The Effect of Temperature on Aroma Extraction During Dry Hopping

INDIVIDUAL EXPERIENCES | In recent years, dry hopping has become part and parcel of a scientific debate at several brewing colleges. But by far not all parameters have been investigated. A very important parameter, so far neglected scientifically, is temperature during dry hopping. Every brewer has made his own experiences in that field.

A GERMAN-US survey showed that more than 30 per cent carry out dry hopping at 0-5 °C, 26 per cent at 6-15 °C and 20 per cent at 16-25 °C [1]. Several studies on dry hopping reported that the resulting hop aroma is very fragile and that changes in dry hopping (apart from variety, also changes in terms of quantity, year of harvest, provenience, time, temperature, contact time etc.) have immediate effects on sensory perception. However, the aroma substances having a major impact on sensory perception during dry hopping have still not been fully identified. Hop aroma analysis is ambitious and, aside from aroma substances such as linalool, geraniol and myrcene that can be analysed quite easily, it is difficult to quantify the multitude of hop aroma substances in beer. It can be a real challenge to analyse sulphurous aroma substances in particular, such as 4-methyl-4-mercaptopentan-2-one (4MMP) responsible for fruity aromas.

Many brewers use an aqueous hop mixture, the so-called hop slurry, for dry hopping. A relatively large quantity of hops is mixed with water. This mixture is added to the beer stream and, if required, circulated. In our tests, we opted for a concentration of 1000 g/hl. On the one hand, this can be a relatively large addition for dry hopping or, on the other hand, a less concentrated hop slurry. The concentration of such hop slurry can be up to 6 kg/hl. Even though many aroma substances mentioned and presented for analysis may be of sensory importance on account of their low threshold values (such as e.g. linalool, geraniol or also myrcene), the exact composition of the

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LIST OF AROMA SUBSTANCES ANALYSED AND DEGREE OF ENRICHMENT IN PER CENT IN PELLETS 90 AND 45…

… of HallertauerTradition

	Tradition pellet 90 [mg/kg]	Tradition pellet 45 [mg/kg]	Enrichment in per cent compared to pellet 90
α-pinene	5	5.2	104
β-pinene	21.3	64.7	304
myrcene	925	1463	158
limonene	26.5	35.1	132
cis-linalool oxide	5	5	100
trans-linalool oxide	5	5	100
linalool	85.2	154.9	182
α-terpineol	5	6.6	132
nerol	5	5	100
geraniol	5	5	100
geranyl acetate	12.1	13.9	115
β-caryophyllene	333	310	93
humulene	773	737	95
caryophyllene oxide	13.4	46.8	349
citronellol	5	5	100
sum	**2224.5**	**2862.2**	**129**

