

# SURVIVABLE COMPOUNDS

A BREWER'S HANDBOOK

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Yakima Chief Hops Yakima, Washington USA

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# CULTURE OF INNOVATION

Yakima Chief Hops is a 100% farmer-owned global hop supplier with a mission to connect the multi-generational family hop farms of the Pacific Northwest with the world's finest brewers. Serving the brewing community for more than 30 years, YCH has become more than a hop supplier. We are a resource for brewers, providing solutions-based products and industry-leading research. We are advocates of sustainability and meaningful social causes, working to support the environment and communities around us.

From hop farming pioneers to artisan craft brewers, we continue to be inspired by the entrepreneurial spirit of the hop and brewing industries. We strive to make continuous improvements across the entire supply chain, from collaborating with farmers and breeders to improve hop quality and develop new varieties, to pioneering new hop processing technologies and research. With this culture of innovation at our core, we have established a robust and talented Research & Development team dedicated to creating solutions and novel brewing innovations. All research is done for the betterment of our growers and brewers, and to enrich our entire supply chain through industry-leading hop discoveries.

# R&D TEAM

#### **R&D LAB**

Our state-of-the-art facility is responsible for creating and refining analytical standards in the hop industry.

#### **SENSORY TEAM**

Our hop and beer sensory staff are among the most experienced in the world. Each lot is analyzed by a team of validated panelists to provide standardized sensory feedback.

#### **RESEARCH BREWERY**

Operated by our dedicated Brewing Innovations team, this facility is responsible for continuous product trialing, allowing constant improvement of YCH products.







# BEER SOLUBLE HOP COMPOUND RESEARCH

Yakima Chief Hops has pioneered the use of cutting-edge hop lab analysis techniques to further unlock the maximum potential of aroma hops. The YCH R&D facility houses one of the only labs in the world with the capability to analyze hops via GC-QTOF and GC-SCD technology and study previously undetectable aromatic components. This technology allows us to explore the aroma potential of novel hop compounds—specifically beer-soluble compounds that survive the brewing process.

GC-QTOF and GC-SCD technology unlocks the potential to identify hop compounds that work synergistically and have greater potential of surviving into finished beer. Much historical attention has been paid to components that do not tend to make an impact in finished beer aroma, leaving brewers grasping to understand how to better translate raw hop aroma into the final product. Utilizing GC-QTOF and GC-SCD technology, the Yakima Chief Hops R&D Team is able to quantify concentrations of beer-soluble compounds within hop varieties, creating a framework that helps brewers utilize hop varieties to their maximum effect. This research provides a massively important link in answering the persistent question:

How can I have more control over the aroma characteristics in my finished beers?

THE PROBLEM OF TRANSLATING RAW
HOP AROMA TO FINISHED BEER AROMA
HAS BEFUDDLED BREWERS FOR YEARS.
THIS NEW DISCOVERY HELPS BRIDGE
THE GAP BY FOCUSING SPECIFICALLY
ON SOLUBILITY.



 $\mathbf{6}$ 

#### THE SURVIVABLES GRAPH

GC-QTOF and GC-SCD technology is useful for research purposes, as well as in the development of practical tools which help brewers make more informed decisions about when and how to use hops.

#### **ANSWERS SUCH QUESTIONS AS:**

- What variety should I use?
- Where in the process should I use it?
- Which hops work together in combination?
- How can I use a variety to its maximum effect?



#### 1. USE HIGH SURVIVABLES HOPS EARLY (OR LATE)

Hops with higher concentrations of survivable compounds have a better likelihood of being successful when used earlier in the brewing process than hops with low concentrations of these same compounds. Early additions include late kettle, whirlpool, and active fermentation dry hopping (AFDH).

#### **EXAMPLE**

Idaho  $7^{\text{@}}$  is likely a better choice for high-impact whirlpool hopping than Cascade.

This is because Idaho 7® contains higher concentrations of beer soluble compounds that can survive heat and fermentation activity.

#### 2. USE LOW SURVIVABLES HOPS LATE

Similarly, we can say that hops with lower concentrations are likely to find better success and a more positive impact in beer when used later in the process, such as post fermentation dry hopping (PFDH).

#### **EXAMPLE**

Cashmere will likely make a higher impact in finished beer if used later in the brewing process.

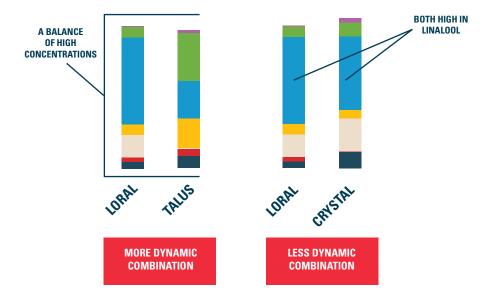
This is because Cashmere contains smaller concentrations of beer soluble compounds that can survive heat and fermentation activity.

## 3. BLEND HOPS TO MAXIMIZE BENEFICIAL CONCENTRATIONS

Focus on balancing high concentrations when creating blends.

#### **EXAMPLE**

Because Loral® is high in linalool and Talus™ is high in geraniol, the two of them are likely to work well in concert. Loral® and Crystal are both high in linalool and would therefore likely create a less dynamic and more one-dimensional blend.



