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#ElevateBeer

Influence of time, temperature and hop oil content on aroma extraction during dry hopping

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BARTH-HAAS GROUP
FOR YOUR SUCCESS

(Session 6: Hops 1 pres. 19)

Dry hopping

- Addition of hops in the cold block of brewery and / or into finished beer
- Different products can be used:

  Cones, Pellets, Extract, Hop oils, Pure Hop Aroma
- Cold extraction of essential oils from hops in a low alcohol solution to get an intensive hop aroma
- Different philosophies → many different ways of dry hopping in the industry

Dry hopping parameters

- **System:**
  - Static dry hopping: addition of hops into ZCVs or casks, with longer contact times (classic dry hopping)
  - Dynamic dry hopping: Circulation by pumping or stirring of hops dissolved in beer (different solutions available)
  - Slurry technique: High concentrated hop dispersion added to beer
- **Oil content (variety, pellet type, amount):**

  The more essential oils are available the more can be extracted
- **Contact time:**

  Few hours up to two weeks
- **Temperature:**

  Higher temperature and pressure increase the extraction yield (however flavour impact of temperature so far is unclear)

Experimental set-up

Chosen parameters for this study

- Different **temperatures** were chosen

  0/13/ 20 °C

- **Time** :
  - 20/60/180/360 min for 0/13/20 °C
  - 1440 min for 20°C
- Two different Pellet types
  - Type 90
  - Type 45

  → for different **oil contents**
- Static and dynamic system

  (magnetic stirrer)

Experimental set-up

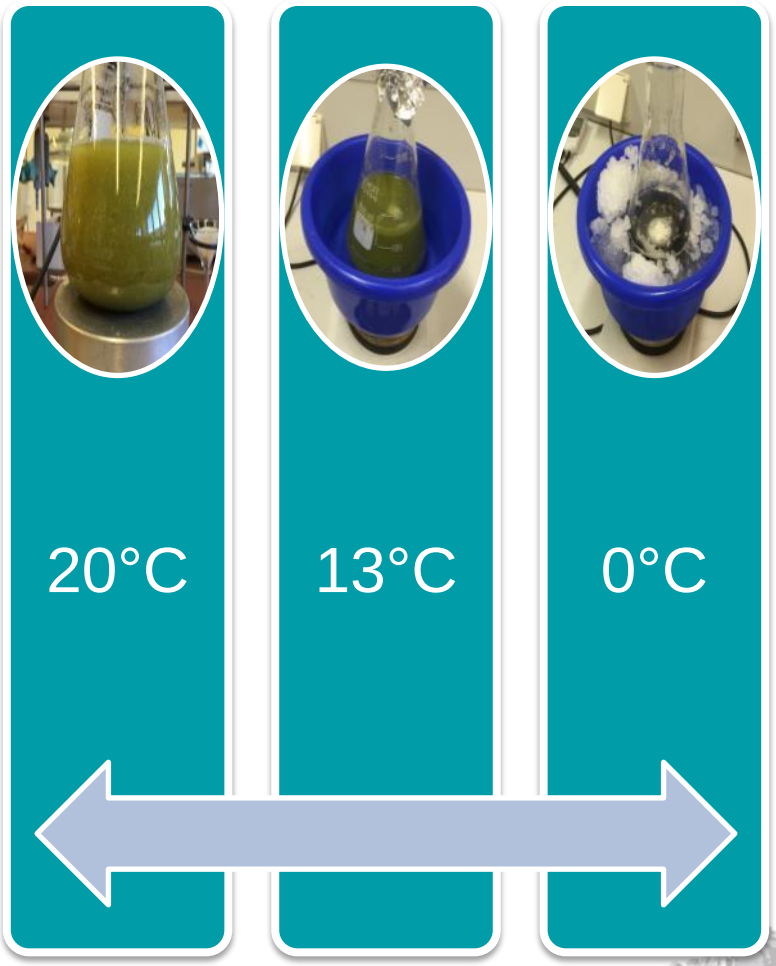
- Lab scale trials in 1 l Erlenmeyer flasks
- Sample size: 0.66 l beer
- Neutral and filtered beer

  → free from yeast

  → no biotransformation of hop oil components possible
- Pressure less extraction in open vessels

  → no reduce of aroma compounds through CO_2 discharge
- Beer was degassed with ultrasonic for 10 min

Experimental set-up

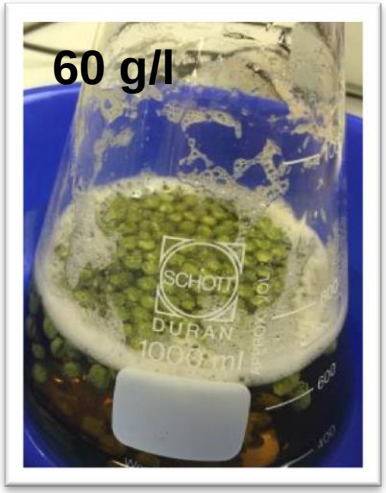


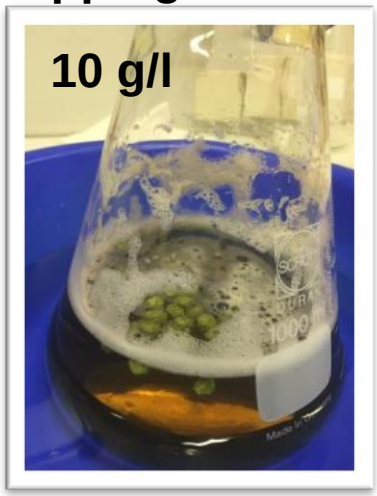
Temperature adjustment

- 20°C: No water cooling (tempered lab)
- 13°C: Water cooling with cold water + air conditioning
- 0°C: Water cooling with ice cubes and sodium chloride