Table 1

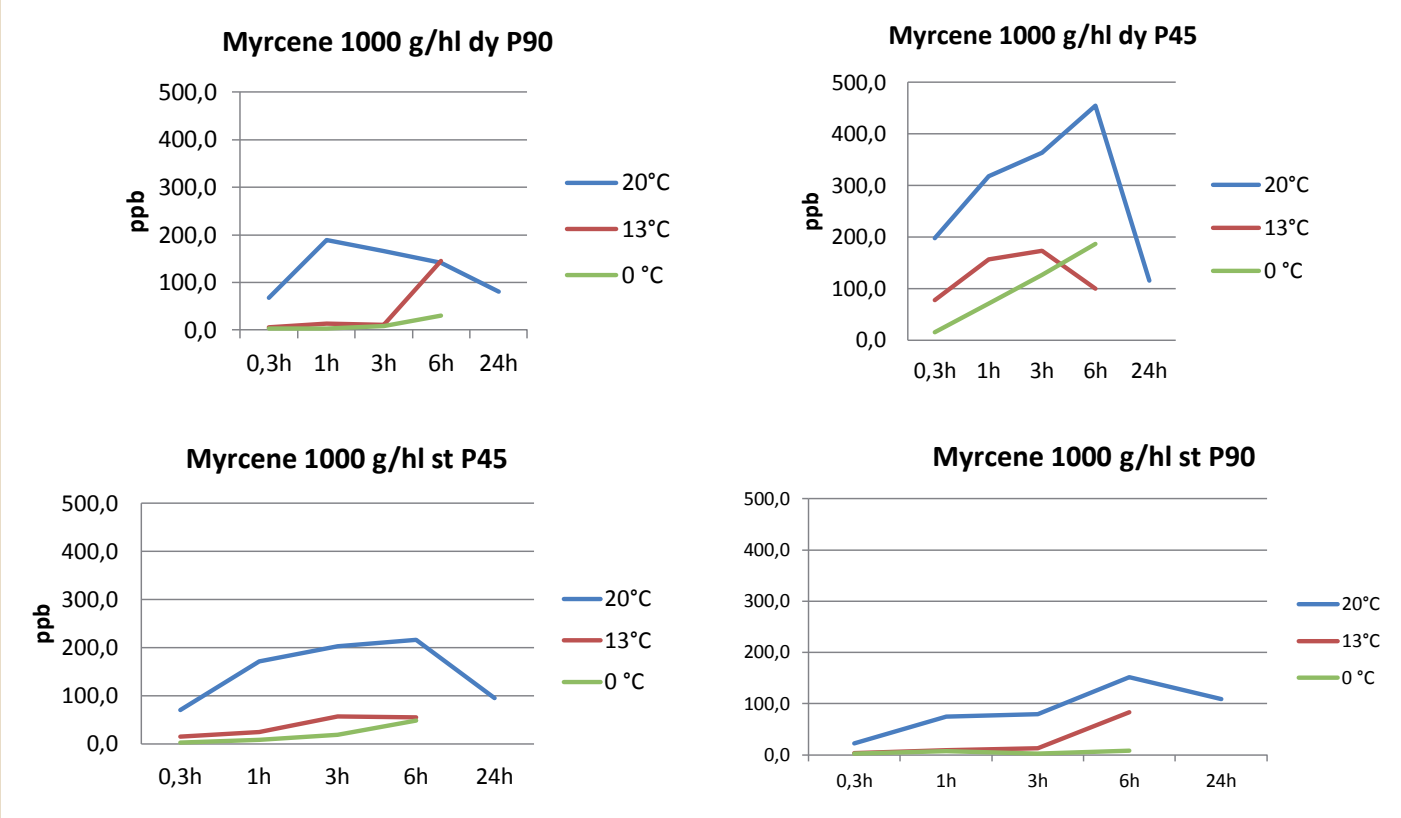

Fig. 1 Extraction of myrcene using dynamic (dy) and static (st) dry hopping

aroma substances is the deciding factor, in addition to highly potent sulphurous aroma substances in specific varieties (e.g. 4MMP) [2, 3, 4].

Test Arrangement

We simulated dry hopping with 1000 g/hl on a very small scale in our study. This corresponded to an oil dosage of 7.5 ml/hl using pellet type 90 (Hallertauer Tradition was used in all tests) and 9.75 ml/hl using pellet type 45. In line with enrichment (Table 1), tests with pellets type 45 contained 1.3 times the amount of aroma substances.

Three different temperatures were used (0 °C, 13 °C, 20 °C), each in a static and in a dynamic system. Samples were investigated after 0.3, 1, 3, 6 and 24 hours using CG-MS/MS. Many brewers are facing the important question: when can extraction in dry hopping be regarded as completed or is there an optimum point in time when dry hopping is finished? Some recent studies have indicated that a plateau concentration is reached already after six to eight hours for measurable aroma substances such as linalool, geraniol and myrcene [5]. The extraction process of individual aroma substances in tests with pellet type 45 is described by way of example below (dy = dynamic dry hopping

