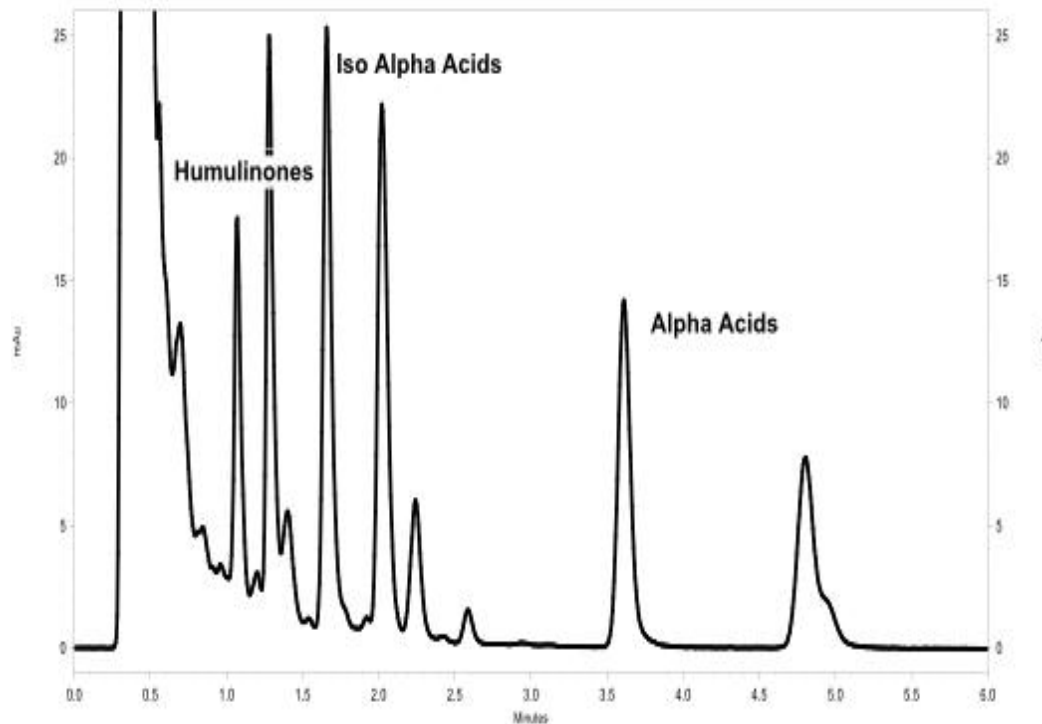
Iron

Hydrogen Peroxide



Humulinone Concentration in Dry Hopped Beers

We analyzed 29 commercial IPA's and found the Humulinone concentration to range from 3 ppm to 24 ppm = ~ 2 to ~16 IBU





Question # 1:

What percent of humulinones in hop pellets get into beer when one dry hops?



Dry Hopping Experiment #1 Humulinone Utilization

Conditions:

Centennial hop pellets assayed 0.35 w/w% Humulinone the day of dry hopping.

Dose Rate: 0, 0.5, 1.0, and 2.0 lbs/barrel

Hop pellets were simply dumped on top of the beer.

Beer Type: Low IBU and High IBU

Temperature of dry hopping, 16 °C

Contact Time: 5 Days



Centennial hop pellets assaying 0.35% Humulinone were added to a low and high IBU beer and dry hopped for 5 days

Sample	lbs pellets Barrel of beer	ppm of Humulinone in beer	% Utilization Humulinone	ppm of Iso-a-acid in beer	*Calculated Bitterness Intensity
Low IBU Beer (8.6)	0	0.8	-	8.6	9.1
	0.5	8	98	8.1	13
	1.0	14	91	7.9	17
	2.0	28	88	7.5	26
High IBU Beer (48)	0	1	-	48	49
	0.5	8	98	39	44
	1.0	14	91	35	44
	2.0	27	87	30	47

*Calculated bitterness = (0.66 x ppm Humulinone) + ppm isoalpha acids



Question #2:

How fast does humulinone dissolve into beer?

How fast are isoalpha acids lost?

What else dissolved into beer when one dry hops?



Dry Hop Experiment #2

What Dissolves Into Beer and How Fast?