Experimental set-up

Static dry hopping





Dynamic dry hopping

Dry hopping methods

- **Two different hop dosages**
  - heavy dry hopping (10 g/l)
    → Hop oil dosage: 7.5 ml/hl
  - hop slurry (60 g/l)
    → Hop oil dosage: 45 ml/hl

- **st = static dry hopping**

  No stirrer used

- **dy = dynamic dry hopping**

  Magnetic stirrer (300 rpm) for simulating circulation

Analysis with GC-MS/MS

Hop Aroma Method

- GC-MS/MS is rarely used in brewing, because of the costs
- An isotopically labeled internal standard is necessary
  - Similarity to the analyte
  - Molecular mass differs marginal
- Challenge for hop aroma
  - Multiple analytes
  - Wide concentration range
  - Chemical properties differ

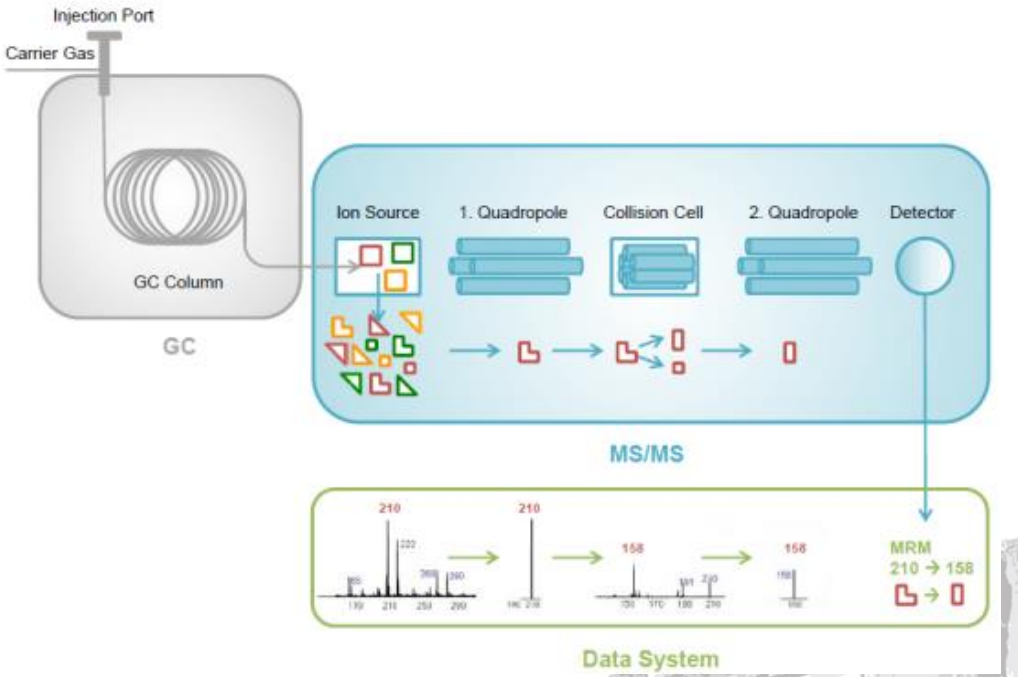
Analytes

Substances

- α-pinene
- ß-pinene
- **myrcene**
- limonene
- cis-linalool oxide
- trans-linalool oxide
- **linalool**
- α-terpineol
- nerol
- **geraniol**
- geranyl acetate
- **ß- caryophyllene**
- humulene
- caryophyllene oxide

Peserske, 2016

Analysis with GC-MS/MS



- Operation range: 1 – 100 µg/l
- Linearity: $R^2 > 0.99$
- Relative Standard Deviation:

