HOP OILS

(Maximizing Hop Flavor)

Over 1000 Different Oil Compounds are Contained Within the Lupulin Gland of Hops

we will Concentrate on Fruit-Forward Oils in Hops

• Essential Oils of Hops

• Breakdown of different Hop Oils

• Hop Oil Usage for Maximum Survivability

- Maximize Oils in different Stages of Brewing (i.e. Whirlpool)
- Flavor Impact in Hop Varieties
 - Favor/Aroma Extraction of Oils in Different Hop Varieties (i.e. Mosaic, etc..)
- Tables on Hop Oils and Summary Table
 - Popular Hops & Oils in the Brewing Process

Essential Oils of Hops Chart

- 40-80%: Hydrocarbons (Terpenes volatile unsaturated hydrocarbons found in essential oils of plants)
 - Most are woody, herbal, pine, spicy.
 - Myrcene (herbal/woody) most prevalent up to 75% of hop's Total Oil. (i.e. Citra)
- 30%: Oxygenated Hydrocarbons (Terpene Alcohols or Oxygen Containing Compounds)
 - Most are citrus, tropical, berry, floral, ethereal.
 - Linalool, Geraniol, Citronellol byproduct of Geraniol. (i.e. Centennial)
 - Minor amounts (15% of total hop oils) are Ketones and Esters (i.e. Mosaic)
- <1%: Sulfur Containing Compounds (Hydrocarbons with Chemically Bound Sulfur)
 - (Polyfunctional) Thiols free and locked, VERY potent (i.e. Idaho 7-free)

CHEMICAL COMPOSITIONS OF THE ESSENTIAL OILS OF HOPS

Based on general averages, actual percentages vary depending on hop variety and other factors.



Notes on Essential Hop Oils

Hop Oils are volatile – vaporize easily and at high temps.

• Hydrocarbons (Terpenes)

- Hydrocarbons 50% lost in 10min boil, 100% 60 min.
- More viscous protein rich base encourages myrcene to say in solution, hence more hop bite in high concentrations.
- Flaked oats limited to 10% due to protein, can add malted wheat (not flaked).

Oxygen Containing Compounds

- Linalool booster for fruity flavors. (80% loss in 5min boil). Geraniol survives much better
- Geraniol to Citronollel mostly in whirlpool & fermentation.
- Keytones and Esters Hops high in Alpha Acids generally contain more fatty acids that can turn into Keytones/Esters during fermentation.

- <1%: Sulfur Containing Compounds
 - Most Thiols are bound (i.e., Sulphur/ Carbon needs to be broken)
 - Needs beta-glucosidase (in yeast) to free bound thiols most do a poor job.
 - New bio-engineered yeast does a much better job freeing thiols.
 - For every one microgram (µg) of free 3MH in Cascade hops, there are 35 µg of the Cyst-3MH precursors and 1,574 µg of the Glut-3MH precursors.

Survivability

• Usage Timing

- Boil
 - Both myrcene and linalool drop off quickly during boil (both have high extraction rate during dry hop tho)
- Whirlpool
 - Whirlpool 203deg more citrus, spicy, ester; Whirlpool 185deg more linalool measured; floral and herbal; Whirlpool 167deg woody.
 - 170-180deg F probably best to maximize terpene alcohols into solution/beer.
 - Free thiols 3MH can increase and 4MMP can increase during whirlpool.
 - Can increase geraniol rich hops for more beta-citronellol production (in Fermentation).
 - About 5oz whirlpool hop rate.



Figure 1-4. Behavior of hop-derived terpenoids during wort boiling.

Fermentation Dry Hop (DH)

- Early DH additions (before completed fermentation) could lessen aromas
- Early DH additions will strip more resinous compounds (hydrocarbons).
- Linalool drops off during fermentation.
- Early fermentation DH can lead to increase haze (particle light reflection).
- Hops high in geraniol are best early in fermentation and can increase betacitronellol. (i.e. Motueka)
- Up to 80% Esters/Keytones survive late DH (After Fermentation) – original state can change during fermentation.