Cascade Hop Pellets

Compound	Concentration, %
Alpha acids (ICE-3)	5.6
Beta acids (ICE-3)	5.8
Humulinones (DCHA humulinones, 65.9%)	0.26
Xanthohumol (99.7% pure, in-house std)	0.26
Hulupones (DCHA hulupones, 67.0%)	0.05

54 IBU All Malt Beer

Dry Hop Dose Rate: 0, 0.5, 1.0, 2.0 lbs per barrel

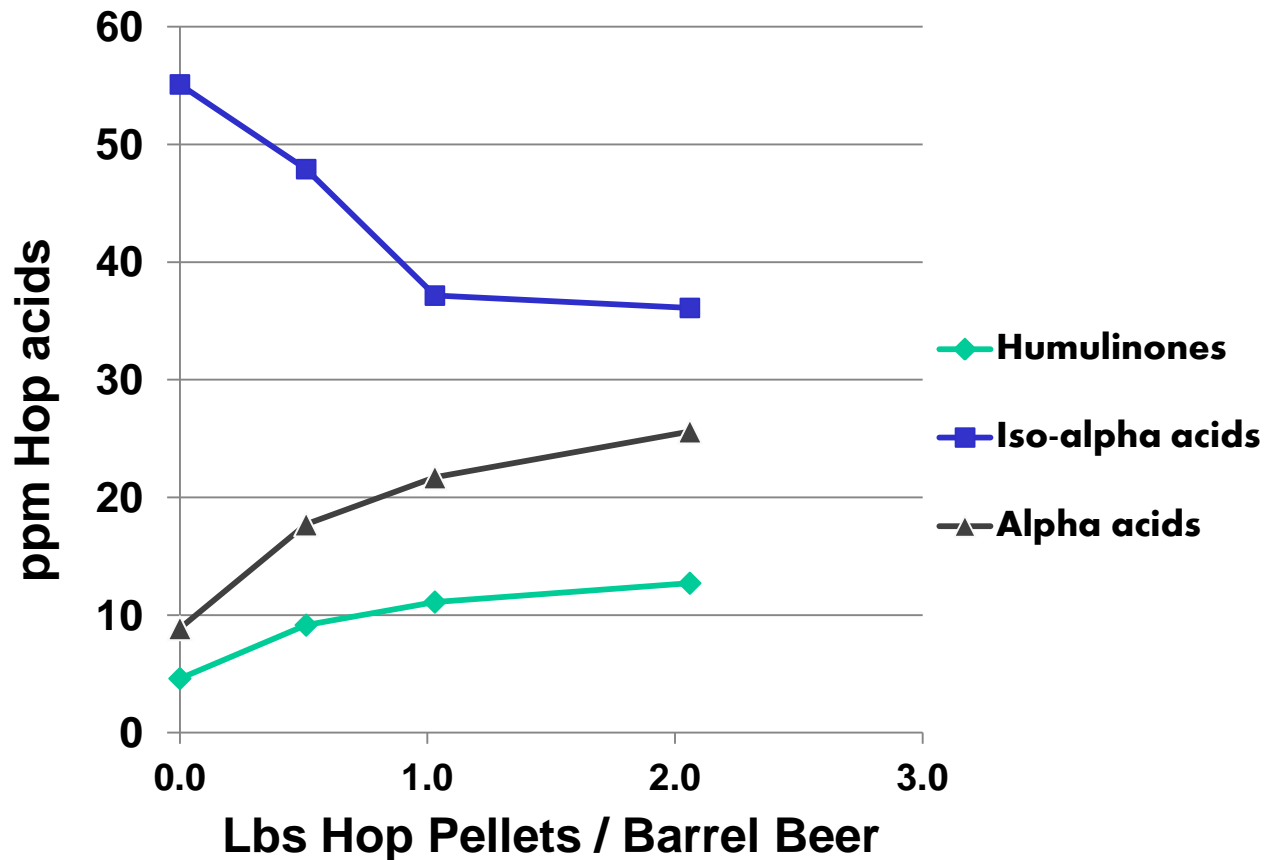
Contact Time: 1, 2, 5 days

Dry Hop Temperature: 16 °C

All Results Reported by HPLC



Concentration of Hop Acids After One Day of Dry Hopping



1 lb/barrel (Day 1)