  < 10 %

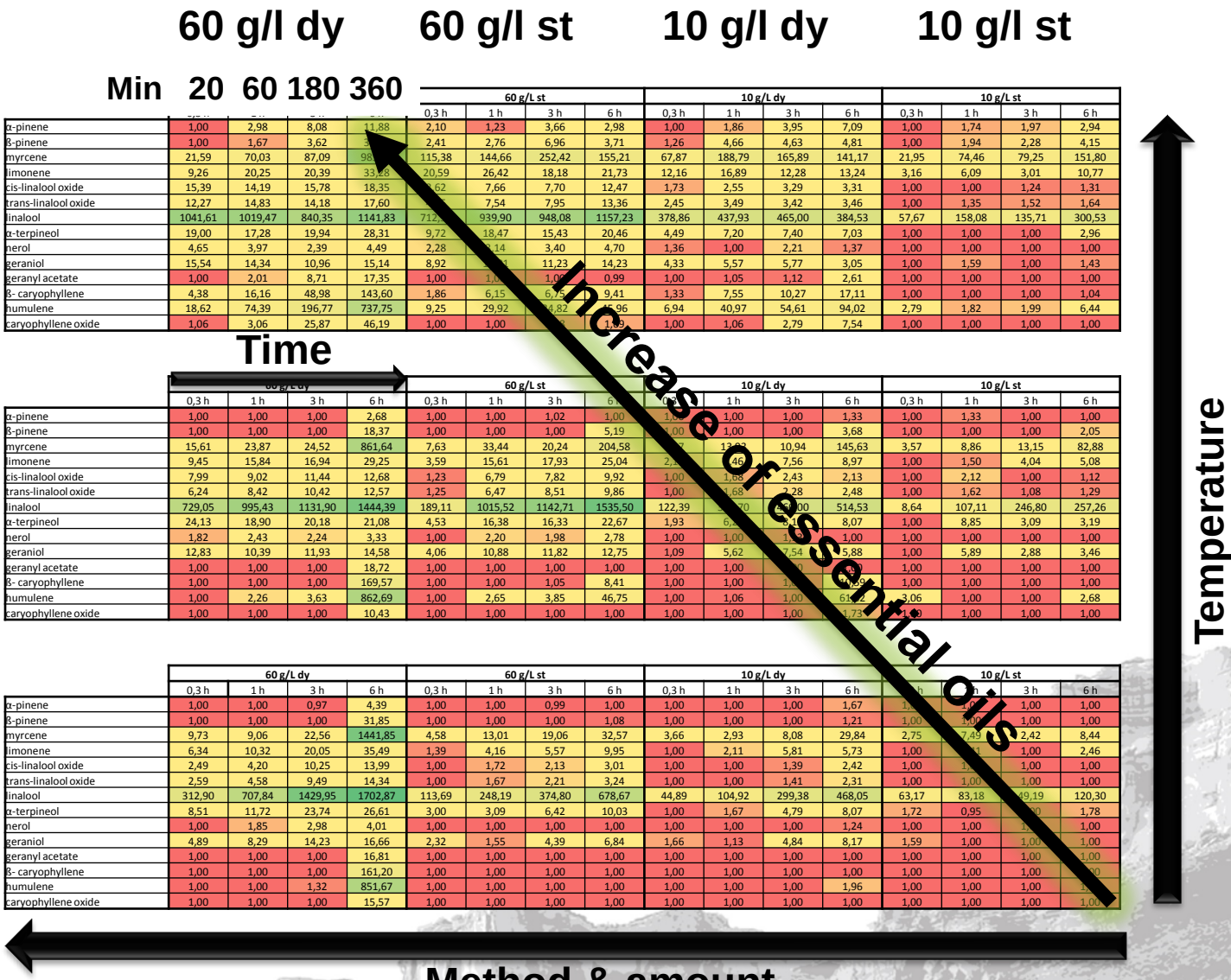
Peserske, 2016

Analysis with GC-MS/MS

- Advantages of GC-MS/MS:
  - Solvent-free extraction
  - Small sample volume (1-3 ml)
  - Minimum of manual handling
- It is a simple analysis for finished beer
- But especially for hop slurries sampling is more complicated, because of the hop particles
  → It need to be filtered

Peserske, 2016

Influence of dry hopping parameters



20°C

	60 g/L dy				60 g/L st				10 g/L dy				10 g/L st			
	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h
α-pinene	1,00	2,98	8,08	11,88	2,10	1,23	3,66	2,98	1,00	1,86	3,95	7,09	1,00	1,74	1,97	2,94
ß-pinene	1,00	1,67	3,62	[illegible]	2,41	2,76	6,96	3,71	1,26	4,66	4,63	4,81	1,00	1,94	2,28	4,15
myrcene	21,59	70,03	87,09	98	115,38	144,66	252,42	155,21	67,87	188,79	165,89	141,17	21,95	74,46	79,25	151,80
limonene	9,26	20,25	20,39	33,28	20,59	26,42	18,18	21,73	12,16	16,89	12,28	13,24	3,16	6,09	3,01	10,77
cis-linalool oxide	15,39	14,19	15,78	18,35	62	7,66	7,70	12,47	1,73	2,55	3,29	3,31	1,00	1,00	1,24	1,31
trans-linalool oxide	12,27	14,83	14,18	17,60		7,54	7,95	13,36	2,45	3,49	3,42	3,46	1,00	1,35	1,52	1,64
linalool	1041,61	1019,47	840,35	1141,83	712,	939,90	948,08	1157,23	378,86	437,93	465,00	384,53	57,67	158,08	135,71	300,53
α-terpineol	19,00	17,28	19,94	28,31	9,72	18,47	15,43	20,46	4,49	7,20	7,40	7,03	1,00	1,00	1,00	2,96
nerol	4,65	3,97	2,39	4,49	2,28	3,14	3,40	4,70	1,36	1,00	2,21	1,37	1,00	1,00	1,00	1,00
geraniol	15,54	14,34	10,96	15,14	8,92	11,	11,23	14,23	4,33	5,57	5,77	3,05	1,00	1,59	1,00	1,43
geranyl acetate	1,00	2,01	8,71	17,35	1,00	1,0	1,08	0,99	1,00	1,05	1,12	2,61	1,00	1,00	1,00	1,00
ß- caryophyllene	4,38	16,16	48,98	143,60	1,86	6,15	6,75	9,41	1,33	7,55	10,27	17,11	1,00	1,00	1,00	1,04
humulene	18,62	74,39	196,77	737,75	9,25	29,92	24,82	46,96	6,94	40,97	54,61	94,02	2,79	1,82	1,99	6,44
caryophyllene oxide	1,06	3,06	25,87	46,19	1,00	1,00	[illegible]	1,00	1,00	1,06	2,79	7,54	1,00	1,00	1,00	1,00