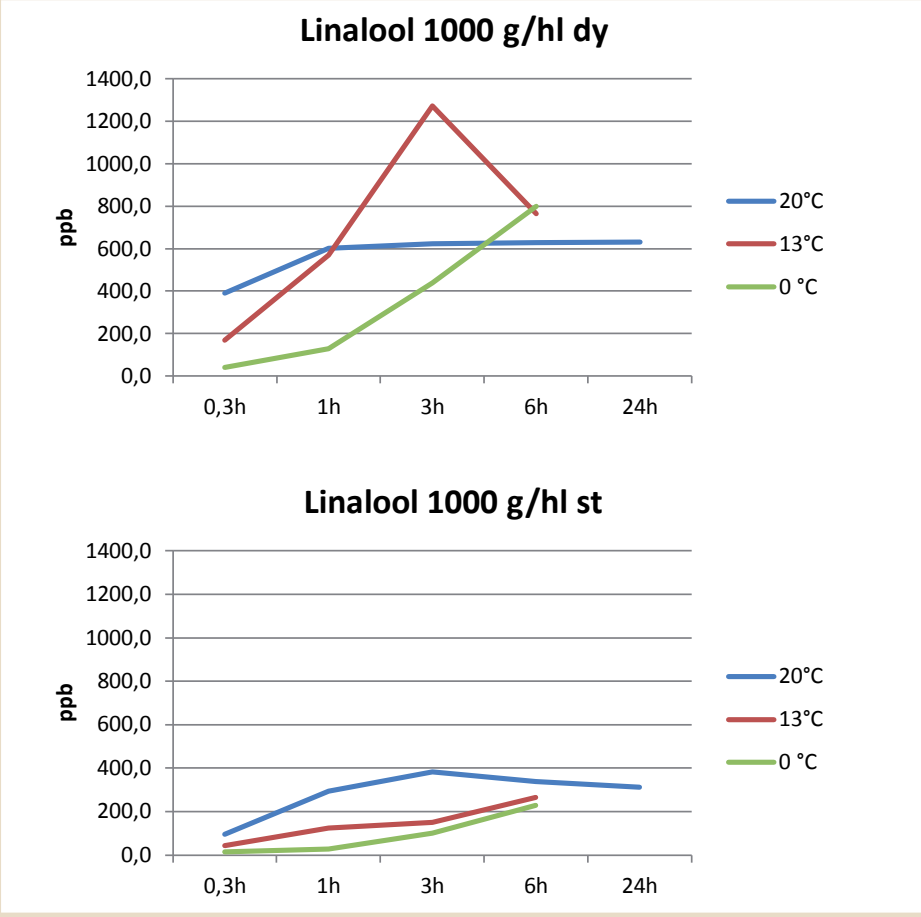

Fig. 2 Extraction of linalool during dynamic and static dry hopping

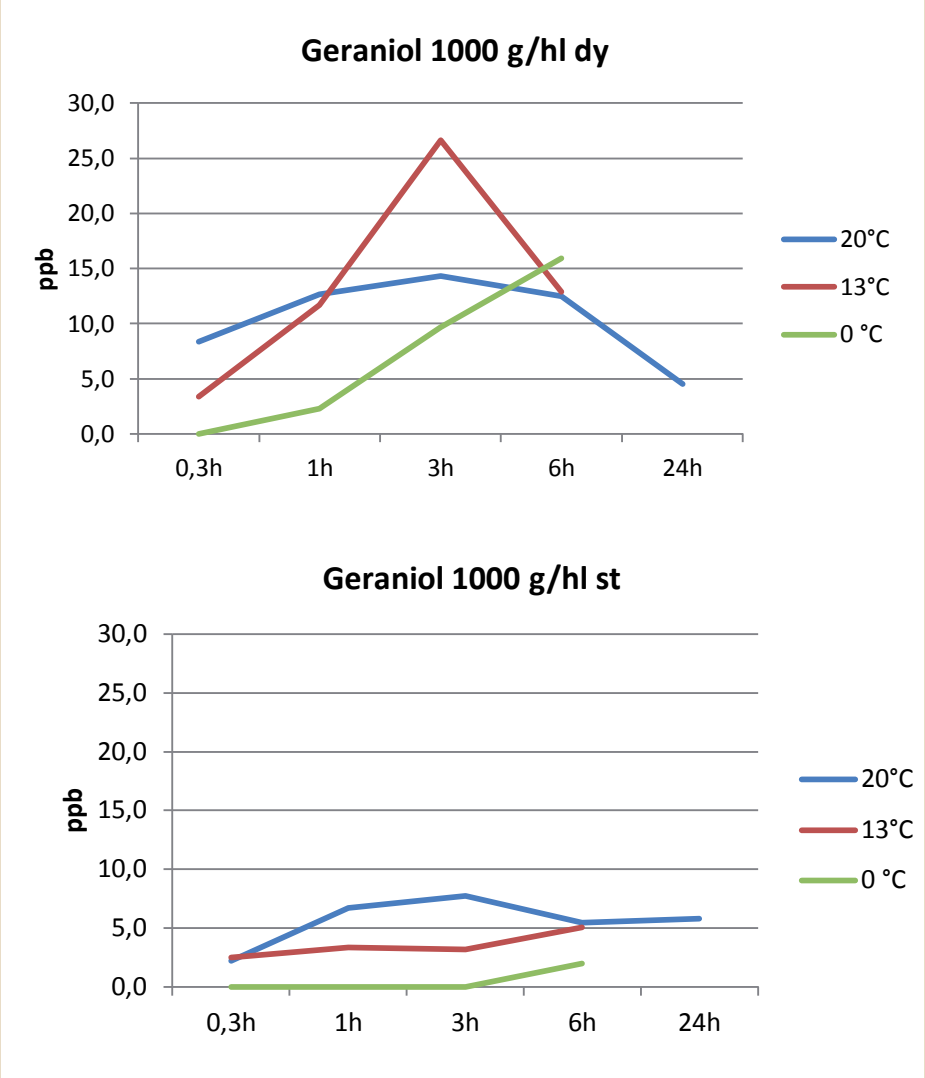

Fig 3 Extraction of geraniol during dynamic and static dry hopping

YIELDS IN PER CENT OF VARIOUS AROMA SUBSTANCES AT A DOSAGE OF 1000 G/HL

	Yield in % in beer	Taste threshold	max. concentration in model solution
α-pinene	0-6	140	7
β-pinene	0-3	6	20
myrcene	0-2	1-500	440
limonene	0-5	100	25
linalool	5-61	0,1-8	1250
α-terpineol	5-30	1-300	22
nerol	0-8	80-500	5
geraniol	5-53	70-200	27
geranyl acetate	0-3		6
β-caryophyllene	0-1	64-450	50
caryophyllene oxide	0-10		27

Table 2

i.e. in circulation; st = static dry hopping i.e. the beer with hops is not in motion).

Results

Extraction of myrcene is better when using dynamic extraction and at higher temperatures. Differences are greater between 13 °C and 20 °C than between 0 °C and 13 °C. However, after extraction, breakdown sets in rapidly (Fig. 1).

Extraction of linalool is also better at higher temperatures and in a moving system. Interestingly enough, the highest linalool levels were obtained at 13 °C in these tests, followed by breakdown. Analyses after 24 h showed that linalool was not broken down (Fig. 2).

Geraniol quantities extracted are, naturally, much lower than levels of linalool but the curve was similar. The 20 °C sample observed for 24 h already showed geraniol breakdown (Fig. 3).

In contrast to the above aroma substances, caryophyllene continued to enrich even after six hours. Again, efficiency of extraction goes up with increasing temperatures. After 24 h at 20 °C, less than 2 ppb dissolved out in the static system (Fig. 4).

Extraction of caryophyllene oxide proceeds similar to that of caryophyllene. In a static system, extraction sets in only at a temperature of 20 °C. Even after six hours, concentration is still rising progressively.