(from Dresel, Praet, Opastaele, Van Holle, Van Nieuwenhove, Naudts, Keukeleire, Aerts, and Cooman)

Abbreviations

w/o hops: after 15' boiling – just before early hopping after EH: after 75' boiling – just before late hopping after LH: after 5' cooling
before ferm: after 10' cooling – just before fermentation after lag: after lagering – just before centrifugation after past: after pasteurization beer ND: bottled beer without dry hopping

Post Fermentation (Late) DH

- Post Fermentation DH increases polyphenols (perceived bitterness); decrease during fermentation.
- 5°F below low yeast range to minimize scrubbing of oils (hop creep); esp. for Thiols.
- Cooler DH doesn't extract as much woody, spicy, and resinous compounds (hydrocarbons).
- Dry hopping 3oz (per 5 gal) per charge maintain citrus qualities of hop (up to 6oz total).
- Green/Oniony flavor when heavily dry hopped after fermentation high in myrcene.
- Between 48 to 72 hours per DH stage (maximize hop surface contact).
- Longer DH, myrcene and linalool levels didn't increase, increases risk resinous vegetative.



7

Flavor Impact in Hop Varieties

• Hydrocarbons (Terpenes)

- Popular Myrcene-rich hops: Citra, Mosaic, Sabro, Centennial
- Nelson high alpha hop that could contribute to spicy/earthy kettle aroma

• Oxygen Containing Compounds

- Good Hot side hops Citra, Mosaic, Simcoe, Centennial, Ekuanot
- Good IBU hops to neutralize (Hydrocarbon) aroma - Citra, Mosaic, Galaxy, Loral, Wiamea
- Great Whirlpool hops for oil survivability Idaho7, Mosaic, Citra, Ekuanot, Simcoe
- Most free geraniol Motueka, Cascade, Chinook, Citra, Mosaic (best early in fermentation)
- **Simcoe** hop free thiols great 83% linalool extraction rate during dry hopping
- **Centennial** huge on all survivable oils.

- Popular Linalool/Geraniol rich hops: Citra, Loral, Centennial, Sabro, Motueka, Chinook
- Popular Ester/Keytone rich hops: Nelson, Ekuanot, Mosaic, Simcoe, Idaho7, Sabro, Centennial, Citra, Chinook, El Dorado

<1%: Sulfur Containing Compounds</p>

- Amarillo and Mosaic most bound geraniol needs beta-glucosidase (B-lyase) enzyme to free geraniol.
- Dry hopping at the end of fermentation, with hops high in free thiols (Sabro and Mosaic)
- **Citra** is such a popular hop when brewers are trying to target 4MMP.
- **Citra** also has linalool and geraniol. So that makes Citra synergistic for Whirlpool and DH.
- Top Hops with 4MMP: Citra, Cascade, Chinook, Sabro, Galaxy

Hop Acid and Oil Chart

* - ml/100g ** - % of Total Oils # - Total Geraniol/Linalool Oils and Top 10 Source = Yakima Chief Hops @ yakimachief.com

Hop Pellet	Aroma Profile	Alpha Acid	Beta	Total Oil*	Myrcene**	Linalool**	Geraniol**	#
			Acid					
Cascade	Floral,Grapefrt,Herbal,pine	4-9	5-9	0.5-2.0	40-60	0.1-0.6	0.1-0.5	1.1
Centennial	Flral, <mark>Lemn</mark> ,Ornge,Trop,Wdy	8-12	3-6	1.0-3.5	60-75	0.4-0.8	0.7-1.7	2.5
Citra	Citrus,Stone,Tropicl,Woody	10-16	3-5	1.0-3.0	50-70	0.5-1.0	0.2-0.7	1.7
Ekuanot	Bbblgm <mark>,Cit,Stone,Trop,Wdy</mark>	14-16	4-6	2.5-4.5	30-40	0.2-0.5	0.5-1.3	1.8
El Dorado	Citrus,Stone,Tropicl,Woody	13-16	5-8	1.5-3.0	45-60	0.3-0.6	0.1-0.3	0.9
Galaxy	Citrus, Stone, Tropical	13-19	6-12	1.9-2.9	32-56	0.5-1.0	0.1-0.3	1.3
ldaho7	Berry,Bbblgm,Cit,Stne,Trpc	12-15	3-6	1.0-3.0	40-55	0.2-0.6	0.5-1.0	1.6
Krush	Bry,Mngo,Cit,Stn,Trop,Wdy	10-14	7-9	0.5-3.0	40-60	0.5-1.0	0.1-1.0	2.0
Loral	Citr,Florl,Hrbal,Lemn,Trpcl	10-13	4-7	1.0-3.0	45-55	0.6-1.2	0.2-0.7	1.9
Mosaic	Berry, Citrus, Stone, Tropical	10-15	3-5	0.5-3.0	45-65	0.4-0.8	0.4-1.0	1.8
Motueka	Fruity, Lemon, Lime, Tropical	6-8	5-6	0.8-1.5	45-60	0.6-0.9	0.8-1.5	2.4
Nelson-NZ	Citrus, Tropical, White Wine	10-13	5-8	0.8-1.5	35-45	0.2-0.6	0.1-0.4	1.0
Riwaka	Apricot,Cit,Resinous,Stne	9-13	4-6	0.8-2.0	45-55	0.4-0.8	0.1-0.3	1.1
Saaz	Earthy,Floral,Spicy,Woody	2-4	4-6	0.4-1.0	25-35	0.1-0.4	0.1-0.4	0.8
Sabro	Cit,Cocont,Herbl,Stne,Trpcl	12-17	5-8	1.004	55-70	0.3-0.6	0.8-1.6	2.4
Simcoe	Cit,Grapfrt,Stone,Trpcl,Wdy	10-16	3-6	0.5-3	40-60	0.3-0.8	0.5-1.2	2.0
Wiamea	Citrus,Stone,Sweet,Tropicl	14-17	7-9	1.5-2.5	50-60	0.6-0.8	0.8-1.2	2.0
HBC638	Cit,Herbl,Stne,Swet,Tropcl	13-16	4-6	2-4	30-40	0.2-0.4	0.4-1.0	1.4
HBC682	Cit, Earthy, Herbl, Stne, Wdy	16-21	5-8	2-4	60-70	0.3-0.6	0.1-0.6	1.29
Superdelic	Berry, Citrus, Sweet, Tropical	9-12	3-5	1.5-2.2	30-38	0.4-0.7	1.2-1.8	2.5