13°C

	60 g/L dy				60 g/L st				10 g/L dy				10 g/L st			
	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h
α-pinene	1,00	1,00	1,00	2,68	1,00	1,00	1,02	1,00	1,00	1,00	1,00	1,33	1,00	1,33	1,00	1,00
ß-pinene	1,00	1,00	1,00	18,37	1,00	1,00	1,00	5,19	1,00	1,00	1,00	3,68	1,00	1,00	1,00	2,05
myrcene	15,61	23,87	24,52	861,64	7,63	33,44	20,24	204,58	2,7	13,0	10,94	145,63	3,57	8,86	13,15	82,88
limonene	9,45	15,84	16,94	29,25	3,59	15,61	17,93	25,04	2,2	4,6	7,56	8,97	1,00	1,50	4,04	5,08
cis-linalool oxide	7,99	9,02	11,44	12,68	1,23	6,79	7,82	9,92	1,00	1,68	2,43	2,13	1,00	2,12	1,00	1,12
trans-linalool oxide	6,24	8,42	10,42	12,57	1,25	6,47	8,51	9,86	1,00	1,68	2,28	2,48	1,00	1,62	1,08	1,29
linalool	729,05	995,43	1131,90	1444,39	189,11	1015,52	1142,71	1535,50	122,39	270	514,53	8,64	107,11	246,80	257,26	
α-terpineol	24,13	18,90	20,18	21,08	4,53	16,38	16,33	22,67	1,93	6,2	8,07	1,00	8,85	3,09	3,19	
nerol	1,82	2,43	2,24	3,33	1,00	2,20	1,98	2,78	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
geraniol	12,83	10,39	11,93	14,58	4,06	10,88	11,82	12,75	1,09	5,62	7,54	5,88	1,00	5,89	2,88	3,46
geranyl acetate	1,00	1,00	1,00	18,72	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
ß- caryophyllene	1,00	1,00	1,00	169,57	1,00	1,00	1,05	8,41	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
humulene	1,00	2,26	3,63	862,69	1,00	2,65	3,85	46,75	1,00	1,06	1,00	6,02	1,06	1,00	1,00	2,68
caryophyllene oxide	1,00	1,00	1,00	10,43	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,73	1,00	1,00	1,00	1,00

0°C

	60 g/L dy				60 g/L st				10 g/L dy				10 g/L st			
	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h	0,3 h	1 h	3 h	6 h
α-pinene	1,00	1,00	0,97	4,39	1,00	1,00	0,99	1,00	1,00	1,00	1,00	1,67	1,0	1,0	1,00	1,00
ß-pinene	1,00	1,00	1,00	31,85	1,00	1,00	1,00	1,08	1,00	1,00	1,00	1,21	1,00	1,00	1,00	1,00
myrcene	9,73	9,06	22,56	1441,85	4,58	13,01	19,06	32,57	3,66	2,93	8,08	29,84	2,75	7,49	2,42	8,44
limonene	6,34	10,32	20,05	35,49	1,39	4,16	5,57	9,95	1,00	2,11	5,81	5,73	1,00	1,1	1,00	2,46
cis-linalool oxide	2,49	4,20	10,25	13,99	1,00	1,72	2,13	3,01	1,00	1,00	1,39	2,42	1,00	1,0	1,00	1,00
trans-linalool oxide	2,59	4,58	9,49	14,34	1,00	1,67	2,21	3,24	1,00	1,00	1,41	2,31	1,00	1,00	1,00	1,00
linalool	312,90	707,84	1429,95	1702,87	113,69	248,19	374,80	678,67	44,89	104,92	299,38	468,05	63,17	83,18	49,19	120,30
α-terpineol	8,51	11,72	23,74	26,61	3,00	3,09	6,42	10,03	1,00	1,67	4,79	8,07	1,72	0,95	1,00	1,78
nerol	1,00	1,85	2,98	4,01	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,24	1,00	1,00	1,0	1,00
geraniol	4,89	8,29	14,23	16,66	2,32	1,55	4,39	6,84	1,66	1,13	4,84	8,17	1,59	1,00	1,00	1,00
geranyl acetate	1,00	1,00	1,00	16,81	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
ß- caryophyllene	1,00	1,00	1,00	161,20	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
humulene	1,00	1,00	1,32	851,67	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,96	1,00	1,00	1,00	1,00
caryophyllene oxide	1,00	1,00	1,00	15,57	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00

Results

- Trials showed that for short contact times (< 6 h) dynamic dry hopping **improves aroma utilization** significantly
- **Reduction** of the **particle size** through stirring, leads to higher exploration of aroma compounds
- An increase of **temperature accelerates** the **transfer of compounds** into beer