## 4. LOAD WORT STREAMS WITH SURVIVABLES EARLY

High concentrations of survivables in whirlpool and active fermentation dry hopping can create conditions necessary for beneficial biotransformation.

#### **EXAMPLE**

A whirlpool addition of Idaho 7® combined with an active fermentation dry hopping addition of Sabro® and Simcoe® is likely to yield huge flavor impact because it loads the wort stream with a diverse array of "raw materials" needed to favor biotransformation.





# BEER SOLUBLE HOP COMPOUND RESEARCH

In 2017, Yakima Chief Hops launched a line of innovative hop products known as Cryo Hops<sup>®</sup> using a cryogenic hop-processing technology that separates whole cones into two components—concentrated lupulin and bract. These concentrated lupulin pellets provide brewers with maximum aroma impact while reducing the negative effects often experienced with today's high hopping rates.

We combined this novel process with GC-QTOF and GC-SCD technology to create TRI 2304CR, a hop blend containing very high concentrations of the most beer-soluble aromatic components—monoterpene alcohols, esters, and polyfunctional thiols. This resulted in the official release of Cryo Pop™ blend—a supercharged pellet that provides brewers with a dynamic solution for juicy, fruit-forward, highly aromatic applications, showing massive tropical, stone fruit, and citrus aromas.



In a study by the YCH R&D Team, an NEIPA was brewed with the Cryo Pop<sup>TM</sup> blend. Corresponding NEIPAs were brewed with the individual corresponding parts of the Cryo Pop blend, dosed at an equivalent rate. The corresponding beers were then blended post fermentation using the same ratios as the Cryo Pop blend and packaged. Both packaged products were analyzed by the YCH beer sensory panel. The two beers show distinctly different flavor profiles though the constituent hop components were the same.

This research suggests a powerful feature of the Cryo Pop™ blend: these hop varieties have a more compelling flavor impact when fermented in concert than they do when fermented individually.





#### **POST-PACKAGE BLEND OF CONSTITUENTS**

APPLE • PEAR • CANTALOUPE • BANANA LEMON • BUBBLEGUM (38% each)

#### CRYO POP™ ORIGINAL BLEND

PEACH • PINEAPPLE • STRAWBERRY (50% each)
GUAVA • MANGO • ORANGE (38% each)













Percentage of trained panelists (n=8) reporting the presence of major flavor complexes in beer. The Post-Package Blend of Constituents represents a beer made by blending all of the blend constituents together after they were finished.

### CRYOPOP\*

### **USAGE SCENARIOS** & RECIPES



#### **SINGLE-HOP BEERS**

Because Cryo Pop<sup>TM</sup> pellets have already been engineered with specific component ratios in mind, they can be used for 100% of the hop bill as an all-in-one solution for brewers desiring juicy peach, pineapple, grapefruit, and daiquiri-like aromas. They provide such powerful and dynamic aroma and flavor profiles that they can create a robust "single hop" beer with the use of one hop blend.

#### **YCH037**

#### CRYO POP™ ORIGINAL BLEND NEIPA

TASTING NOTES: MANGO • RUBY RED GRAPEFRUIT PEACH • FLORAL

#### **SPECIFICATIONS**

Original Gravity	1.065
Final Gravity	1.016
IBU	25
ABV	6.5%

#### INGREDIENTS

GRAINS	AMOUNT	<b>YEAST &amp; ADJUNCTS</b>	AMOUNT
2-Row or Pilsner Malt.	60%	London III	16 million cells/mL
White Wheat	25%	Whirlfloc	Variable
Flaked Oats	15%	Yeast Nutrient	Variable

HOPS	TYPE	AA%	ADDITION	<b>AMOUNT</b>
Cryo Pop™ Original Blend	Cryo Hops® Pellets	18.5%	Flame Out	1.9 g/L
Cryo Pop™ Original Blend	Cryo Hops® Pellets	18.5%	Dry Hop 1	5.8 g/L
Cryo Pop™ Original Blend	Cryo Hops® Pellets	18.5%	Dry Hop 2	1.9 g/L

#### INSTRUCTIONS

STEP	Perform an infusion mash to achieve a mash temp of 154°F/68°C for 60 min.
STEP	Vorlauf until the wort has cleared and is free of grain particles.
STEP	3 Runoff into the kettle and sparge with 180°F/82°C water.
STEP	4 Bring the wort to a boil.
STEP	5 After 45 min, add Whirlfloc for clarity and yeast nutrient for yeast health.
STEP	6 After 60 min, turn off the burner. Let the wort cool to about 204°F/96°C. Add the whirlpool hop additions.
	Note: All whirlpool additions are calculated based on a 15 minute whirpool starting at 204°F/96°C.
STEP	7 Gently create a whirlpool in the kettle.
STEP	8 Quickly cool the wort to 64°F/18°C, aerate it, and transfer in into a sanitized fermenter.
STEP	Pitch the appropriate amount of yeast and add either an airlock or blowoff
	tube to the fermenter.
STEP	10 Dry Hop 1: Add hops at middle of active fermentation, with approximately 1.024 – 1.032 specific gravity left before final gravity.
STEP	11 Dry Hop 2: After final gravity is hit dry hop for two days at 72° F/ 22° C,

Elevated hopping rates tend to produce hop creep often resulting in

diacetyl production. After beer passes forced diacetyl test, drop temperature to

rousing once at 24 hours with CO2. Dump hops from

bottom of FV after 48 hours.

