Discussion for results of aroma vs drying temperature of hops

Altwies, James R (Hopnology LLC), Dettmers, Daniel (Thermastor, Inc), Molling, Christine (Gorst Valley Hops, LLC). 2019.

Introduction

Hops (humulus lupulus var. lupulus) are a critical flavor and aroma component in beer brewing and have recently experienced a production renascence due to the proliferation of local craft brewing. Hundreds of small-scale growers seeking a niche crop have planted thousands of acres to capitalize on craft beer popularity. However new smaller, non-traditional hop growers face large industry barriers competing with hop farms in the Pacific Northwest and Europe where infrastructure and know-how are passed down through multiple generations, leaving the newly established smaller grower heavily disadvantaged.

Small scale regional growers must compete on attributes other than sale price to the brewer since they cannot achieve operational and cost efficiencies of their larger scale competitors and as such utilize their smaller scale to their advantage. The vast majority (>99%) of hops consumed by the craft brewing industry in North America are in a dry (8-10% moisture content) form. Traditional growers utilize high temperatures to drive off moisture quickly so the space may be utilized for the next harvest batch. Small scale growers are not constrained by such harvest requirements and therefore dry more slowly.

This study was designed to identify the impact of drying temperature on several critical hop aroma components know to the heat sensitive. Hops from the same variety (var. Cascade) harvested at the same time period from the same hop yard were exposed to four different drying temperatures and dried to the same moisture content (10%). Samples were analyzed in the laboratory using SMPE gas chromatography to determine the impact to aroma components in each treatment. Concurrently professional brewers sampled each treatment organoleptically and scored them based on a standard spider chart.

Materials and Methods

Hops. Cascade hops were harvested from Arendt's Hop Haven (Nekoosa, WI) at 74% moisture content as determined by the oven-dry method. Bines were cut and stripped using a Wolf 220 hop harvester. Hop subsamples were taken from the cleaning bel (cleaning belt?), placed in a temperature-controlled cooler at 20C and immediately transported to the testing facility for drying.

Dryer. A dryer was constructed to accept four, 15lb wet hop samples with bed dimensions 2ft x 2ft and a bed depth of 1ft. The floor of the drying chamber was constructed such that air could pass through unrestricted. A reverse-incline centrifugal fan provided approximately 8000 cfm of air flow at 1" W.C. pressure drop. Drying uniformity was achieved by drawing air downward through the hop bed and exhausting out of the building. Heat was added to three of four treatments via indirect propane combustion with no opportunity for treatment cross-over.

Dryer Instrumentation. Thermocouples were positioned at the heat inlet, top of the hop bed, center of the hop bed, and bottom of the hop bed to record air temperature and hop cone temperature. Anemometers were located at the air inlet and within the lower plenum of the dryer to record incoming and outgoing air velocity.

Treatments. Four treatments were as follows: No heat added (average 80F) + dehumidification, 110F heat only, 135F heat only, and 155F heat only. Each sample was dried to 10% moisture content as determined by over-dry weight analysis. Each treatment was sub-divided into four 1.25lb units and packed in triple-laminate barrier bags under inert gas per industry standards. Packages were placed in frozen storage (-20F) to await analysis.

Organoleptic Aroma Analysis. A 1.25lb vacuum-packaged sample from each treatment was removed from cold storage and allowed to come to room temperature. Trained subjects were presented with 8 blind samples (two from each treatment) in non-sequential order. Subjects placed a bolus of dry hops in their palm and vigorously rubbed their hands together to crush the cone. Subjects opened and cupped their hands, placing the sample under the nose and inhaling sharply. Each sample was evaluated for aroma quality utilizing a 1-5 scoring system (1=very low aroma, 5=high aroma) for each of 7 aroma attributes (Citrus, Floral, Fruity, Herbal, Pine, Tropical Fruit, Woody).

Laboratory Aroma Analysis. Individual oil components were quantified by diluting a portion of the oil recovered in distillation and adding an internal reference standard used in ASBC Hops 17 *Hop Essential Oils by Capillary Gas Chromatography-Flame Ionization Detection.*

Hop Essential Oils by HS-SPME-GCMS (Headspace-Solid Phase Microextraction). Samples were analyzed by a Gerstel MPS automated HS-SPME autosampler equipped with heated agitator set to 70C, and 2cm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) SPME fiber. Keeping as many variables with the programming and optimization constant were key to simply assessing the differences in oil composition between samples of varying drying temperature. Reference materials were purchased from Sigma Aldrich (Milwaukee, WI) and retention times and mass spectra verified with separation of analytes using a DB-5 wax column 30m x 0.25ID x 0.25um film thickness installed in a gas chromatograph equipped with a mass spectrometer with conditions similar to those outlined in Hops-17. Sample weight was optimized by reducing the sample weight to the point where saturation of myrcene was effectively reduced.

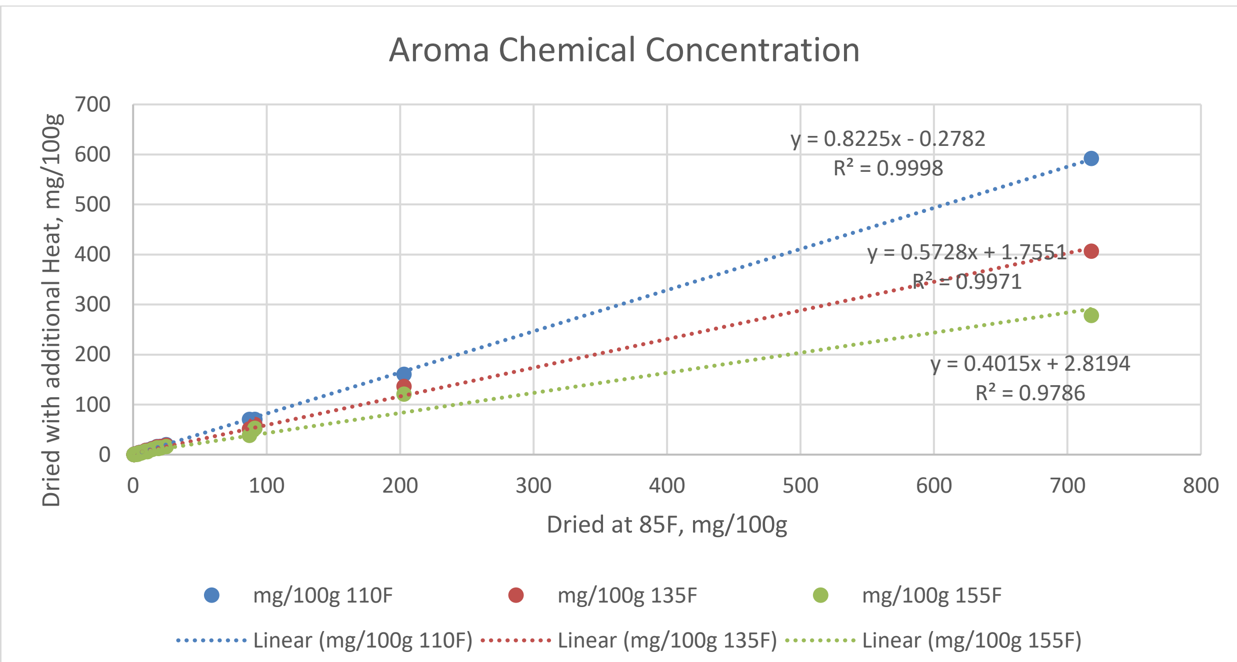
Samples from each treatment were analyzed in triplicate and the chromatograph peak area integration averaged within 1 standard deviation. Data are presented as both mg/100g of sample and as a percent change compared to the control (no heat + dehumidification). For simpler interpretation the compounds were grouped according to the organoleptic categories from the sensory analysis.