Influence of time

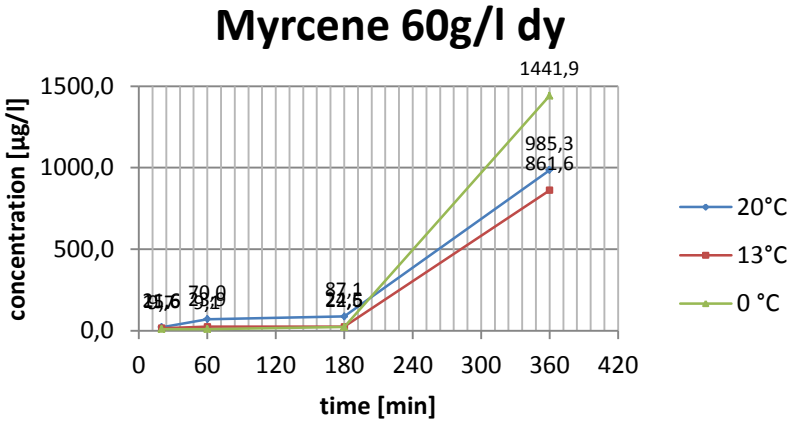
Thresholds

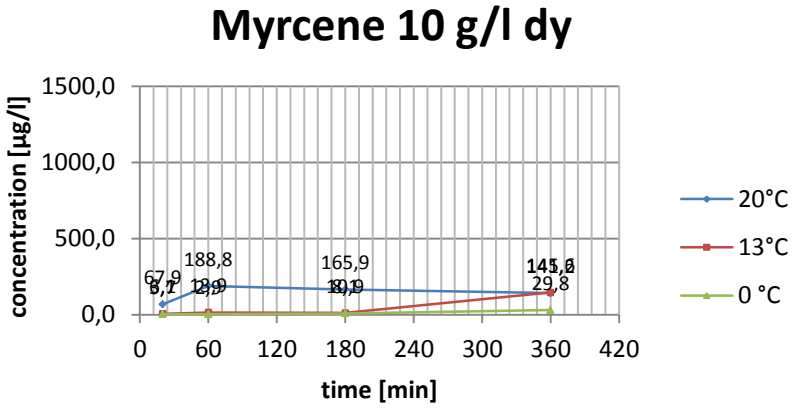
Analyte	Min. [µg/l]	Max. [µg/l]
myrcene	10	200
linalool	9	80
α-terpineol	1000	NIF
nerol	500	NIF
geraniol	10	70
ß- caryophyllene	160	450
humulene	800	NIF
caryophyllene oxide	NIF	NIF

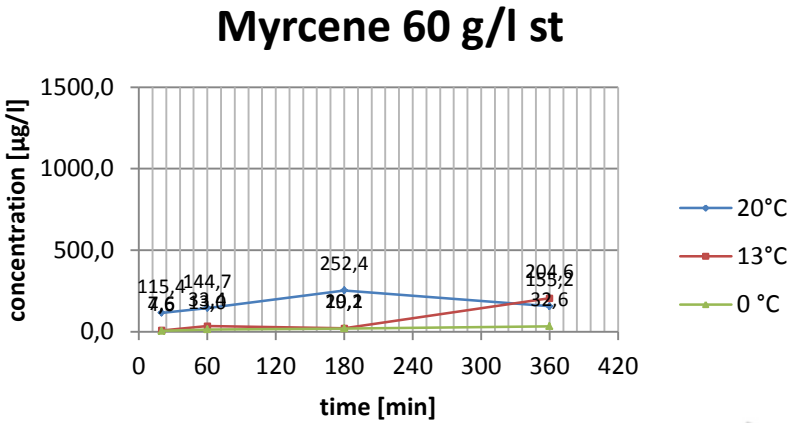
ASBC Beer Flavor Database

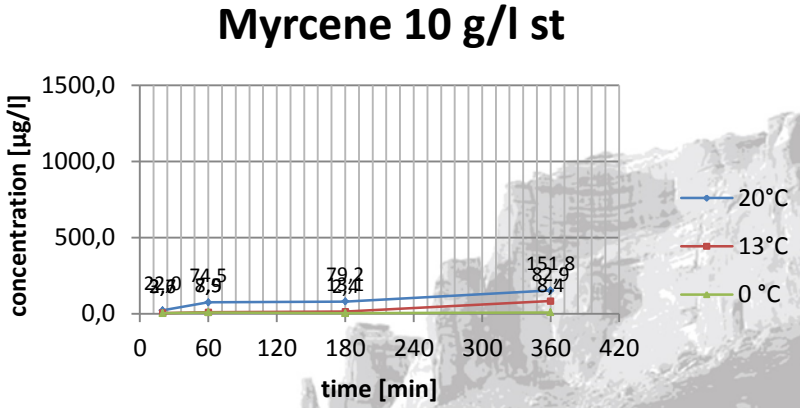
- In slurries and dynamic systems the content of the major analytes goes beyond their thresholds after 20 min
- With extension of time from 3 h to 6 h the concentration further increases up to 2.5 times