32° F/ 0° C.

#### **BLEND AMPLIFIER**

Cryo Pop pellets can be used to amplify the character of other existing hop combinations. When used as a 20-40% portion of a hop bill, Cryo Pop pellets will elevate levels of geraniol, linalool, esters, and polyfunctional thiols, enhancing and elevating the characteristics of other hop varieties.

#### **YCH038**

#### CRYO POP™ ORIGINAL BLEND AMPLIFIER WEST COAST IPA

**TASTING NOTES**: PINEAPPLE • STONE FRUIT • PEACH GRAPEFRUIT • PINE • CEDAR

#### **SPECIFICATIONS**

Original Gravity 1.059
Final Gravity 1.010
IBU 58
ABV 6.2%

#### INGREDIENTS

GRAINS	AMOUNT	<b>YEAST &amp; ADJUNCTS</b>	AMOUNT
2-Row or Pilsner Ma	lt 85%	English Ale Yeast	14.5 million cells/mL
Malted Wheat	5%	Whirlfloc	Variable
Crystal 60 Malt	5%	Yeast Nutrient	Variable
Acidulated Malt	As Needed		

HOPS	TYPE	AA%	ADDITION	<b>AMOUNT</b>
Warrior® Brand	T-90 Pellets	. 16.0%	60 min	0.5 g/L
Talus™ Brand	.T-90 Pellets	. 9.0%	Whirlpool	3.9 g/L
Cryo Pop™ Original Blend	. Cryo Hops® Pellets		Dry Hop 1	1.0 g/L
Simcoe® Brand	. T-90 Pellets		Dry Hop 1	3.9 g/L
Cryo Pop™ Original Blend	. Cryo Hops® Pellets		Dry Hop 2	1.0 g/L
Citra® Brand	Cryo Hops® Pellets		Dry Hop 2	1.0 g/L
Mosaic® Brand	. T-90 Pellets		Dry Hop 2	2.0 g/L

Mosaic®	Brand 1-90 Pellets	Dry Hop 2 2.0 g/L
INSTRU	CTIONS	
STEP 1	Perform an infusion mash to achieve a mash temp of 152	2°F/67°C for 60 min.
STEP 2	Vorlauf until the wort has cleared and is free of grain pa	rticles.
STEP 3	Runoff into the kettle and sparge with 180°F/82°C water.	
STEP 4	Bring the wort to a boil, and add 60 minute hop addition.	
STEP 5	After 45 min, add Whirlfloc for clarity and yeast nutrient	for yeast health.
STEP 6	After 60 min, turn off the burner. Let the wort cool to abowhirlpool hop additions.  Note: All whirlpool additions are calculated based on a 15 minut at 204°F/96°C.	
STEP 7	Gently create a whirlpool in the kettle.	
STEP 8	Quickly cool the wort to 66°F/19°C, aerate it, and transfe sanitized fermenter.	r in into a
STEP 9	Pitch the appropriate amount of English Ale yeast and a	dd either an airlock or
	blowoff tube to the fermenter.	
STEP 10	Dry Hop 1: Add hops at middle of active fermentation, wi 1.032 SG left before terminal gravity.	th approximately 1.024-
STEP 11	After final gravity has been reached, add second Dry Ho	p for 2 days at 22°C/72°F.
STEP 12	After 2-3 days and the beer has passed forced diacetyl t	est, cool the fermenter

to 32°F/0°C. Transfer to a keg and carbonate or bottle condition.

#### RAW MATERIAL FOR BIOTRANSFORMATION

Recent research suggests that high levels of monoterpene alcohols and polyfunctional thiols in a wort stream can create the conditions necessary for the yeast metabolism of hop-derived compounds, otherwise known as "biotransformation." Cryo Pop pellets are a perfect choice for loading whirlpool and active fermentation dry hop additions with these components, thus creating a dynamic environment for yeast and hops to provide maximum aroma expression.

#### **YCH039**

#### CRYO POP™ ORIGINAL BLEND BIOTRANSFORMATION JUICY PALE ALE

TASTING NOTES: TANGERINE • PINEAPPLE • PEACH GRAPEFRUIT • CEDAR

#### SPECIFICATIONS

Original Gravity1	.059
Final Gravity 1	.014
IBU	27
ABV	5.9%

#### INGREDIENTS

GRAINS	AMOUNT	<b>YEAST &amp; ADJUNCTS</b>	AMOUNT
Pilsner Malt	90%	London III	14.5 million cells/mL
Malted Wheat	5%	Whirlfloc	Variable
Munich II Malt	5%	Yeast Nutrient	Variable
Acidulated Malt	As Needed		

HOPS	TYPE	AA%	ADDITION	AMOUNT
Cryo Pop™ Original Blend	Cryo Hops® Pellets	18.5%	. Whirlpool	2.9 g/L
Cryo Pop™ Original Blend	Cryo Hops® Pellets		. Dry Hop 1	3.9 g/L
Idaho 7® Brand	. T-90 Pellets		Dry Hop 1	3.9 g/L
Citra® Brand	Cryo Hops® Pellets		Dry Hop 2	1.9 g/L