Figs. 5 and 6 provide an overview of all aroma substances measured in tests with pellet type 90 and pellet type 45. It is obvious that concentrations tested with pellet type 45 in a dynamic system are, in summary, significantly above those in tests with pellet type 90 and that yield of aroma substances is better despite the fact that oil levels are higher in pellet type 45. These differences are less pronounced in the static system, yields tended to be somewhat higher when using pellet type 45.

Table 2 is a summary of yield ranges (transfer rates) for various aroma substances. Other research showed much higher yields for linalool. The relatively low yields here can be attributed to the relatively high hop addition of 1000 g/hl.

Apart from linalool, concentrations measured for other aroma substances are either just within or mostly below the threshold value range. However, it should be kept in mind that interaction of different aroma substances may involve a sensory contribution [6].

YIELD IN FACTORS AT 1000 G/HL IN A DYNAMIC DRY HOPPING SYSTEM WITH PELLET TYPE 45 COMPARED TO PELLET TYPE 90 …

… in accordance with aroma substance (e.g. linalool was extracted to the tune of 1.59 after 24 hours, compared to tests with pellet type 90)

10 g/l dynamic						
	Temperature	0.3h	1h	3h	6h	24h
myrcene	20 °C	2.91	1.68	2.19	3.22	1.43
	13 °C	12.70	11.24	15.88	0.69	
	0 °C	4.15	24.21	15.64	6.24	
limonene	20 °C	1.14	1.21	1.72	1.78	2.18
	13 °C	2.24	2.05	3.31	1.80	
	0 °C	1.29	1.39	1.60	2.74	
linalool	20 °C	1.03	1.37	1.34	1.63	1.59
	13 °C	1.38	1.69	2.76	1.49	
	0 °C	0.91	1.22	1.46	1.71	
α-terpineol	20 °C	1.32	1.34	1.36	1.38	1.55
	13 °C	1.72	1.47	2.64	1.36	
	0 °C	1.01	1.33	1.61	1.56	
nerol	20 °C	1.72	3.45	1.64	3.08	1.80
	13 °C	1.00	2.18	3.98	2.47	
	0 °C	1.00	1.00	1.76	1.80	
geraniol	20 °C	1.94	2.27	2.48	4.10	4.51
	13 °C	3.12	2.08	3.53	2.20	
	0 °C	0.60	2.04	2.00	1.95	
caryophyllene	20 °C	2.49	0.88	1.63	1.52	2.71
	13 °C	1.00	1.81	6.58	0.74	
	0 °C	1.00	1.00	1.42	4.60	
caryophyllene oxide	20 °C	1.71	3.88	2.21	1.27	2.06
	13 °C	1.09	1.00	3.14	0.71	
	0 °C	1.00	1.02	1.98	2.68	