Discussion

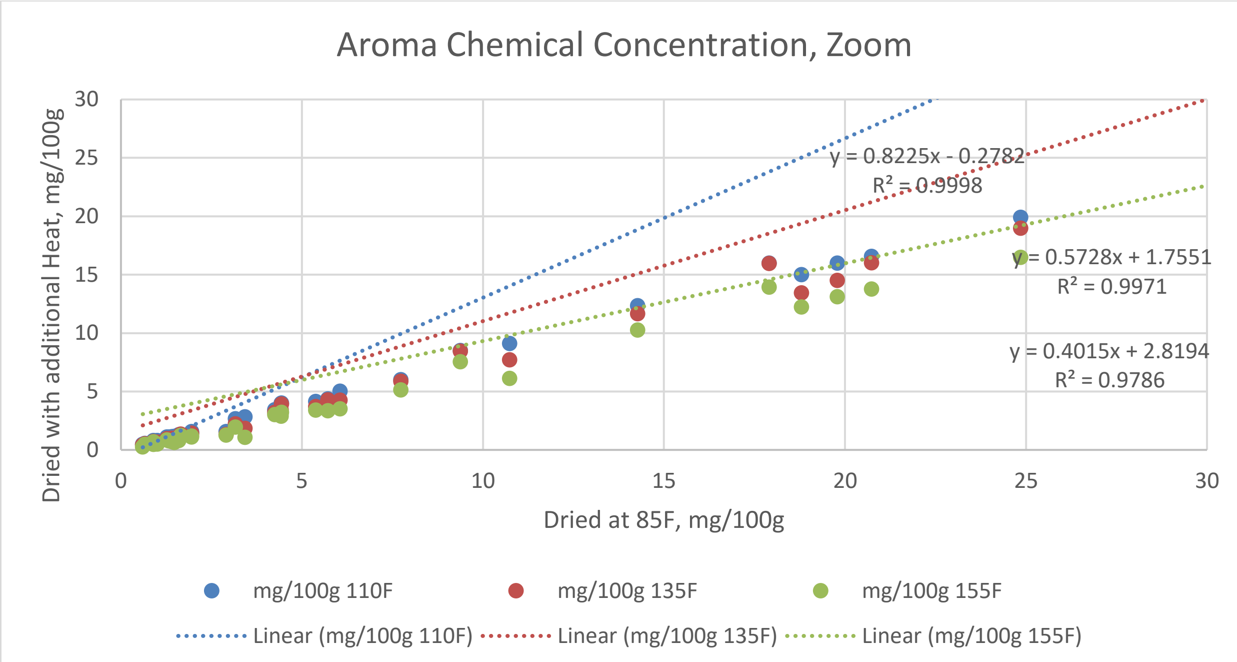
Raw data from laboratory. The values reported by the laboratory are the mass concentrations for each chemical tested for in the dried hops. Units are mg of chemical per 100g of dried sample. Results from three samples were averaged to smooth any variation that may have occurred among the three subsample analyses. So effectively, N=3.

For each treatment (no additional heat=85F, 110F, 135F, 155F), the lab reported mass concentrations for 38 different chemicals. Thirty-six of these chemicals have known aroma profiles for their initial forms. Two oxidation forms were also tested for. We hypothesize that the higher the temperature at which the hops are dried, more aroma chemicals will be driven off from the hops and more oxidation chemicals formed. We expect to see aroma chemicals at lower concentrations in samples dried with added heat compared to concentrations in the hops dried with no additional heat (85F). We expect to see higher concentrations of the two oxides for hops dried with additional heat.

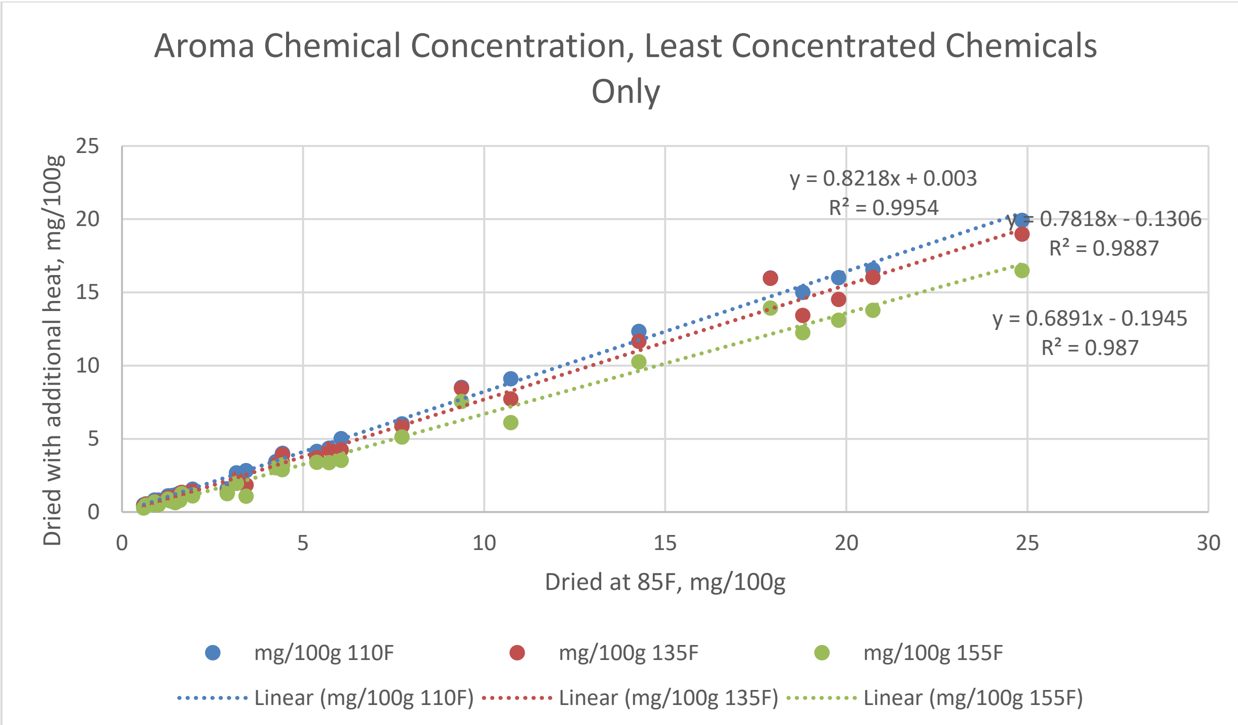
The next figure shows the concentrations of all aroma chemicals from the analysis (no oxides) for the additional heat samples (y-axis) vs. the no additional heat samples (x-axis). The relationship be tween heated vs. unheated is quite linear, with R^2 of the linear fit ranging from 0.98 to 0.99. The slopes of the linear fit support the hypothesis that more heat drives off more aroma chemical, with 82%, 57%, and 40% of the aroma chemicals remaining in the samples heated to 110F, 135F, and 155F, respectively. However, there are a few chemicals at high concentrations that are dominating this relationship.