INSTRUCTIONS	
STEP 1	Perform an infusion mash to achieve a mash temp of 154°F/68°C for 60 min.
STEP 2	Vorlauf until the wort has cleared and is free of grain particles.
STEP 3	Runoff into the kettle and sparge with 180°F/82°C water.
STEP 4	Bring the wort to a boil.
STEP 5	After 45 min, add Whirlfloc for clarity and yeast nutrient for yeast health.
STEP 6	After 60 min, turn off the burner. Let the wort cool to about 204°F/96°C. Add the whirlpool hop additions.  Note: All whirlpool additions are calculated based on a 15 minute whirlpool starting
STEP 7	at 204°F/96°C. Gently create a whirlpool in the kettle.
STEP 8	Quickly cool the wort to 66°F/19°C, aerate it, and transfer in into a sanitized fermenter.
STEP 9	Pitch the appropriate amount of yeast and add either an airlock or blowoff tube
	to the fermenter.
STEP 10	Dry Hop 1: Add hops at middle of active fermentation, with approximately 1.024- 1.032 SG left before final gravity.
STEP 11	After final gravity has been reached, add second Dry Hop for 2 days at 22°C/72°F.

STEP 12 After 2-3 days and the beer has passed forced diacetyl test, cool the fermenter to 32°F/0°C. Transfer to a keg and carbonate or bottle condition.

#### **HOP & BEER**

# **SENSORY LEXICON**

Both hops and beer contain hundreds of flavor-active compounds which contribute to aroma, taste, and mouthfeel. While this complexity can make sensory science feel overwhelming, it is possible to create a "dictionary" of flavors to help organize the chaos. Creating a universal language to describe hop and beer flavor allows us to be descriptive, quantitative, and replicable in our research and discussions. Most of the aromas listed here can be found in both hops and in beer, though some will be more common in one or the other. The lexicon is intended to provide an overview of potential flavors and is not an exhaustive list. Descriptions of flavor tend to vary from region to region and culture to culture. With that in mind, it should also be noted that a lexicon is never truly finished and will continue to evolve as new hop varieties and brewing methods are adopted.



#### **AROMA**



#### **DRIED FRUIT**

Date • Dried Apricot Dried Fig • Raisin

MELON

Cantaloupe • Cucumber

Honeydew • Watermelon



BERRY

Black Currant . Blueberry Grape • Raspberry • Strawberry



#### STONE FRUIT

Apricot . Cherry Peach • Plum



**POMME** 

Apple • Pear



**CITRUS** 

Banana • Coconut • Guava Grapefruit • Lemon Lemongrass • Lime • Orange Passion Fruit • Pineapple



#### FLORAL

Cherry Blossom . Geranium Jasmine • Rose • Soapy



#### HERBAL

Black Tea • Dill • Green Tea Mint • Rosemary • Thyme



TROPICAL

Lychee • Mango

VEGETAL

Cabbage . Celery Green Pepper • Tomato Plant



GRASSY

Green Grass • Hay



#### **EARTHY**

Barnvard . Compost . Geosmin Leather • Mushroom • Soil



#### WOODY

Cedar • Pine • Resinous Sawdust • Tea Tree • Tobacco



Anise • Black Pepper Cinnamon • Clove • Ginger



#### **SWEET AROMATIC**

Bubblegum • Caramel Chocolate • Creamy • Vanilla



#### **ONION / GARLIC** Garlic • Green Onion • Onion



Cannabis . Skunky

DANK



NUTTY Almond • Peanut • Walnut



**BREADY** 

Biscuit . Dough Graham Cracker Oatmeal • Rye



**ROASTED** 

Coffee • Dark Malt



**OFF-NOTES** 

Burnt Rubber • Cardboard • Catty Cheesy . Diesel . Mustv Plastic/Waxy • Smoky • Sulfur • Sweaty

> \* Acetaldehyde • Butyric Acid Diacetyl • DMS • Lactic Acid Light Strike • Metallic



#### **TASTE**

**BITTER** SALT **SOUR SWEET** UMAMI

#### MOUTHFEEL

**ALCOHOL** 

**ASTRINGENCY** Drying • Grippy

**BODY** 

**CARBONATION** 

Warming . Boozy

Thickness • Fullness

Bubble Size . Density

#### **HOP & BEER**

# RESEARCH VOCABULARY

The brewing process is inherently reliant upon chemistry. The ability to bridge the gap between brewing processes and principles of basic chemistry can help all brewers gain a better understanding of how chemical compounds interact in each batch of beer. The following is intended to be a general-use guide for brewers desiring to better understand hop compounds and functions. Information is organized into three sections: Brewing Terms, Equipment/Methods, and Critical Compounds. All are intended to help brewers have a better understanding of Cryo Pop and how they can use the research behind it for better decision-making in their breweries.

#### **BREWING TERMS**

#### **Active Fermentation Dry Hop Addition (AFDH)**

Dry hop additions occurring before fermentation is complete. A relatively new practice employed by many modern brewers. Traditional wisdom suggested that such a process would result in reduced aromatic compounds from dry hop additions, but newer research proposes that yeast cells can interact with certain hop-derived compounds to produce new and more pronounced flavor attributes (Takoi, et al., 2010). Timing of AFDH additions will vary based on brewery processes. AFDH may create yeast management challenges for brewers as yeast is typically of low quality after dry hopping. AFDH may help mitigate hop creep, since hop enzymes typically complete their conversion before the initial fermentation is complete.