Influence of temperature: Myrcene extraction





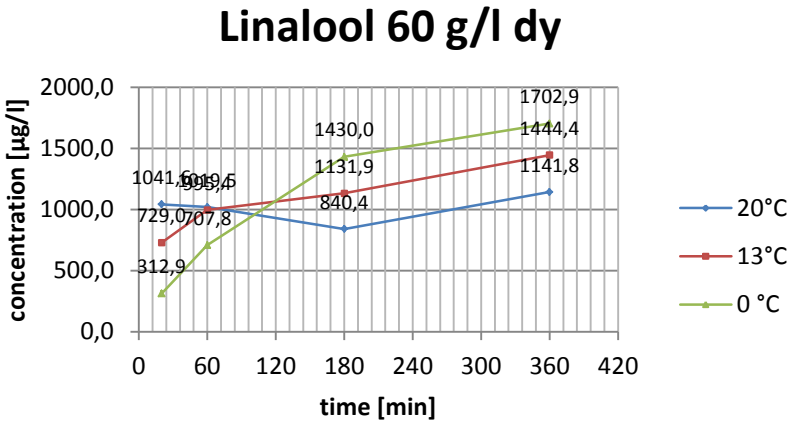


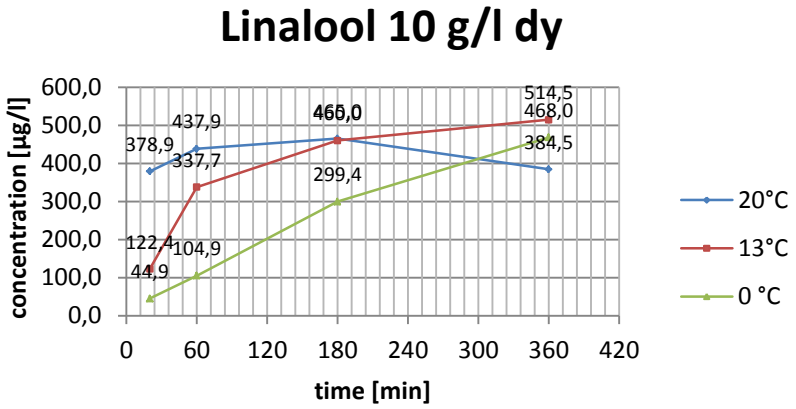


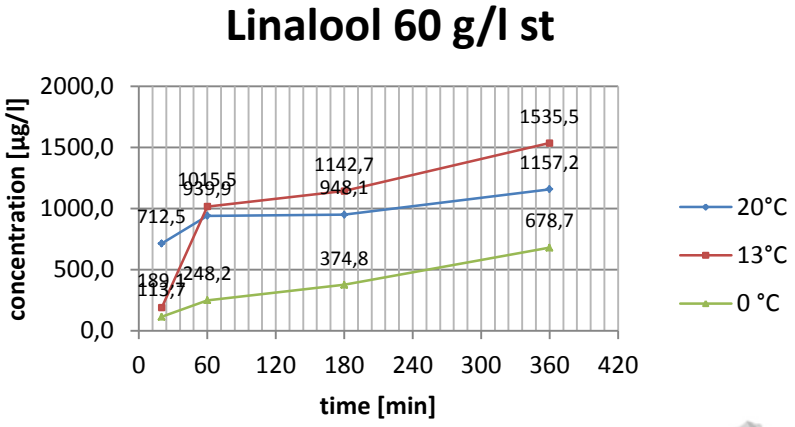
Influence of temperature: Myrcene extraction

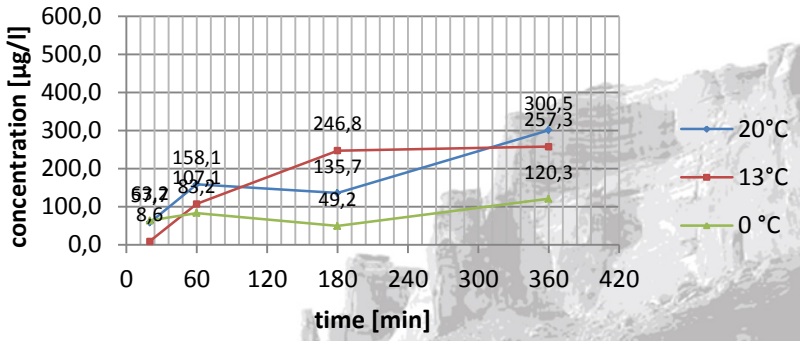
- The lower the temperature the lower the transfer rates into beer
- At higher temperatures a content between 109 and 252 µg/l is possible → this leads to a hoppy, green, fresh cut grass flavour