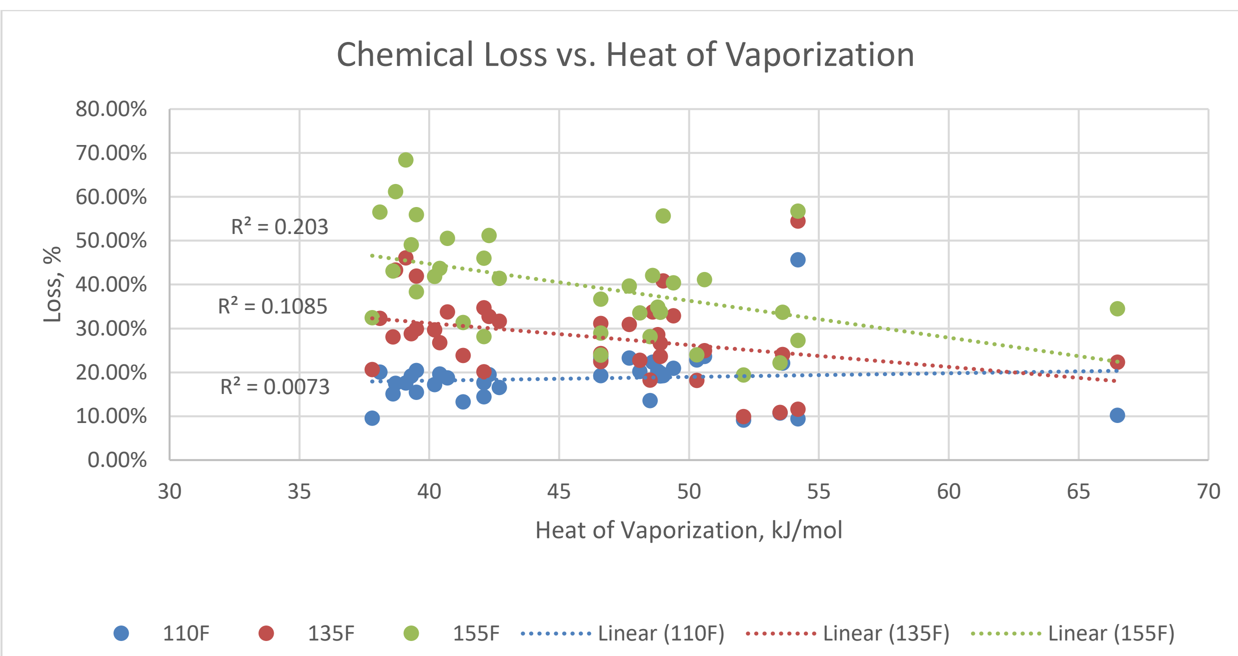
However, if we focus on the chemicals that are found at concentrations below 30 mg/100g (next figure), we see that the slope of the linear fit is not representative of the trend for the two highest heats.



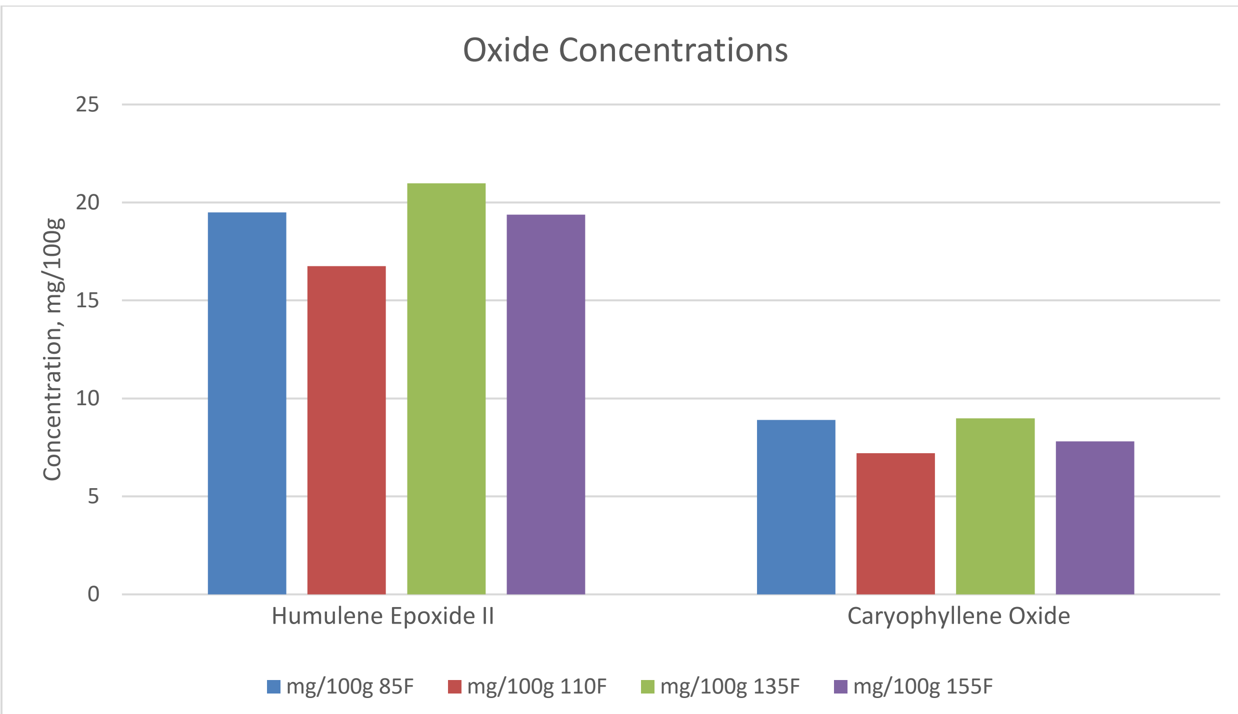
The relationship is still linear though. We can fit a line for these less concentrated chemicals (next figure) and come up with rates of 82%, 78%, and 69% of the aroma chemicals left behind in the 110F, 135F, and 155F samples, respectively. The R^2 are similar. The original hypothesis is still supported that higher heats drive off more aroma chemicals; although we can note that at least at the two highest temperatures tested, chemicals with larger concentrations have been driven off at a higher percentage (less remain) than those aroma chemicals at lower concentrations.