#### Alpha Acids

A group of compounds also known as humulones. Each hop variety has a slightly different distribution of the three most common humulones: humulone, cohumulone, and adhumulone. These alpha acids reside within the lupulin gland and are the precursors for iso-alpha-acids, which are the primary bittering compound in beer. Alpha acids are less bitter and less soluble than iso-alpha-acids, and therefore do not provide much bittering potential in their non-isomerized form. Hop varieties with high levels of alpha acids are more efficient in creating bitterness, and thus are usually used in early kettle additions.

#### **Antagonism**

The opposite of synergy. Example situation: an increased grassy or vegetal note, which may not be unpleasant on its own, "drags down" other positive fruity or tropical notes, reducing overall positive flavor characteristics.

#### **Biotransformation**

A broad term used to describe the process by which an organism changes chemical compounds into new ones. In brewing, an incompletely understood process by which certain strains of yeast can interact with hop compounds during fermentation. A successfully biotransformed beer may theoretically have higher levels of desirable flavor compounds. (Kishimoto, Morimoto, Kobayashi, Yako, & Wanikawa, 2008)

#### **Dry Hopping**

An overarching term for adding hops to beer after wort has begun fermentation. All hop products (except  $\mathrm{CO}_2$  extract) can be used for dry hopping, but different products can have significantly different efficiencies (see: Hop Product Efficiencies).

#### **Early Kettle Addition**

A hop addition occurring toward the beginning of kettle boil, usually for 45-90 minutes of boil time. Due to sustained heat and convection of the boil, most hop-derived aromatics will volatize out of solution. Early kettle additions impart more bitterness as isomerization reactions have ample time to occur. The main considerations when choosing early kettle additions are quantity of alpha acids and efficiency of hop product used (see: Hop Product Efficiencies).

#### **Hop Creep (also: Refermentation)**

A colloquial term used to describe the effects of adding a dry hop addition to beer in the presence of yeast. Enzymes present in hops can break down previously non-fermentable sugars in the beer, providing a new nutrient source for the yeast. This process can cause serious headaches for brewers. More fermentation may cause beers to deviate from the allowed ABV range, and refermentation can produce unexpected diacetyl. Brewers can mitigate the effects of hop creep by performing VDK tests before cold crashing any dry hopped beer.

#### **Hop Product Efficiencies**

Two main efficiency factors affect hop usage.

#### 1. Isomerization Efficiency

Depending on the accessibility of lupulin glands some hop products isomerize more quickly than an equivalent amount of another product. Whole leaf hops are generally least efficient as the hop leaf, or bract, protects some of the lupulin. T-90 pellets are relatively efficient, while Cryo Hops® and CO<sub>2</sub> Extract are significantly more efficient. Isomerization efficiency will vary depending on brewing equipment but should follow this trend in most typical brewhouses.

#### 2. Overall Yield

Any liquid (beer/wort) absorbed by hops and discarded in the brewing process is lost potential profit for a brewery. Different hop products have different absorptive potential. As with isomerization, product types follow the same trend. Therefore, in terms of product yield, Cryo Hops® pellets represent the most efficient dry hop product, followed by T-90 pellets and then Whole Leaf.

#### 'Hop Volcano'/ 'Hop Gusher'

When dry hops are added to an actively fermenting vessel, they supply a substantial number of nucleation points (surfaces from which  $\mathrm{CO}_2$  is released from solution into bubbles). This can cause an eruption of foam, usually through the dry hopping port. This process is what causes the explosive reaction between Diet Coke® and Mentos®. While the name is entertaining, this can cause serious safety issues for uninformed brewers, especially if dry hopping on a ladder. Some brewers minimize the risk of Hop Volcano by adding a small portion of the dry hop charge, closing the dry hop port, and venting the tank to atmosphere to release subsequent off-gassing. After 30 minutes to an hour most foaming should subside, allowing the brewer to add the remainder of the dry hop charge with lowered risk of a Hop Volcano.

#### Isomerization

The transformation of a chemical compound into an entirely new compound while maintaining the same molecular weight and atomic make-up. In brewing, the process of changing the molecular structure of alpha acids to iso-alpha acids, usually via boiling. Degree of isomerization will be dependent upon heat, time, and efficiency of hop product being used. Generally, the longer alpha acids are above 79°C/175°F the more isomerization will occur. Isomerization will also occur in non-boiled liquids (such as whirlpool) at temperatures above 79°C/175°F.

#### **Isomerized Alpha Acids**

As alpha acids (humulones) undergo isomerization, their chemical structure changes slightly (but the molecular weight remains the same). This change causes them to form isomerized alpha acids (also: iso-alpha acids, IAA, isohumulones). Iso-alpha acids are significantly more bitter and soluble than their non-isomerized cousins—this is advantageous to brewers since their main purpose is imparting bitterness to beer.