Table 3

Maximum Yield

After the same quantities of hops were weighted-in, the test make-ups with pellet type 45 contained 1.3 times more aroma substances. Concentrations in dry hopping tests with pellets type 45 should, theoretically, be correspondingly higher. Table 3 lists these yields in per cent in the dynamic system.

An example: at 20 °C using pellets type 45, 2.2 times the amount of myrcene was measured after three hours compared to the dynamic system with pellets type 90. At this point in time, yield was still far above 1.3 times. This was to be expected in view of the higher oil level. It boils down to the fact that ultimately, after 24 hours, just 1.43 times was left over.

Table 3 shows that there is an individual yield maximum for every aroma substance, depending on time and temperature. It is also evident that yields in a dynamic system are better for all aroma substances using pellet type 45 compared to pellet type 90.

Summary

Hop aroma of dry hopped beers is made up of several hundred different aroma substances. Each of them has individual properties in terms of sensory quality, polarity, solubility and volatility.

Our tests on a pilot scale showed that a dynamic system for dry hopping leads to substantially faster extraction. Extraction rates are time-dependant. With a time delay, monoterpene alcohols such as linalool and geraniol can get up to the same concentration range. Following maximum extraction, concentration of some aroma substances decreased. Using pellets type 45 in a dynamic system, yields were consistently higher than with pellets type 90 in a dynamic system. In addition to the higher concentration and the associated improved "accessibility", finer milling to smaller particles might also be an influencing factor. Differences in extraction between pellet type 90 and pellet type 45 are less pronounced in a static system. As Hallertauer Tradition was used in all tests, further investigations are required to confirm these results for other varieties.

An appreciable concentration of caryophyllene and caryophyllene oxide was extracted only at 20 °C. More recent research revealed that, sesquiterpene oxides in particular, also in low concentrations, are aroma-active and contribute to the hoppy and herbaceous aroma. Should our results be confirmed, this would go to explain the increase in such aroma impressions emanating from dry hopping under relatively warm circumstances. ■