2023 Yakima Chief Hop Oil Survivability Graph

(YAKIMA CHIEF HOPS



GOOD CANDIDATES FOR HIGH IMPACT EARLY IN THE BREWING PROCESS (LATE KETTLE, WP, AFDH) BETTER UTILIZED LATER IN THE BREWING PROCESS (PFDH)

2020 Takima Chief Hop Oil Survivability Graph



- Butanoic acid, 3-methyl butyl ester is an ester with fruity apricot, pear and banana aroma.
- Methyl geranate is a monoterpene ester with floral, green and fruit aroma.
- 2-Methylbutyl isobutyrate (2MIB) is an ester that has a green apple and apricot aroma.
 - Linalool is a monoterpene alcohol with floral and citrus aroma.
- Geraniol is a monoterpene alcohol with rose-like aroma.
 - 2-Nonanone is a ketone with fruit, floral and herbaceous aroma.
- **3**-Mercaptohexanol (3MH) is a thiol with grapefruit and gooseberry aroma. It can be converted by certain yeasts into 3MHA (passionfruit/guava).
- Note Units Part per million (PPM)

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Hop Variety	<mark>Butanoic acid,</mark> 3-methylbutyl	Methyl Geranate	2MIB	<mark>Linalool</mark>	<mark>Geraniol</mark>	<mark>2-Nonanone</mark>	<mark>3MH</mark>	Total
ldaho 7	<mark>19</mark>	92	<mark>153</mark>	148	64	<mark>64</mark>	<mark>189</mark>	<mark>729</mark>
Mosaic	<mark>25</mark>	<mark>192</mark>	64	134	<mark>67</mark>	<mark>31</mark>	<mark>167</mark>	<mark>679</mark>
Citra	6	<mark>195</mark>	45	<mark>239</mark>	33	11	92	<mark>621</mark>
Ekuanot	<mark>28</mark>	86	<mark>145</mark>	120	50	3	136	568
Simcoe	<mark>19</mark>	<mark>164</mark>	56	128	<mark>67</mark>	<mark>25</mark>	95	554
Loral	11	81	33	<mark>306</mark>	36	0	22	490
Chinook	11	109	78	83	<mark>67</mark>	6	120	473
Sabro	17	6	81	111	<mark>100</mark>	0	<mark>156</mark>	470
El Dorado	8	47	<mark>97</mark>	111	11	8	120	404
Amarillo	3	61	25	<mark>156</mark>	11	0	70	326
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	Ester	Ester	Ester	Ester	Keytone	Thiol (Bound)	OVERALL
	2MIB	lsoamyl lsobutyrate	lsobutyl Isobtyrate	Methyl Geranate	2-Nonanone	3MH	RANK
	Fruity,Apricot	Fruity, Tropical	Fruity, Pineapple	Fruity,Floral	Sweet,Fruity	MANY!	
1	Ekuanot (145)	Krush	El Dorado	Centennial	ldaho7 (64)	Chi (120)	EKUANOT
2	Krush	Ekuanot	Ekuanot	Citra (195)	Mosaic (31)	Krush	EL DORADO
3	El Dorado (97)	Sabro	Idaho7	Mosaic (192)	Simcoe (25)	Sabro (156	MOSAIC
4	Sabro (81)	Mosaic	Citra	Simcoe (164)	Citra (11)	El Dorado (120)	KRUSH
5	ldaho7 (153)	Simcoe	Sabro	Chinook (109)	El Dorado (8)	ldaho7 (189)	IDAHO7
6	Chinook (78)	El Dorado	Mosaic	Amarillo (61)	Cascade	Ekuanot (136)	CITRA
7	Centennial	Citra	Krush	Ekuanot (86)	Krush	Mosaic (167)	SABRO
8	Citra (45)	Chinook	Centennial	Loral (81)	Ekuanot (3)	Simcoe (95)	SIMCOE
9	Mosaic (64)	ldaho7	Chinook	ldaho7 (92)	Sabro (0)	Citra (92)	CHINOOK
10	Simcoe (56)	Centennial	Simcoe	Cascade	Loral (0)	Amarillo (70)	CENTENNIAL
11	Cascade	Loral	Cascade	El Dorado (47)	Amarillo (0)	Loral (22)	CASCADE
12	Loral (33)	Cascade	Amarillo	Krush	Chinook (6)	Centennial	LORAL
13	Amarillo (25)	Amarillo	Loral	Sabro (6)	Centennial	Cascade	AMARILLO