#### **Late Kettle Addition**

A hop addition occurring toward the end of kettle boil. Generally boiled for 15 minutes or less, late kettle additions contribute less bitterness, although many volatile compounds will still be lost due to heat. Some wort-soluble compounds (monoterpene alcohols, 3MH) will remain in the wort and be transferred to the fermenter.

#### Post Fermentation Dry Hop Addition (PFDH)

The most common method for adding cold-side hops, still widely employed today. PFDH is typically easier for brewers to manage than AFDH, since breweries have more time to harvest yeast and brew subsequent batches. Additionally, unlike with AFDH, the risk of a 'hop volcano' is much lower.

#### Synergy

In hop parlance, synergy describes potential amplification of overall desirable beer flavor from the interaction of two or more flavor compounds, i.e. "The whole is greater than the sum of its parts".

#### **VDK**

An abbreviation for Vicinal Diketones, which are a class of chemical compounds containing two carbonyl (oxygen double bonded to carbon) groups bonded by a single carbon bond. In beer, important compounds are 2,3-butanedione (diacetyl) and 2,3-pentanedione. VDKs are oxidized byproducts of the conversion process used by yeast to convert sugars into alcohol and carbon dioxide. VDKs have an artificial butter aroma and are considered a flaw in all but a few beer styles. Early in the fermentation process yeast produce an abundance of  $\alpha$ -acetolactate, which has no detectable aroma. Over time,  $\alpha$ -acetolactate oxidizes into VDKs. Problems arise when the undetectable  $\alpha$ -acetolactate is present in a packaged beer since it will inevitably oxidize into VDKs. In a normal fermentation, yeast absorb VDKs and convert them into compounds which do not have a detectable aroma.

#### **Whirlpool Addition**

A hop addition occurring in the whirlpool vessel after kettle boil is complete. Volatile compounds in these additions are more stable due to lower temperatures and the lack of boil convection. Some brewers actively cool their wort before adding a whirlpool addition. While reducing the temperature slightly can reduce the rate of volatilization, extreme cooling (below 82°C/180°F) can lead to infection risk and will most likely not result in significantly different extraction rates.

#### **EQUIPMENT / METHODS**

#### Chromatography

A separation technique consisting of a mobile phase and a stationary phase, by which analytes are separated by their individual affinities/attraction for the mobile phase and stationary phase. The time it takes for each analyte to travel through the stationary phase is called retention time. In brewing, the process of separating individual compounds for identification and quantification.

#### **Gas Chromatography (GC)**

A separation method using a carrier gas (usually helium). Analytes must be to a gaseous state to be carried through the stationary phase. The stationary phase (column) can either be packed (filled with material) or capillary (open tubular). Very versatile, the GC's main purpose is to separate each constituent compound of a complex mixture (a hop or beer sample in our case). The column has an extremely small diameter (0.25mm) and is quite long (about 60m). Different chemical compounds have specific physical properties (vaporization point and molecular weight) which cause them to travel through the column at different rates. Given the correct parameters, compounds will exit the column in a single-file, linear fashion. The string of compounds passes through a detector, such as an MS, SCD, ODP, or QTOF; (see further definitions in Equipment/Methods). Researchers test pure samples of target compounds at specific concentrations, known as reference standards, to calibrate the instrument and compare against compounds detected in hops. YCH's analytical laboratory has identified many key flavor-active compounds using this instrument.

#### High Performance Liquid Chromatograph (HPLC)

A type of chromatography device. Unlike gas chromatography, HPLCs use a liquid mobile phase to carry product samples, which makes liquid testing significantly easier. This instrument is typically used to measure the alpha and beta acids in hops and hop products, along with alpha and iso-alpha acids in beer. These analyses are performed using a Diode Array Detector (DAD)

#### Mass Spectrometer (MS)

A common detector used in combination with a Gas Chromatograph. Compounds eluted from the column of the GC are hit with a stream of electrons, breaking the compounds into pieces of different weights and charges. These weights and charges are subsequently detected by the mass spectrometer, which reports the output as intensity peaks on a graph. An MS is multi-use detector, but has some limitations, especially with sulfur compounds.

#### **Olfactory Detection Port (ODP)**

A sensory detector added on to GC separation processes. A sensory panelist seated in front of the ODP smells individual compounds and indicates identifiable aromas detected, as individual compounds elute off of the column. This is a difficult skill to master, as the operator often smells for more than thirty minutes straight! An ODP is useful in detecting new compounds that might normally be ignored as noise

#### Quadrupole Time of Flight Detector (QTOF)

A more advanced GC detector. Compounds eluting from the GC column are passed through a quadrupole. Ions are separated based on mass-to-charge ratio (m/z). Separated ions are sent into a time-of-flight tube. In this device, ions are propelled into the tube via a high voltage pulse. The subsequent speed of descent determines mass-to-charge ratio. All ions enter the QTOF with the same kinetic energy and are therefore for separated by size. Smaller ions will travel faster than larger ions.

#### **Sensory Analysis**

A scientific discipline that applies principles of experimental design to the use of human senses for the purposes of evaluating consumer products.

#### **Sensory Panel**

A group of individuals who are trained to distinguish and evaluate the taste, flavor and texture of food products. A well-trained panel can act as a measuring tool and is often able to evaluate products for characteristics which cannot be instrumentally measured.