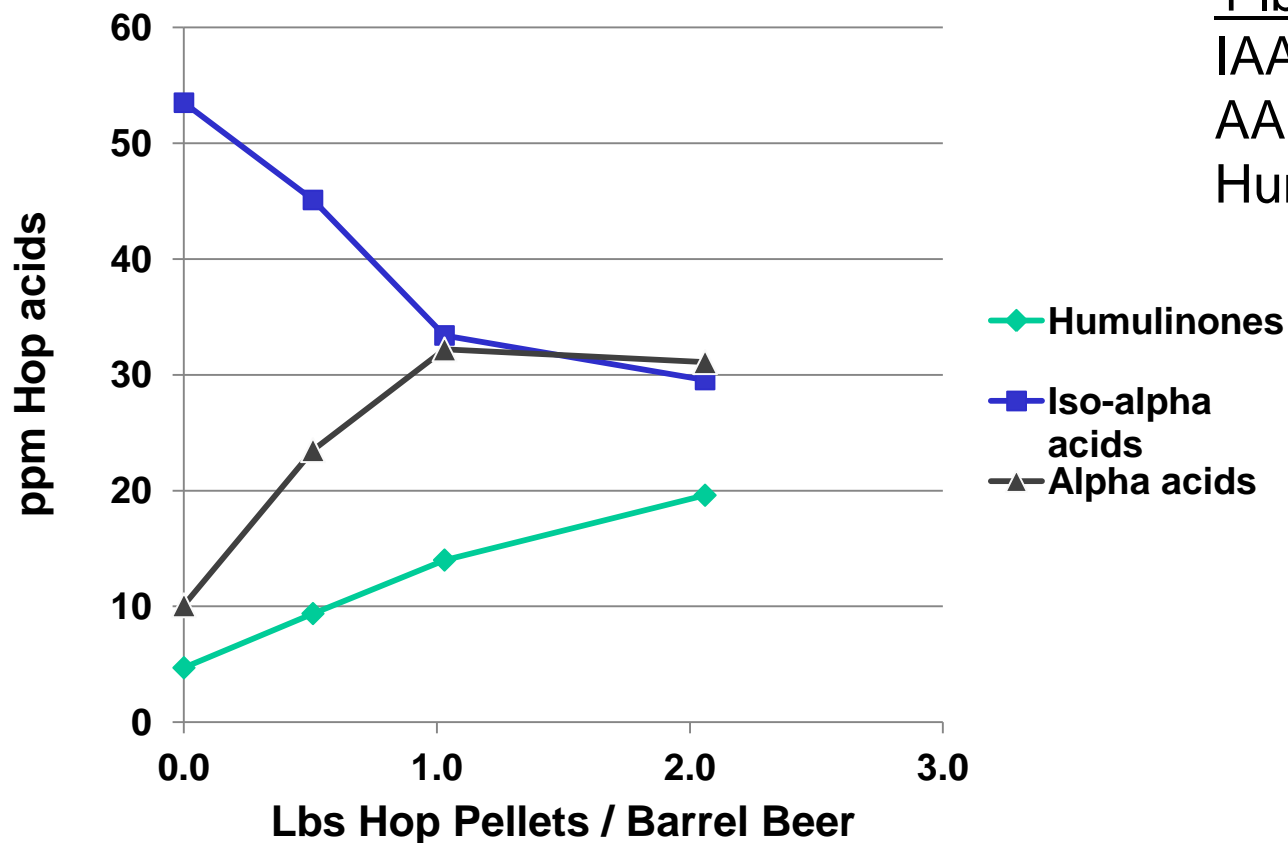
IAA 37 ppm

AA 21 ppm

Hum 11 ppm



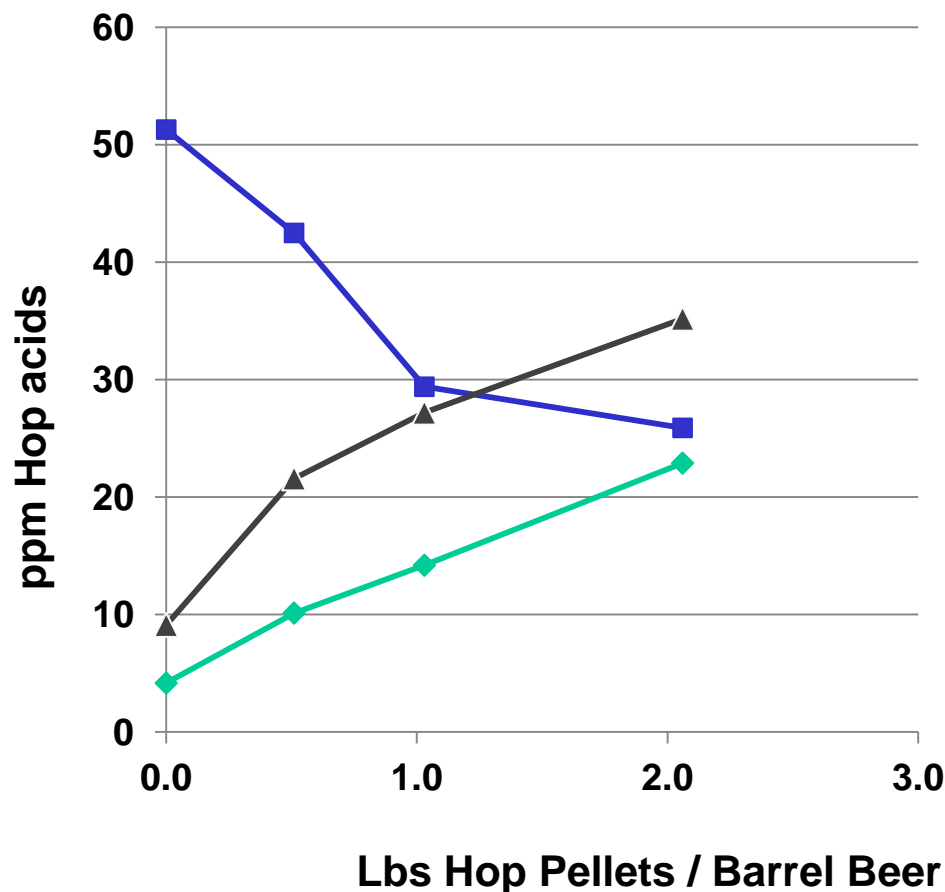
Concentration of Hop Acids After 2 Days of Dry Hopping



Day 2	
1 lb/barrel	(Day 1)
IAA 32 ppm	(37 ppm)
AA 31 ppm	(21 ppm)
Hum 15 ppm	(11 ppm)



Concentration of Hop acids After 5 Days of Dry Hopping



	Day 5	(Day 2)	(Day 1)
1 lb/barrel			
IAA	29 ppm	(32 ppm)	(37 ppm)
AA	28 ppm	(31 ppm)	(21 ppm)
Hum	15ppm	(15 ppm)	(11 ppm)

- ◆ Humulinones
- Iso-alpha acids
- ▲ Alpha acids



HPLC Analysis of Beers Dry Hopped for 5 Days with Cascade Hop Pellets

Lbs Hops per BBL	PPM Iso- α -acid	PPM Alpha Acids	PPM Hum	PPM XN	% Utilization			
					Iso- α	α -acid	Hum	XN
0	51.3	9	4.2	0.24	-	-	-	-
0.5	42.5	21.6	10	0.62	- 17%	11%	100%	12%
1.0	29.4	27	14	0.79	- 43%	8%	97%	8%
2.0	25.9	35	23	0.79	- 49%	6%	90%	4%

Note: No Beta Acids were seen in any of the dry hopped beers.



Calculated Bitterness For Dry Hopping with Cascade Hop Pellets For Five Days

Lbs Hops per BBL	PPM of Iso-a-acid	PPM of Humulinone	Calculated Bitterness*
0	51.3	4.2	54.1
0.5	42.5	10	49.1
1.0	29.4	14	38.6
2.0	25.9	23	41.1

* Calculated Bitterness = ppm IAA + (0.66 x ppm Humulinone)



Question # 3:

Is there a sweet-spot or an IBU above which dry hopping reduces bitterness and below which dry hopping increases bitterness?