Influence of temperature: Linalool extraction





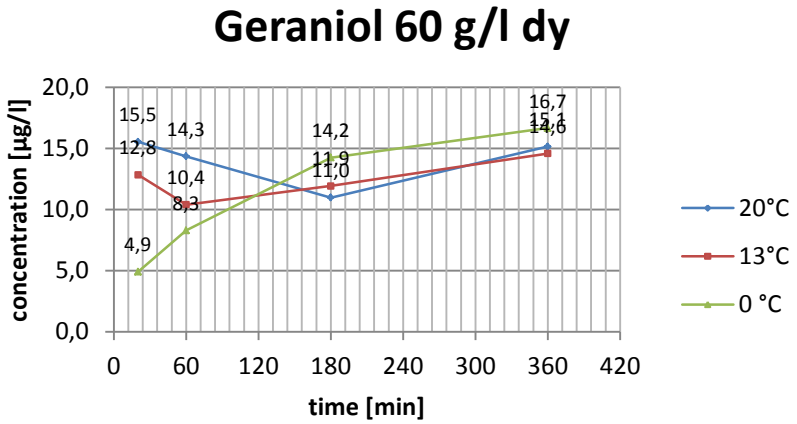


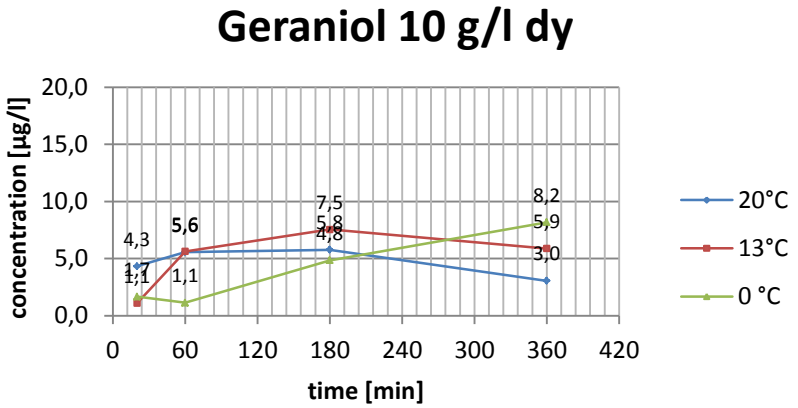


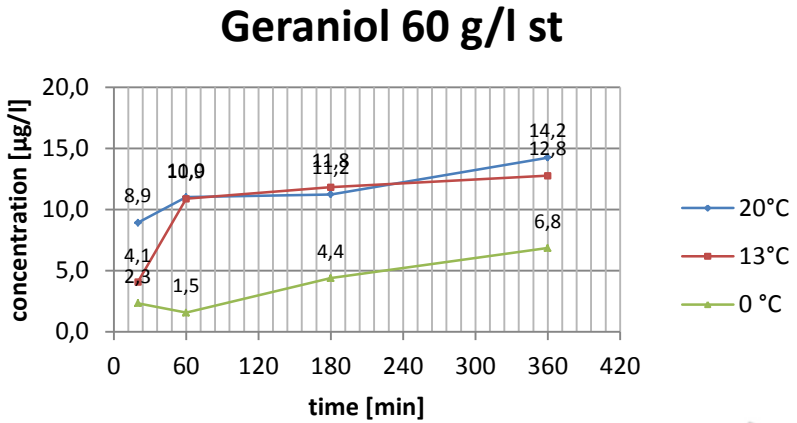
Influence of temperature: Linalool extraction

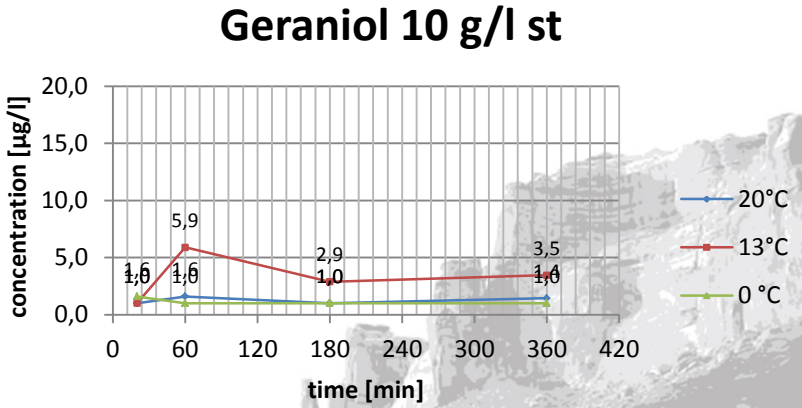
- Linalool has a very good solubility in beer
- At warmer temperatures it goes quickly into solution
- At 0°C the hesitation in the beginning of linalool extraction can be caused by the declined dissolution of pellets at low temperatures → after pellets were broken linalool content reaches similar levels
- Circulation improves utilization of linalool

Influence of temperature: Geraniol extraction





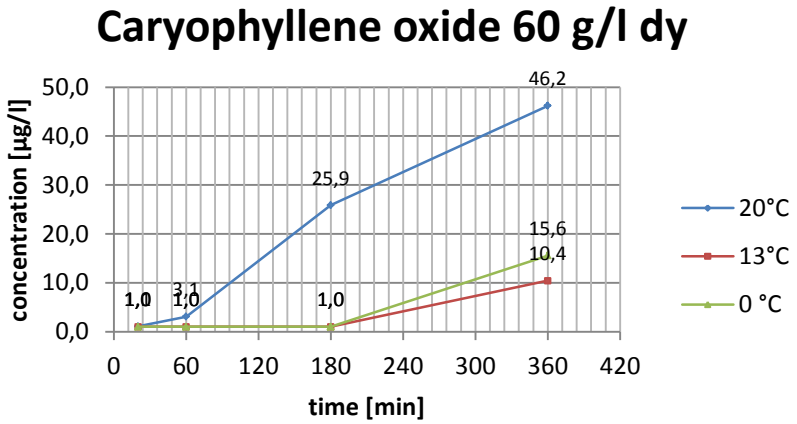


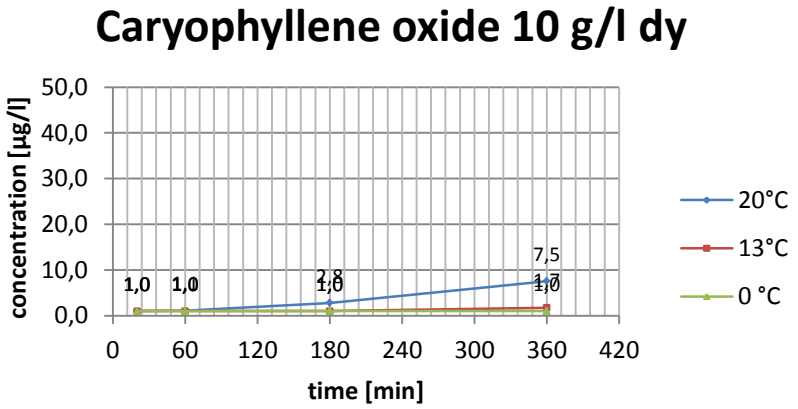


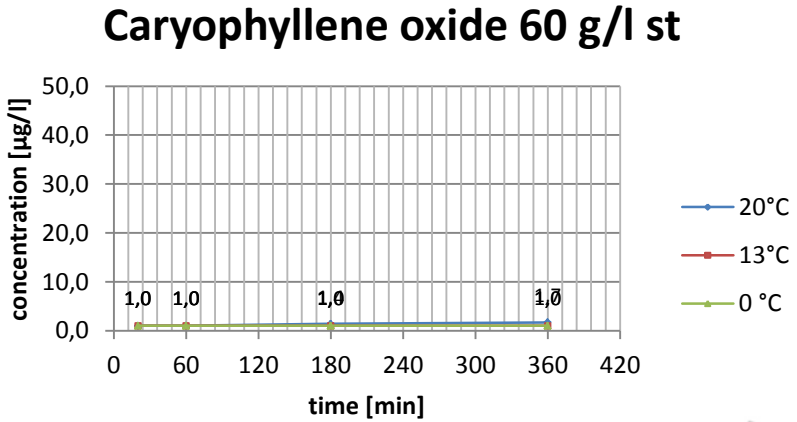
Influence of temperature: Geraniol extraction