#### **Sensory Program**

The formalized use of sensory procedures to support an organization's quality systems and/or research initiatives. YCH uses a trained sensory panel to examine hop samples and ensure high product quality from harvest to finished goods. YCH also employs a trained beer sensory panel which performs evaluations on beers from both the YCH internal brewery and from partner breweries. Both hop and beer sensory programs support various Research and Development efforts, such as new product development. When combined with lab analysis, sensory assessment helps to illuminate the flavor impact of compounds present in hops and beer.

#### Sulfur Chemiluminescence Detector (SCD)

A detector used in combination with a Gas Chromatograph. Commonly used to detect small amounts of sulfur-containing compounds in a sample. Sulfur components are present in hops at relatively low concentrations, and in order to be detected they are combusted at high temperatures to form sulfur monoxide (SO). The SO is subsequently passed through a photomultiplier tube to detect light produced by the chemiluminescent reaction of SO with ozone. This reaction also produces peaks which can be identified and quantified using reference standards (Agilent, 2021).

#### CRITICAL COMPOUNDS

YCH's hop and beer analyses help determine the function of individual compounds. These analyses are the building blocks of Hop Survivable Technology, a research tool that brewers can use to make more informed decisions about hop usage in the brewery. These compounds are broken up in to 4 major groups: Terpenes, Terpene Alcohols, Sulfur-Containing Compounds, and Esters and Ketones.

Hop compounds have extremely varied aroma, taste, and solubility threshold levels. It is worth noting that absolute magnitude of a chemical's concentration is likely less important to its impact in beer than its concentration relative to other varieties and compounds, and its beer-solubility.

An example: the difference between 40% and 44% myrcene in two otherwise equivalent samples would most likely not be as noticeable as a difference of 0.5% and 0.55% linalool. Though myrcene represents a much higher proportion of the hop's oil, linalool is substantially more beer-soluble and therefore more impactful on the finished product.

#### **TERPENES**

Many different terpenes are found throughout the plant world. Terpene is a general term describing compounds made of one or more isoprene groups ( $C_sH_g$ ) (Qian, 2013). Hop analysis typically focuses on mono- and sesqui- terpenes, which consist of 2 and 3 isoprene groups, respectively.

#### Farnesene

A sesquiterpene exhibiting a noble and woody aroma profile. Interestingly, farnesene is only found in trace amounts in most modern varieties, and some actually have no detectable farnesene. Most of the varieties containing high levels of farnesene are traditional European varieties.

#### **Hvdrocarbons**

As the name implies, 'hydrocarbon' can describe any compound that is made up of only hydrogen and carbon atoms. While all terpenes are hydrocarbons, not all hydrocarbons are terpenes.

#### **Monoterpenes**

Hydrocarbons made of 2 isoprene units. All monoterpenes are made of 10 carbon, and 16 hydrogen atoms ( $C_{10}H_{16}$ ). The most common hop monoterpenes are myrcene and  $\beta$ -pinene. Monoterpenes are very volatile and will usually not survive when added in hot-side additions.

#### Myrcene

A monoterpene, usually the largest component of a hop's 'total oil' (up to about 75%, although some varieties have significantly less). Myrcene is extremely volatile, and while it contributes heavily to raw hop aroma, it will generally not survive the brewing process due to low solubility. Myrcene has an herbal, woody, and somewhat carrot-like aroma.

#### **Sesquiterpenes**

Hydrocarbons made of 3 isoprene units. All sesquiterpenes are made of 15 carbon, and 24 hydrogen atoms ( $C_{15}H_{24}$ ). The most common hop sesquiterpenes are  $\beta$ -caryophyllene, farnesene, and  $\alpha$ -humulene. Like monoterpenes, sesquiterpenes are very volatile, and will usually not survive when added in hot-side additions.

#### Terpenes

A class of compounds that consist of varying quantities of isoprene units  $(C_sH_g)$ . Typically representing a large portion of the 'total oil' fraction of a hop, with the monoterpene myrcene usually being the most prevalent.

#### α-humulene

A sesquiterpene exhibiting grassy, herbal, and woody aromas. It is highly volatile and generally will not survive the brewing process.

#### **B**-pinene

A monoterpene,  $\beta$ -pinene smells pine-like. It is far less abundant in hops than myrcene, making up only about 1% of the total oil, maximum. Like myrcene,  $\beta$ -pinene is very volatile, and will only transfer to beer during dry hopping.

#### **β-caryophyllene**

A sesquiterpene with a very woody aroma, sometimes cedar-like. Other aroma notes include floral and spicy.  $\beta$ -caryophyllene contributes to the character of noble hops and is found in lower levels in newer American hops. It generally does not survive the brewing process.

#### **TERPENE ALCOHOLS**

Terpene alcohols are closely related to terpenes. Unlike terpenes, terpene alcohols are oxygenated, making them an alcohol. By their nature, alcohols are more soluble than non-oxygenated terpenes due to their greater polarity. They therefore have a much greater retention rate into the final beer, and hops high in terpene alcohols are widely thought to benefit hot-side additions.

Terpene alcohols are also the subject of recent research investigating biotransformation. In a study by (Takoi, et al., 2012),  $\beta$ -citronellol, a compound not usually found in hops, was found to increase during fermentation. A prominent theory states that during fermentation certain strains of yeast are

capable of metabolizing geraniol into  $\beta$ -citronellol, which has shown to amplify citrus/floral aroma profile in final beer. Enough geraniol must be present in the wort solution for conditions to favor this action.