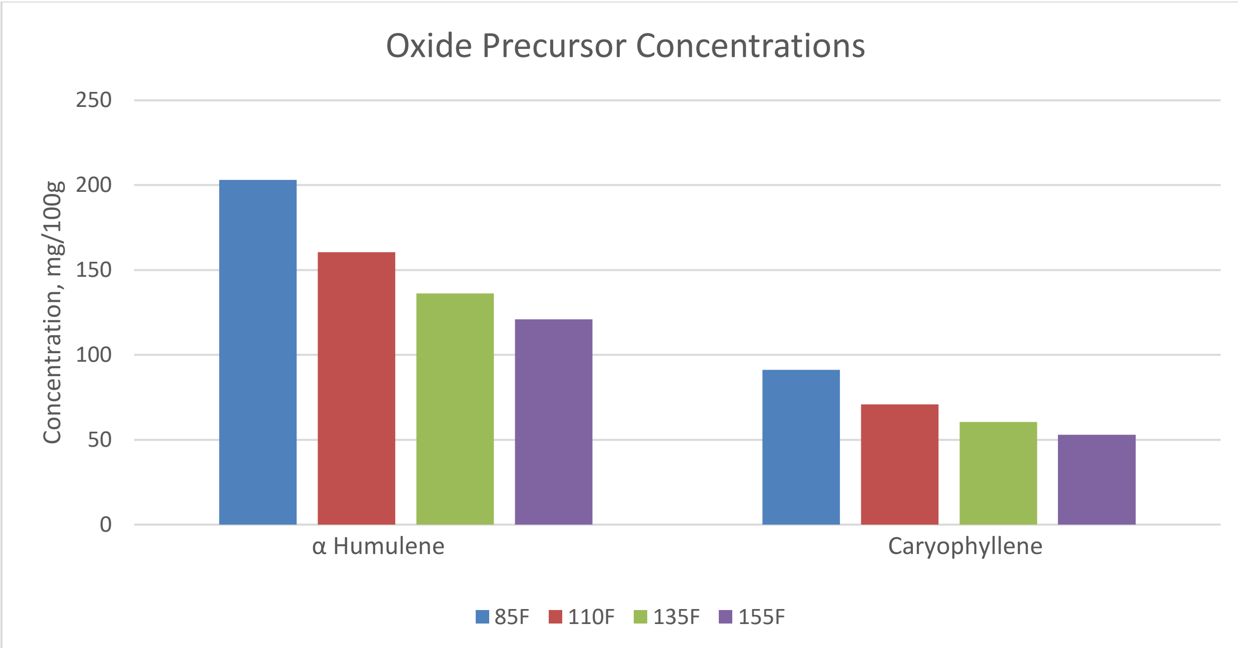
We have heat of vaporization and vapor pressure information for these aroma chemicals. The next figure shows the percent loss of each aroma chemical in the heated samples versus heat of vaporization. The values do show trends and a trend line is apparent however the R^2 data suggests low correlation. This experiment was not designed to normalize environmental conditions associated with heat of vaporization, yet general trending indicated some relationship.



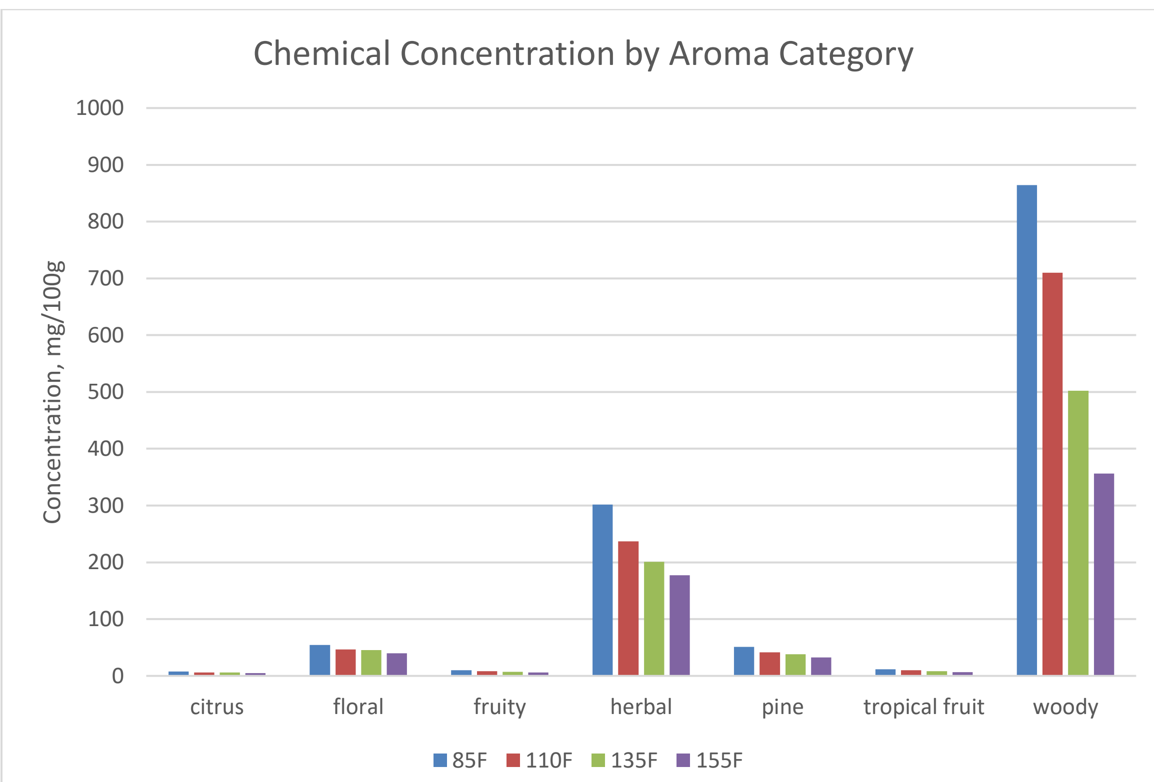
The story for oxidation chemicals is less clear. In the next figure, the concentrations of the two oxides are shown for each treatment. Both humulene epoxide II and caryophyllene oxide show similar behavior, but not a uniform trend. From unheated to 110F, the concentrations of the oxides decrease as with the aroma chemicals. However, from 100F to 135F, the concentrations increase, but then decrease again from 135F to 155F. A possible explanation is as follows. Humulene epoxide II and caryophyllene oxide both exist in hops dried at ambient temperature. In fact, they may even exist in wet hops, possibly even before picking. We do not have data for hops at these stages. However, when heated, two processes are happening. Current chemicals are being driven off, and since these are oxides, new ones are being made from their non-oxidized precursors. Alpha humulene exists in the no-heat-added hops at 203 mg/100g and caryophyllene at 91 mg/100g. As heat is increased over a certain threshold, which appears to be between 110F and 135F, more oxides are created than are being driven off or destroyed. At an additional threshold, the balance again returns to more oxides being driven off or destroyed.