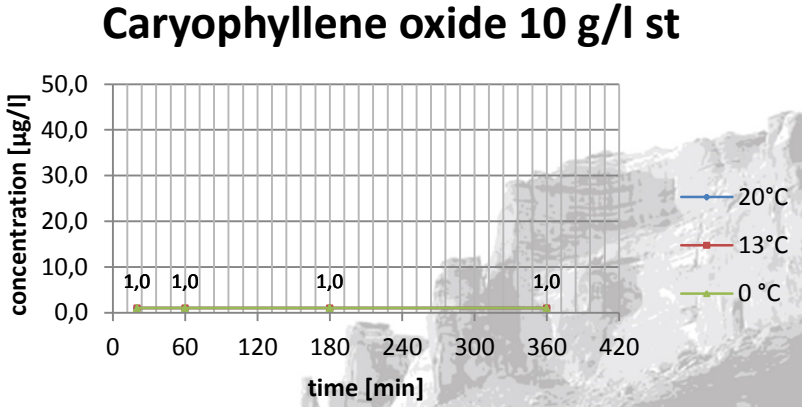
- In Hallertauer Tradition geraniol concentration is very low, the extraction progress is more independent from temperature than seen for other compounds
- Only with the high addition range the threshold conc. for geraniol were reached

Influence of temperature: Caryophyllene oxide extraction









Influence of temperature: Caryophyllene oxide extraction

With static dry hopping caryophyllene oxide and geranyl acetate did not dissolve

→ a circulation is necessary

Influence of oil content

- The comparison of Type 90 and Type 45 showed that the total amount of compounds extracted is about twice higher with the same dosage rate
  - Oil content: HHT PEL90 0.75 ml/100g
  - Oil content: HHT PEL45 1.35 ml/100g

  → Factor = 1.8 (~ 2)

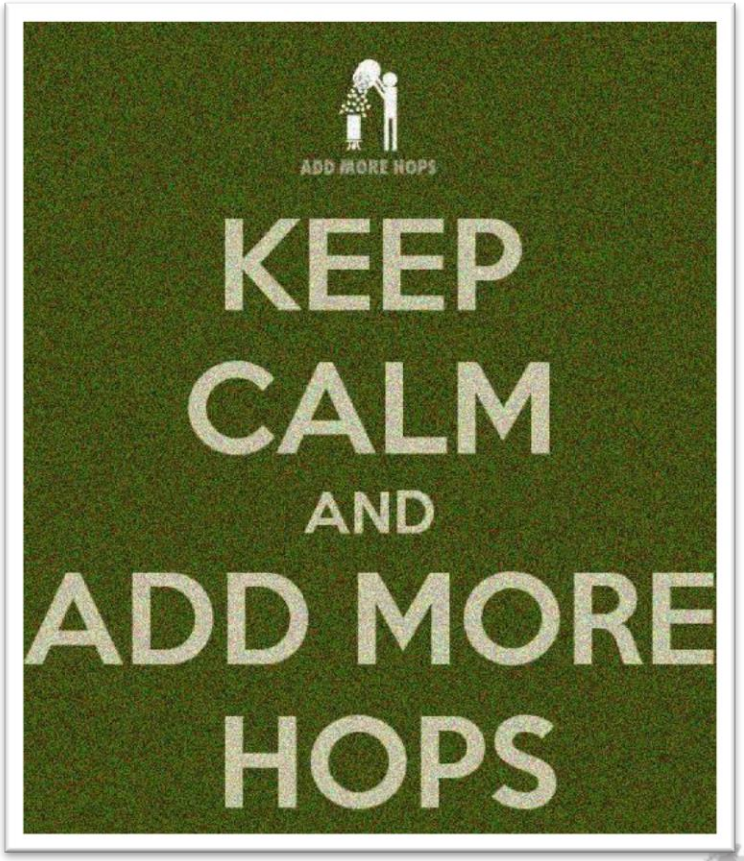
Conclusion

- Even with extremely high dosages there does not seem to be a **saturation limit** (6 kg/hl)
- An **increased hop dosage** yields in **higher extraction** rates
- Linalool goes rapidly into beer → other components don't
- **Dynamic dry hopping** leads to a **faster** and **more efficient** extraction
- The **majority of the aroma** components that can be measured are **transferred** into beer **in first few hours** when circulated
- The measured components do not allow a forecast about the sensory impact

Conclusion

- The **lower** the **temperature** the **lower** the **yield** of total aroma compounds
- Low temperatures **prevent** pellets from **dissolving** fast
- For dynamic dry hopping devices, warmer temperatures can be recommended if contact time is short (< 4 h)
- Extraction progress is different for alcohols compared to terpenes and other components
- Longer contact times (above 24 h) may lead to higher concentrations at low temperatures → this has to be investigated

Thank you for your attention



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BARTH-HAAS GROUP
FOR YOUR SUCCESS

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ZIEMANN CIMC ENRIC HOLVRIEKA CIMC ENRIC

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VLB BERLIN