Dry Hopping Experiment #3

Dry Hop Beers With Different IBU's

Cascade Hop Pellets with 0.25% Humulinones

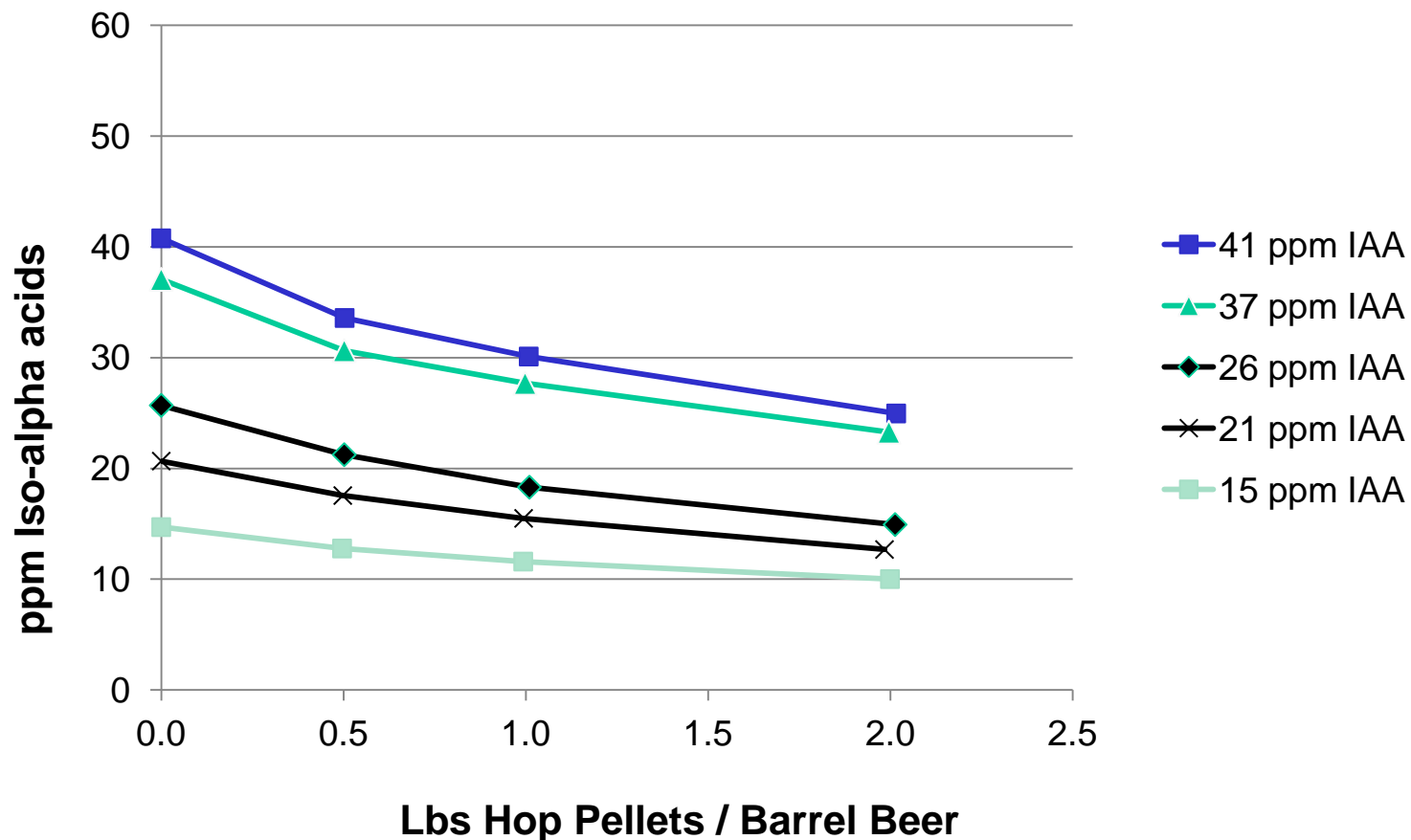
Dose Rate: 0.5, 1.0, 2.0 lbs/barrel