The following figure shows that precursor concentrations for these two chemicals are indeed decreasing by amounts large enough to account for the increase in oxides between 110F and 135F. Further study of this is needed to understand the actual process.



In order to compare aroma concentrations to perceived aroma, we aggregated the individual aroma chemicals into categories. There is one citrus chemical, 6 floral chemicals, 4 fruity chemicals, 6 herbal chemicals, 4 pine chemicals, 6 tropical fruit chemicals, and 9 woody chemicals. The next figure shows the total concentration for each aroma category in mg/100g. As heat increases, total concentration of chemicals monotonically decreases for all categories.

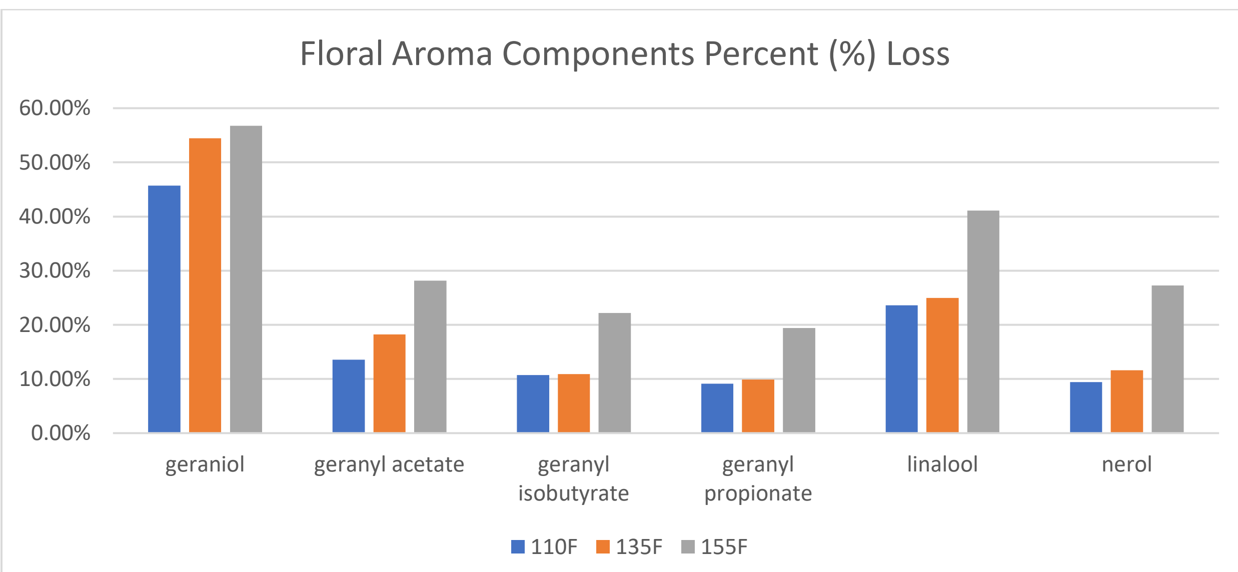


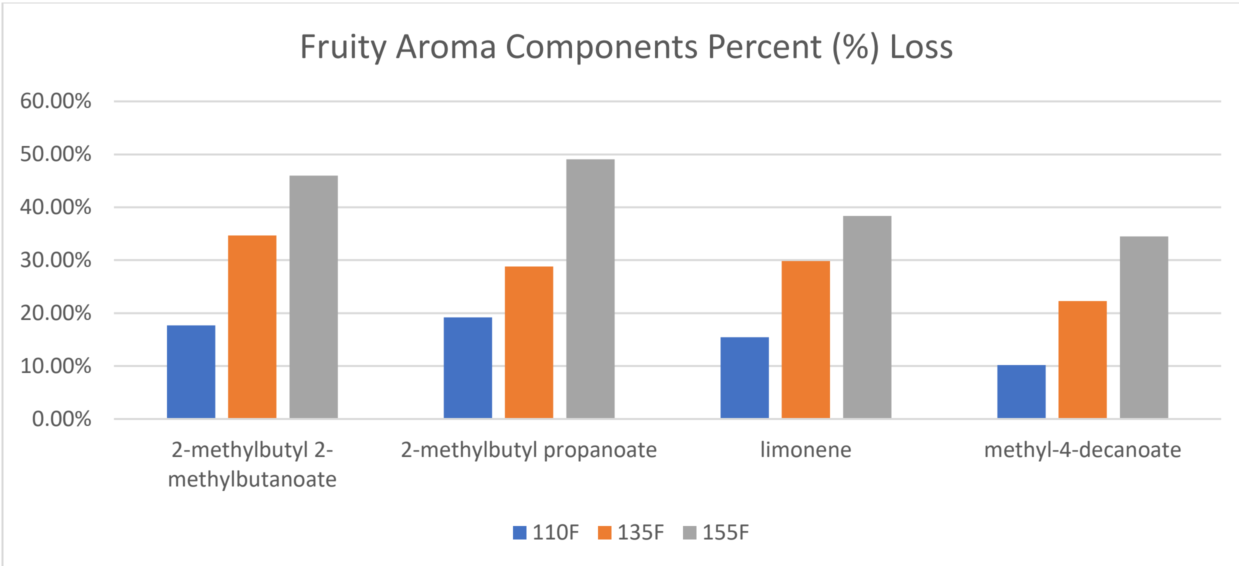
Initially we might hypothesize that as the concentrations of these chemicals decrease in the analysis, they will also decrease as sensed by the human nose. This, however, does not consider any cancelling out, masking, or enhancement of aroma that may occur by a mix of the aroma component chemicals. Most persons know from cooking with spices that flavors (which are highly tied to aroma) can be enhanced, masked, balanced, etc. by adding additional spices to a food. Below is the mean organoleptic score for each aroma category.