Source = Yakima Chief Hops @ yakimachief.com (rankings only)

(78) = 2020 Yakima Hops Table Value in PPM

Compound	Sensory characteristics	Detection threshold (ng/l)
1-Sulfanylpentan-3-ol	Green odor	n/a
2SEA	Onion	n/a
ЗМН	Rhubarb, grapefruit flavor	<mark>60</mark>
ЗМНА	Passion fruit, grapefruit flavor	4.2
3SH	Grapefruit like flavor, rhubarb	0.8
4MMP	Black currant, passion-fruit-like flavor	0.8
4MSP	Tree-like flavor	1.5

SENSORY CHARACTERISTICS OF DESCRIBED SULFUR COMPOUNDS AND THEIR DETECTION THRESHOLD (determined in beer, wine or model solutions) (Copper et al., 2021; Mafata et al., 2018; Michel et al., 2019; Nizet et al., 2013, 2014; Peltz & Shellhammer, 2017; Zott et al., 2011). From Biotransformation of Hops-Derived Compounds – 2022. **1 Million PPM = 1 PPT = 1 ng/L**

SUMMARY

Description	BOIL	WHIRLPOOL	FERM DH	POST FERM DH Want Low %	
Myrcene	Best to use hi %	Ok to use	Ok to use		
Hi Myrcene Hops	Citra, Mosaic, Sabro, Centennial ⁽¹⁾ , Simcoe ⁽²⁾ , Galaxy, Loral, Wiamea ⁽¹²⁾			Ekuanot, Nelson ⁽¹¹⁾ , Saaz	
Geraniol	Most will be lost	Can use	Can use	Want to use	
Hi Geraniol Hops			Motueka, Chinook, Mosaic, Cascade, Citra ⁽⁶⁾	Motueka, Chinook, Mosaic, Cascade, Citra ⁽⁶⁾ , Centennial, Sabro	
Geraniol to Citronellol	Most will be lost	Can use	Want to use early	Won't work	
Hi Geraniol Hops	Mosaic, Amarillo ⁽³⁾	Motueka, Chinook, Mosaic, Cascade, Citra ⁽⁶⁾ , Centennial, Sabro ⁽⁹⁾	Mosaic, Amarillo ⁽³⁾		
Linalool	Will be lost	Can use	Can use	Want to use	
Hi Linalool Hops				Simcoe ⁽⁵⁾ Citra, <mark>Krush</mark> , Loral, Galaxy, Amarillo	
Esters/Keytones	Most will be lost	Most will be lost	Can change	Want to use	
Hi Ester / Keytone Hops				Ekuanot, Mosaic, Simcoe, Idaho7, Sabro, Citra, El Dorado, Krush, Amarillo, Nelson ⁽⁴⁾	
Total Oxygenated Compounds	Most will be lost	Can use	Can use	Want to use	
Hi Total Oil Hops	Centennial	Idaho7, Citra, Simcoe, Mosaic, Ekuanot ⁽⁸⁾ , Centennial, Krush, Sabro, Motueka, Wiamea ⁽¹³⁾		Citra, Ekuanot, Mosaic, Centennial ⁽⁷⁾ , Idaho7, Loral, Sabro, <mark>Motueka</mark> , Chinook ⁽¹⁴⁾	
Free Thiols	Possible Increase	Can use (&4MMH)	Can use	Want to Use	
Hi Free Thiol Hops		Chinook, Krush, Sabro, El Dorado ⁽¹⁰⁾ , Idaho7, Mosaic, Simcoe ⁽¹⁵⁾		Citra, Cascade, Chinook, Sabro, Galaxy ⁽¹⁶⁾	