Contact Time: 3 Days

Dry Hop Temperature: 16 °C

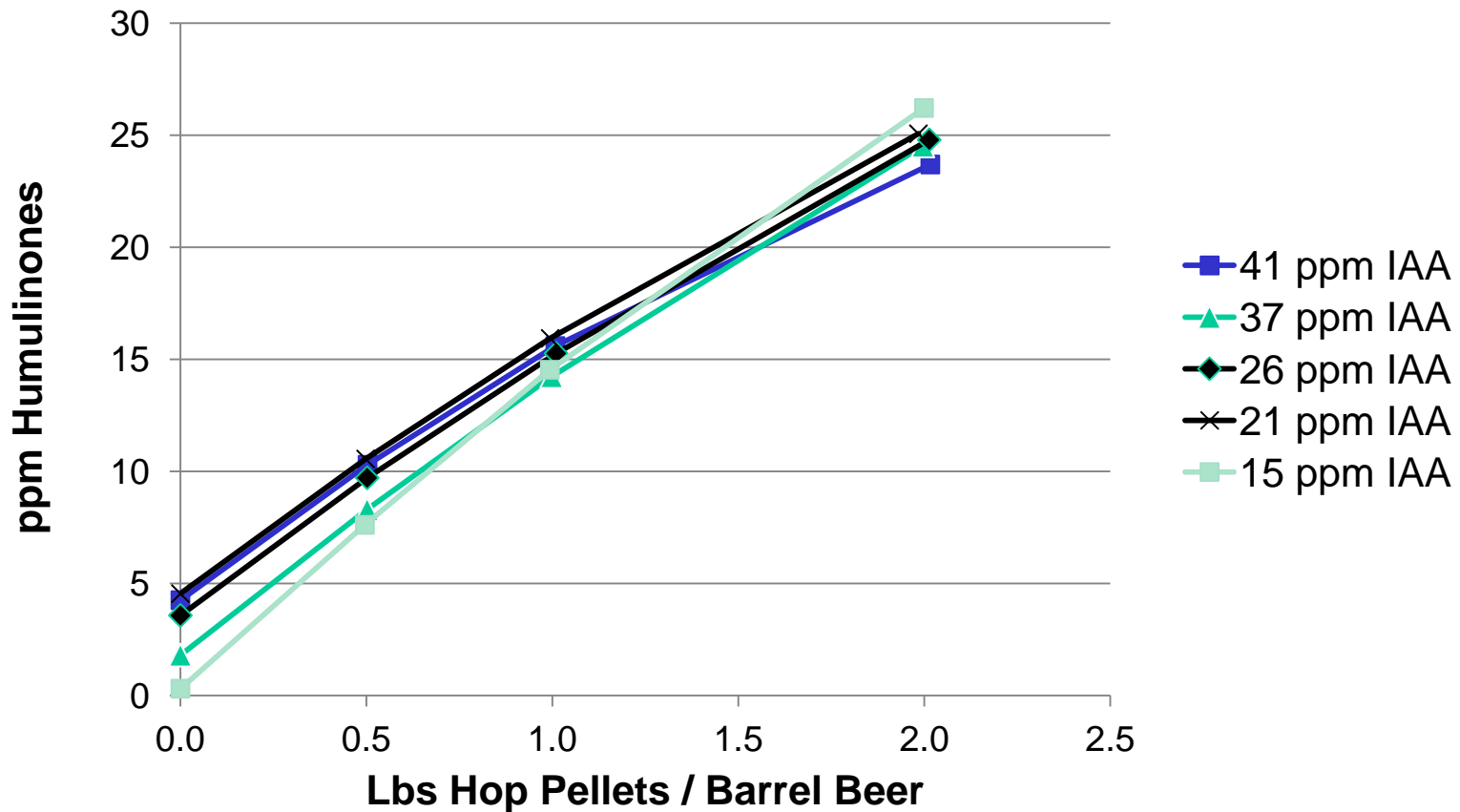


Concentration of Iso-alpha acids after 3 Days of Dry Hopping With Cascade Hop Pellets in Beer