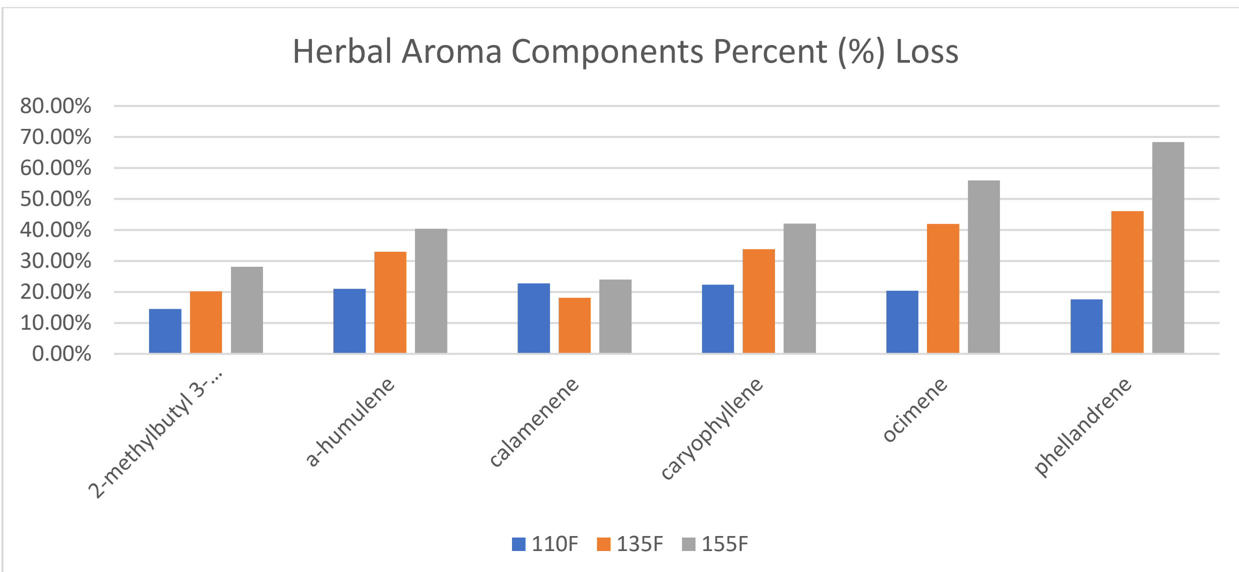
In every instance the target molecule shows concentration reduction as temperature increases. The largest losses occurred at the highest temperature. Floral compounds show relatively little change between 110F and 135F which may account for the relatively small change in the organoleptic score between those treatments.

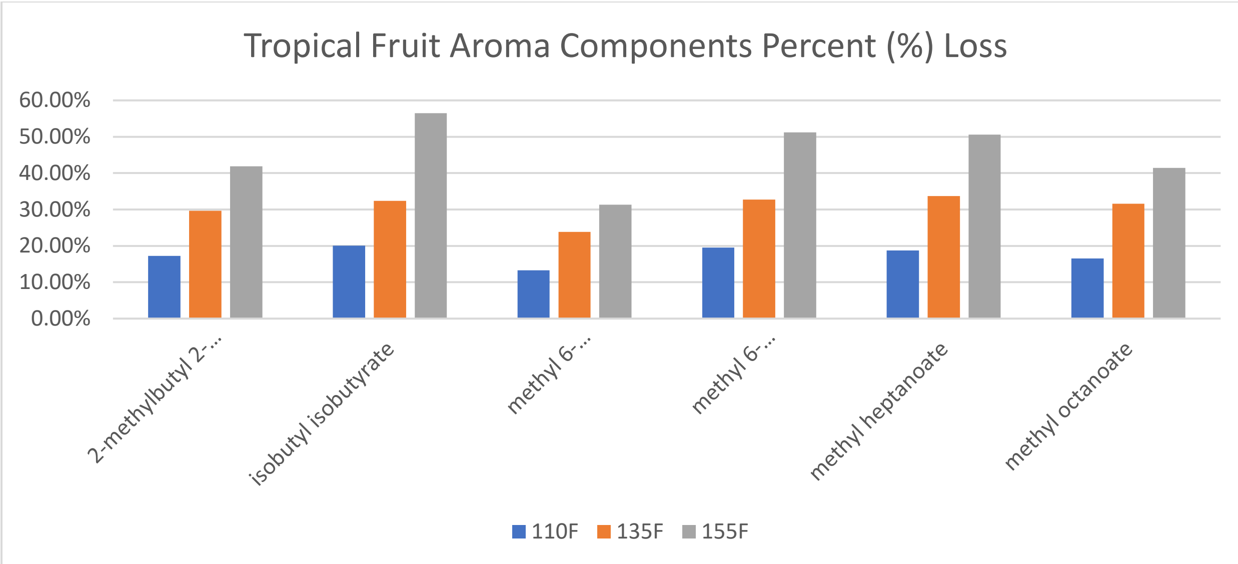
Losses of compounds associated with tropical fruit aroma were linear and elevated as temperature increased. This is especially important given that the craft brewing industry is driven to produce recipes heavy in pineapple, mango, melon, etc. Any variety described as "tropical" can therefore be expected to suffer greatly from traditional large-scale drying techniques utilizing heat.

Perhaps most critical is the steep loss of geraniol even at the lower temperatures. The ratio of geraniol to linalool has been linked to sensory intensity of "dry hop" aroma in beer, otherwise equivalent to the impactfulness of hop aroma in finished beer. While linalool losses were consistent with other aroma compounds as temperature increased, it is the amplified losses of geraniol that alter the "dry hop" aroma ratio. It may be inferred from this observation that hops dried with any heat will experience an impact to "dry hop" aroma indicators especially at the higher range typical of conventional larger scale hop production.

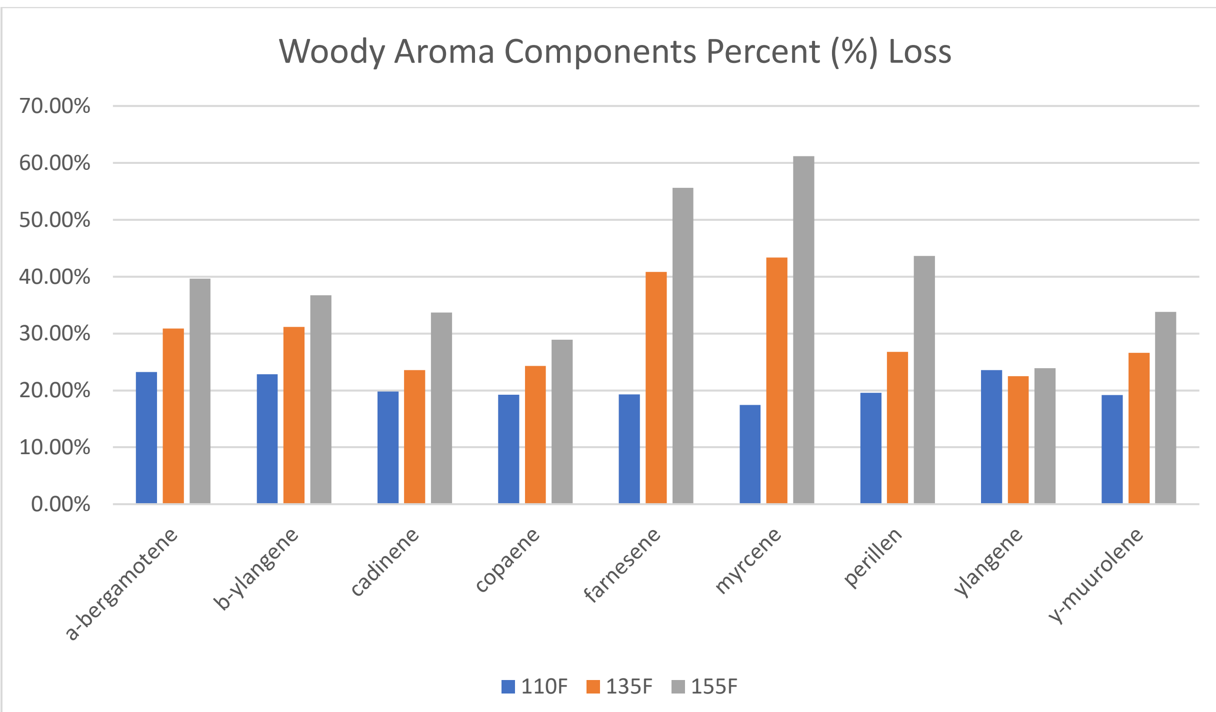



Fruity Aroma Components Percent (%) Loss
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
2-methylbutyl 2-methylbutanoate
2-methylbutyl propanoate
limonene
methyl-4-decanoate
110F
135F
155F