- ⁽¹⁾ Sabro, Centennial also High Geraniol some could survive
- ⁽²⁾ Citra, Mosaic, Sabro, Centennial, Simcoe -Janish Top 5
- ⁽³⁾ Mosaic/Amarillo Most Bound Geraniol some yeasts free them better than others
- ⁽⁴⁾ Also, Amarillo and Nelson Janish
- ⁽⁵⁾ Simcoe has 83% linalool survival rate during DH BUT less than 5% Late kettle or Whirlpool -Janish
- ⁽⁶⁾ Motueka, Chinook, Mosaic, Cascade, Citra -Janish
- ⁽⁷⁾ Total Oil and High Oxygenated Compound hops: Citra, Ekuanot, Mosaic, Centennial Janish
- ⁽⁸⁾ Oil Survivability Hops Janish
- ⁽⁹⁾ Can be used in Whirlpool or Early Fermentation
- ⁽¹⁰⁾ Chinook, Krush, Sabro, El Dorado (Best used in early Fermentation or Mash) - Shanleigh Thomson
- (11) Nelson could contribute to spicy/earthy kettle aroma - Janish
- (12) Kettle hops help to neutralize hydrocarbon (spicy/earthy) aroma - Janish
- (13) Hi total oil hops in whirlpool can impart higher flavor profile than during DH
- (14) Additional Geraniol/Linalool rich hops: Loral, Sabro, Motueka, Chinook – Janish
- ⁽¹⁵⁾ For 4MMP, want 90 deg (F) or less in Whirlpool or DH – Yakima Valley Hops
- (16) Top Hops with free 4MMP: <u>Citra</u>, <u>Cascade</u>, <u>Chinook</u>, <u>Sabro</u>, <u>Galaxy</u> -Yakima Valley Hops

Note – if no Hop reference, then from one of the above referenced Tables.

Hop Variety	<u>Cascade</u>	<u>Centennial</u>	Citra® Brand	Ekuanot® Brand	El Dorado® Brand	<u>Galaxy™ - AU</u>
Brand	N/A	N/A	HBC 394	HBC 366	N/A	N/A
Aroma Profile	Floral	Lemon	Citrus	Bubblegum	Citrus	Citrus
	Grapefruit	Orange	Stone Fruit	Citrus	Stone Fruit	Stone Fruit
	Grassy	Tropical	Tropical	Stone Fruit	Tropical	Tropical
	Herbal	Woody	Woody	Tropical	Woody	
	Pine	Floral		Woody	,	
Alpha Acid Range Low	4	8.5	10	14	13	13
Alpha Acid Range Hi	9	12	16	16	16	18.5
Beta Acid Range Low	5.5	3.5	3	4	5.5	6.1
Beta Acid Range Hi	9	5.5	4.5	5.5	7.5	11.6
Total Oil Range Low	0.5	1	1	2.5	1.5	1.9
Total Oil Range Hi	2	3.5	3	4.5	3	2.9
Co-Humulone Low	29	23	20	30	30	32
B-Pinene Low	0.5	0.8	0.6	0.4	0.6	0.3
B-Pinene Hi	1	1.2	1	0.7	0.9	0.6
Myrcene Low	40	60	50	30	45	32
Myrcene Hi	60	75	70	40	60	56
Linalool Low	0.1	0.4	0.5	0.2	0.3	0.5
Linalool Hi	0.6	0.8	1	0.5	0.6	1
Caryophyllene Low	4	3	4	9	6	7
Caryophyllene Hi	10	7	8	12	10	14.7
Farnesene Low	4.5	0.1	0.1	0.1	0.1	2.8
Farnesene Hi	8.5	0.5	1	1	1	5.1
Humulene Low	10	7	7	17	8	0.8
Humulene Hi	20	12	12.5	22	15	2.2
Geraniol Low	0.1	0.7	0.2	0.5	0.1	0.1
Geraniol High	0.5	1.7	0.8	1.3	0.3	0.3