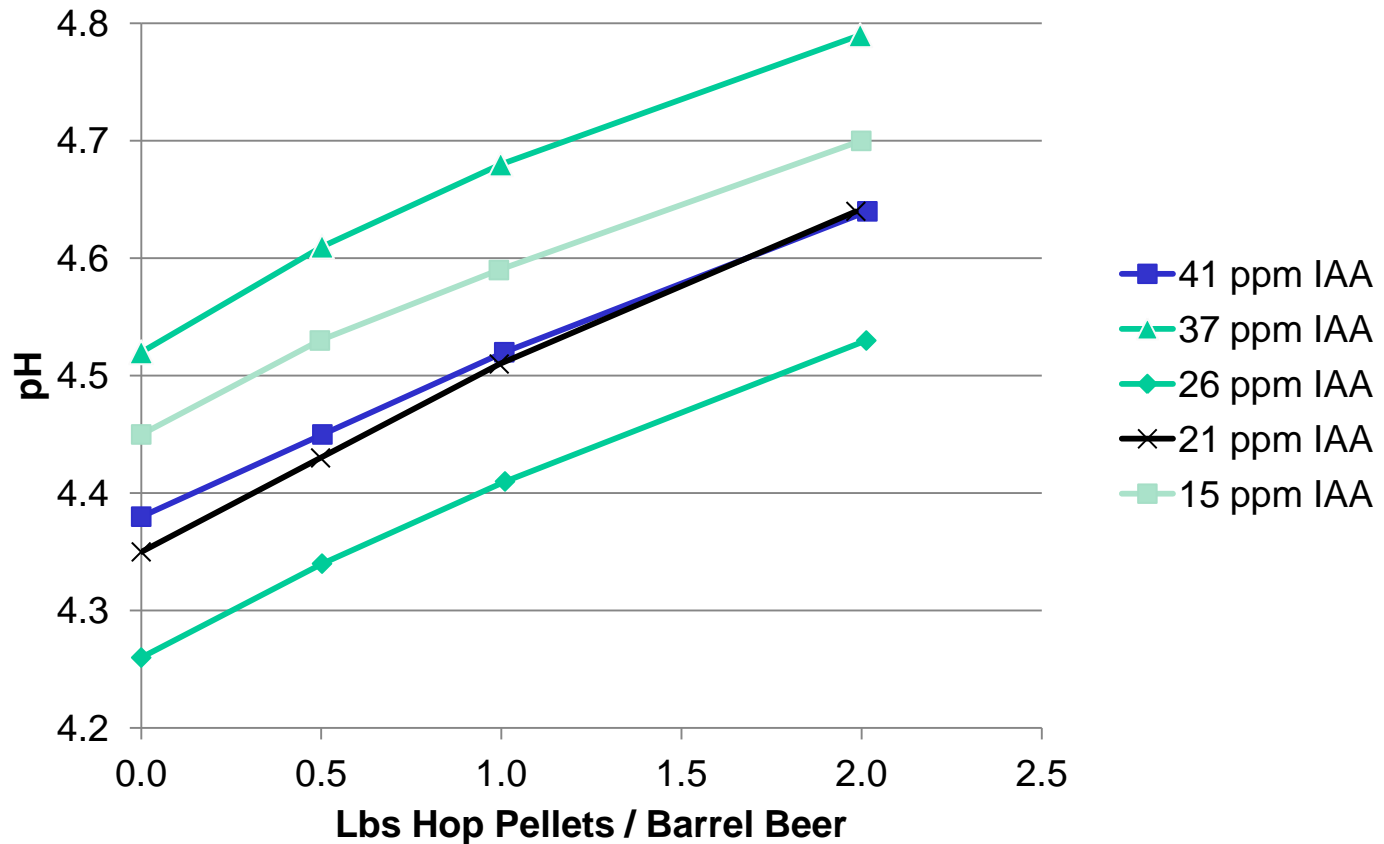


Concentration of Humulinones After Dry Hopped 3 Days With Cascade Hop Pellets in Beer





The Change in Beer pH after 3 Days of Dry Hopping With Cascade Hop Pellets on pH of Beer





Effects of 3 Days Of Dry Hopping With Cascade Hop Pellets vs Starting IBU's of Beer

The higher the IBU the greater the loss of Iso-alpha Acids

Humulinone incorporation is nearly 100% at low dry hopping dosages and greater than 89% at high dry hopping dosages.

~ 26 IBU's seems to be the sweet-spot or cut-off line. Dry hopping beers above 26 IBU's one loses total bitterness and below this level dry hopping increases a beer's 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.



Conclusion

Leaf hops 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.

CO₂ Hop Extract contains 0% humulinones.



Dry hopping under the conditions tested show the higher the starting IBU the greater the loss in isoalpha acids.

Dry hopping beers below 26 IBU can increase a beers bitterness while dry hopping beers above 26 IBU can reduce a beers bitterness.

Because humulinone are 66% as bitter as isoalpha acids their incorporation into high IBU dry hopped beers helps off-sets the bitterness loss of isoalpha acids.

Dry hopping increases a beers pH by about 0.14 pH units per lbs of hops per barrel dosed.

No beta acids were seen in any of the dry hopped beers and very small quantities if any of hulupones were seen.



Acknowledgements

Bob Smith & Jeremy Leker

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Thank You For Your Kind Attention