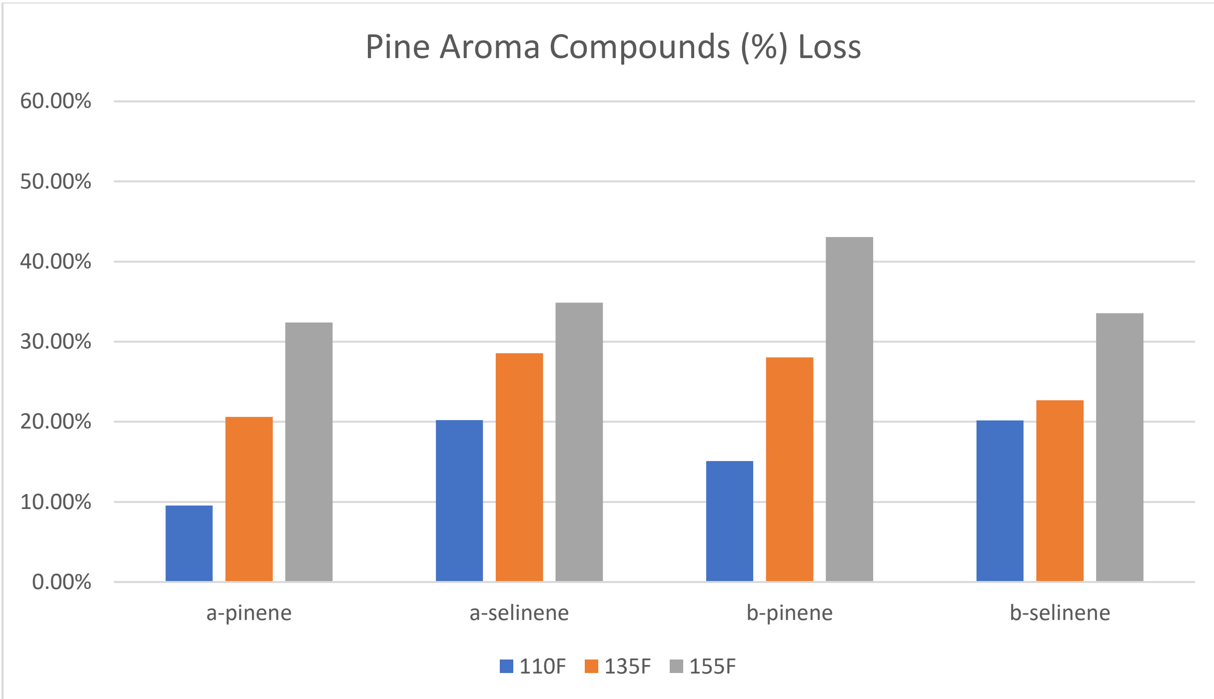

Herbal Aroma Components Percent (%) Loss
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
2-methylbutyl 3-...
a-humulene
calamenene
caryophyllene
ocimene
phellandrene
110F
135F
155F



Tropical Fruit Aroma Components Percent (%) Loss
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
2-methylbutyl 2-...
isobutyl isobutyrate
methyl 6-...
methyl 6-...
methyl heptanoate
methyl octanoate
110F
135F
155F



Woody Aroma Components Percent (%) Loss
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
a-bergamotene
b-ylangene
cadinene
copaene
farnesene
myrcene
perillen
ylangene
y-muurolene
110F
135F
155F



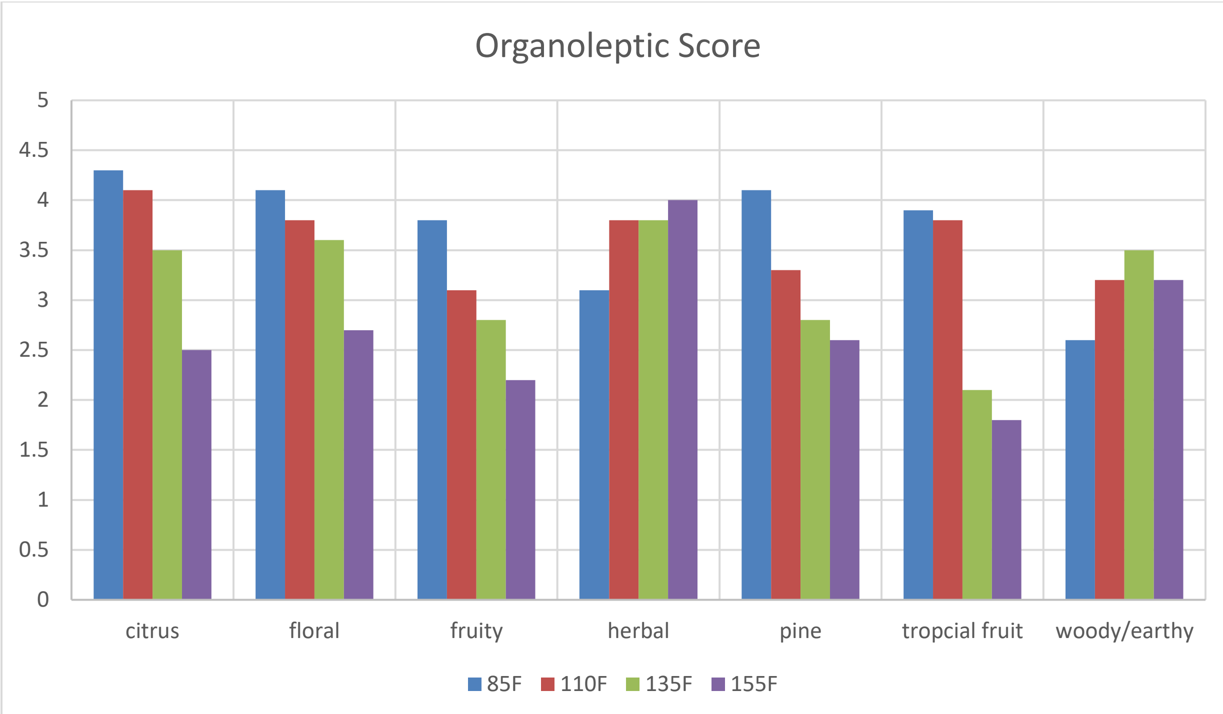
Pine Aroma Compounds (%) Loss
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
a-pinene
a-selinene
b-pinene
b-selinene
110F
135F
155F