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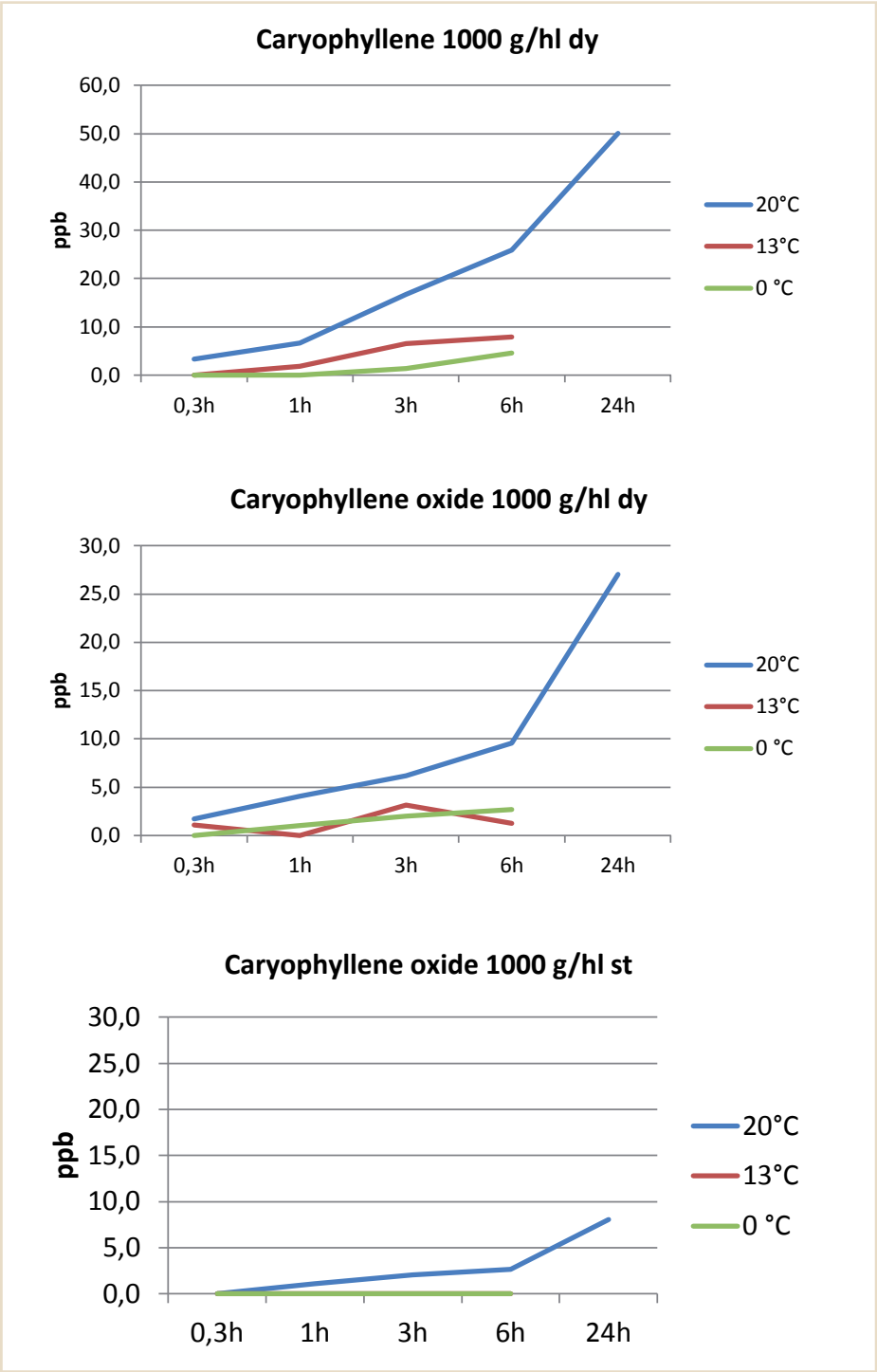

Fig. 4 Extraction of caryophyllene in dynamic and static dry hopping

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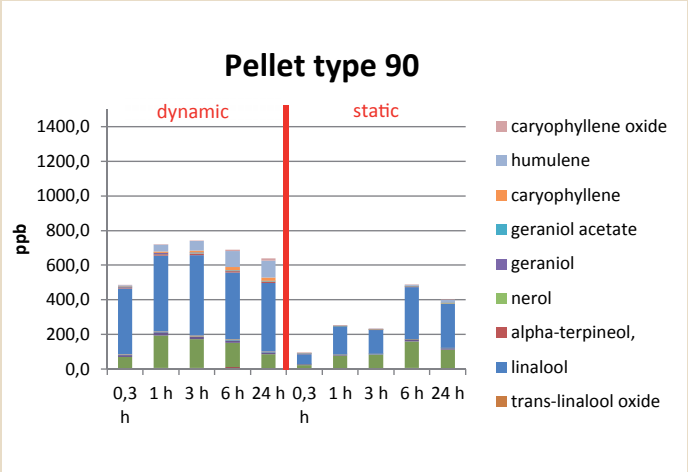

Fig. 5 Overview of aroma substance composition at 1000 g/hl and pellet type 90 in a dynamic and static system

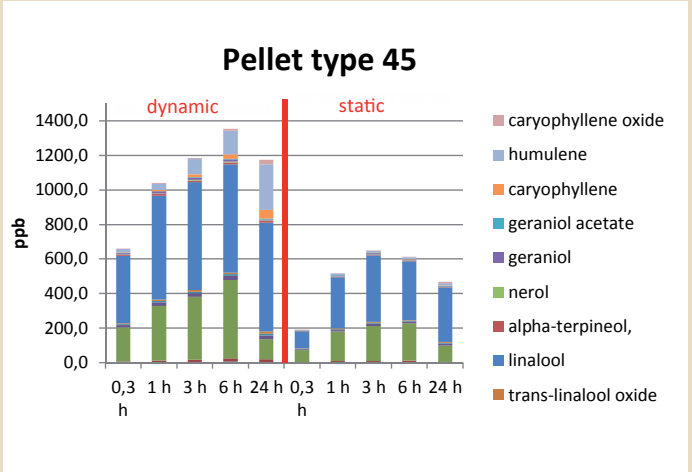

Fig. 6 Overview of aroma substance composition at 1000 g/hl and pellet type 45 in a dynamic and static system