#### Geraniol

Like linalool, geraniol is a monoterpene alcohol which commonly survives late boil and whirlpool additions. Its aroma profile is geranium-like and citrusy. Geraniol is thought to be at least partially biotransformed by certain strains of yeast into β-citronellol during fermentation.

#### Linalool

A monoterpene alcohol commonly used as a fragrance and flavoring in cosmetics and candy. It has a strong fruity and floral aroma, commonly described as similar to the aroma of Froot Loops™ cereal. High levels of linalool can act as a 'booster' to increase fruity flavor in beer. Linalool is beer-soluble and commonly survives the brewing process.

#### Nerol

A monoterpene alcohol with a rose and citrus aroma. An isomer of geraniol. Not usually detectable by YCH analysis.

#### **B-citronellol**

A monoterpene alcohol with an aroma similar to citronella candles. Not thought to be found in hops, but has been detected in beer. It is believed that this compound is produced by metabolism of geraniol by yeast during fermentation.

#### **SULFUR-CONTAINING COMPOUNDS**

Sulfur compounds represent an increasingly important area of study in hop aroma science. They are difficult to detect using a traditional GC-MS and are usually found in extremely small concentrations in hops, potentially two orders of magnitude less than terpenes (ASBC). However, the human nose is excellent at detecting sulfur compounds. An example: the aroma threshold for myrcene is about 20ppb, while 4MMP (a common sulfur compound found in hops) is detectable at around 0.05ppb, or about 400 times less (ASBC)! Sulfur-containing compounds are now thought to be an integral part of the aroma profile of a beer, incentivizing brewers to harness their power in the brewing process.

Common confusion surrounds the prefixes mercapto and sulfanyl, which are generally interchangeable. Using mercapto- is not now suggested by the IUPAC. However, much of previously completed research on sulfur-containing compounds use the mercapto- prefix, along with much of modern brewer parlance. In the following descriptions, the sulfanyl- prefix will be used in text, but the mercapto- abbreviation will also be listed.

#### **Polyfunctional Thiol or Thiol**

In chemistry, a blanket term for an organic compound containing a sulfhydryl functional group(-SH). In the brewing world, it is a broad term covering a group of compounds, often contributing positive beer flavor and aroma.

#### 4-methyl-4-sulfanylpentan-2one (4MSP or 4MMP)

A polyfunctional thiol, and one of the better-known sulfur compounds in the brewing world.

Research suggests that 4MSP is not present in European varieties (Kishimoto, Morimoto, Kobayashi, Yako, & Wanikawa, 2008). 4MSP is usually described as having a blackcurrant aroma. At higher concentrations the aroma can become unpleasant, expressing as a "catty" or cat-urine-like.

Interestingly, the threshold at which 4MSP becomes unpleasant varies substantially among

individuals, similar to the flavor perception of cilantro. When dissolved in a beer matrix, it is thought to add tropical and wine grape-like flavors.

#### 3-sulfanylhexan-1-ol (3SH or 3MH)

A polyfunctional thiol commonly found in hops. It has a tropical and grapefruit aroma. 3SH can be converted by yeast into 3SHA (3MHA).

#### 3-sulfanylhexyl acetate (3SHA or 3MHA)

This compound is found readily in hoppy beers, but not usually found in hops (Kishimoto, Morimoto, Kobayashi, Yako, & Wanikawa, 2008). Like its relative 3SH, it has a grapefruit and tropical aroma. When present in high concentrations it can provide a passionfruit flavor. Whirlpool and active-fermentation dry hopping additions containing varieties high in 3SH are thought to maximize the potential for 3SHA by maximizing contact time between hop compounds and actively fermenting veast.

#### 3-sulfanyl-4-methylpentyl acetate (3S4MPA or 3M4MPA)

A polyfunctional thiol with a rhubarb and grapefruit aroma. In a study by Takoi Et al. on Sauvignon Blanc wines, it was concluded that 3S4MP and 3S4MPA worked synergistically to enhance flavor (Takoi, et al., 2009).

#### 3-sulfanyl-4-methylpentan-1-ol (3S4MP or 3M4MP)

A polyfunctional thiol with an aroma of rhubarb and grapefruit. It has an extremely low odor threshold of 0.07ppb. Like 3SHA, its concentration increases during fermentation (ASBC).

#### **ESTERS AND KETONES**

#### 2-methylbutyl isobutyrate

An ester derived from hops which typically survives the brewing process. Like most esters, it lends a fruity aroma, specifically apricot.

#### 2-nonanone

A ketone with a variety of different aromas. It can range from sweet and fruity to cheesy, buttery, and waxy.

#### Methyl geranate

A methyl ester derived from hops which typically survives the brewing process into finished beer. It lends a fruity and floral aroma and is usually the only hop-derived methyl ester that survives into beer.

#### **Butanoic acid 3-methylbutyl ester**

An ester derived from hops which typically survives the brewing process. It lends a fruity, sweet, and tropical aroma.

#### **QUESTIONS?**

Email us at brewinghelp@yakimachief.com





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