Aroma [C]

organoleptic sector	chemical name	mg/100g 85F	110F	135F	155F
citrus	citronellol	7.73241	6.02434	5.87234	5.12908
floral	geranyl propionate	9.376635	8.520031	8.450862	7.555821
floral	geranyl isobutyrate	17.90635	15.98465	15.95672	13.93582
floral	nerol	4.43123	4.013487	3.91774	3.22182
floral	geranyl acetate	14.26903	12.33418	11.66784	10.25445
floral	linalool	5.716863	4.366121	4.289736	3.36627
floral	geraniol	2.906049	1.578599	1.32412	1.257628
fruity	methyl-4-decanoate	4.426419	3.974434	3.44022	2.900725
fruity	2-methylbutyl propanoate	1.402006	1.132731	0.998343	0.714089
fruity	limonene	3.159784	2.672387	2.216056	1.946758
fruity	2-methylbutyl 2-methylbutanoate	0.896576	0.738222	0.585414	0.484263
herbal	calamenene	1.648938	1.273264	1.350194	1.253122
herbal	2-methylbutyl 3-methylbutanoate	0.655086	0.560439	0.523156	0.470744
herbal	a-humulene	203.0221	160.4905	136.2065	121.0041
herbal	caryophyllene	91.229	70.8586	60.41289	52.8592
herbal	ocimene	1.472072	1.171674	0.854678	0.648573
herbal	phellandrene	3.429846	2.826465	1.84829	1.084652
pine	a-pinene	0.896576	0.811028	0.711873	0.605935
pine	b-selinene	20.73621	16.55469	16.02683	13.77533
pine	b-pinene	10.73306	9.110948	7.723934	6.111351
pine	a-selinene	18.79953	14.99584	13.43183	12.24489
tropical fruit	methyl 6-methylheptanoate	1.270036	1.101125	0.966943	0.871812
tropical fruit	2-methylbutyl 2-methylpropanoate	6.053589	5.012348	4.258337	3.52018
tropical fruit	methyl octanoate	1.319695	1.101125	0.902423	0.773018
tropical fruit	isobutyl isobutyrate	0.601345	0.48086	0.406908	0.261717
tropical fruit	methyl 6-methyloctanoate	1.006777	0.810464	0.677032	0.491196
tropical fruit	methyl heptanoate	1.597919	1.298097	1.058992	0.790004
woody	ylangene	0.897256	0.685734	0.695528	0.682891
woody	cadinene	24.84903	19.92635	18.98573	16.4802
woody	copaene	4.248873	3.430362	3.216119	3.019278
woody	y-muurolene	19.7893	15.99651	14.51878	13.10457
woody	perillen	1.953692	1.570697	1.431059	1.100945
woody	a-bergamotene	1.945529	1.493376	1.344602	1.17374
woody	b-ylangene	5.380137	4.14996	3.703462	3.40544
woody	farnesene	87.10121	70.30888	51.55813	38.65092
woody	myrcene	717.969	592.5508	406.8204	278.6405

Percent Change by Treatment Compared to No-Heat

Aroma Sector	Chemical Name	% loss 110F	135F	155F
citrus	citronellol	22.09%	24.06%	33.67%
floral	geranyl propionate	9.14%	9.87%	19.42%
floral	geranyl isobutyrate	10.73%	10.89%	22.17%
floral	nerol	9.43%	11.59%	27.29%
floral	geranyl acetate	13.56%	18.23%	28.13%
floral	linalool	23.63%	24.96%	41.12%
floral	geraniol	45.68%	54.44%	56.72%
fruity	methyl-4-decanoate	10.21%	22.28%	34.47%
fruity	2-methylbutyl propanoate	19.21%	28.79%	49.07%
fruity	limonene	15.43%	29.87%	38.39%
fruity	2-methylbutyl 2-methylbutanoate	17.66%	34.71%	45.99%
herbal	calamenene	22.78%	18.12%	24.00%
herbal	2-methylbutyl 3-methylbutanoate	14.45%	20.14%	28.14%
herbal	a-humulene	20.95%	32.91%	40.40%
herbal	caryophyllene	22.33%	33.78%	42.06%
herbal	ocimene	20.41%	41.94%	55.94%
herbal	phellandrene	17.59%	46.11%	68.38%
pine	a-pinene	9.54%	20.60%	32.42%
pine	b-selinene	20.17%	22.71%	33.57%
pine	b-pinene	15.11%	28.04%	43.06%
pine	a-selinene	20.23%	28.55%	34.87%
tropical fruit	methyl 6-methylheptanoate	13.30%	23.86%	31.36%
tropical fruit	2-methylbutyl 2-methylpropanoate	17.20%	29.66%	41.85%
tropical fruit	methyl octanoate	16.56%	31.62%	41.42%
tropical fruit	isobutyl isobutyrate	20.04%	32.33%	56.48%
tropical fruit	methyl 6-methyloctanoate	19.50%	32.75%	51.21%
tropical fruit	methyl heptanoate	18.76%	33.73%	50.56%
woody	ylangene	23.57%	22.48%	23.89%
woody	cadinene	19.81%	23.60%	33.68%
woody	copaene	19.26%	24.31%	28.94%
woody	y-muurolene	19.17%	26.63%	33.78%
woody	perillen	19.60%	26.75%	43.65%
woody	a-bergamotene	23.24%	30.89%	39.67%
woody	b-ylangene	22.87%	31.16%	36.70%
woody	farnesene	19.28%	40.81%	55.63%
woody	myrcene	17.47%	43.34%	61.19%



Some of the aroma categories, namely every category except herbal and woody, show a decrease in score with increasing heat. Herbal and woody, however, tend to increase for the heated treatments as compared to the unheated hops even though their concentrations are decreasing by large amounts mass-wise. What we may be seeing is an unmasking of the herbal and woody aromas as the brighter and sweeter aromas are driven off. It is interesting to note that either before or after heating, neither herbal nor woody aromas are dominating this hop variety. That is, even though those chemicals exist in much higher concentrations than the other aroma categories have, they score about the same. Of course, the humans smelling the hops are perceiving relative sensations, so perhaps they tend to report near some mean value. Perhaps the threshold for sensing these chemicals is much higher and the human nose can get overwhelmed by the other aromas bombarding the receptors in the nose.

Conclusions

Chemical analysis reveals that as hops are dried at higher and higher temperatures, more and more aroma chemicals are driven off. This results in the perceived aroma decreasing for floral, fruity, and piney categories, while increasing for herbal and woody aromas. As these aromas are a key differentiator in hop varieties and the reason they are used in brewing, it follows that their impact on aroma/flavor of beer brewed with hops that were dried at different temperatures would yield a similar result.