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Optimization of the Hop Kilning Process to Improve Energy Efficiency and Recover Hop Oils

In 2010 the company Wolf Anlagen-Technik GmbH & Co. KG (Geisenfeld) and the VLB Berlin e.V. started a two year project focusing on energy recovery during hop kilning. A heat exchanger was installed in an industrial scale hop kiln in order to decrease the consumption of primary energy. The efficiency of heat recovery using exhaust air of the hop kilning process was determined and potentially saved primary energy calculated. Heat recovery from exhaust air produces certain volumes of condensate. The collected condensate was analysed for eight selected hop oil components which were also determined in green and kilned hops. Before the heat exchange process the exhaust air was forced through a filter cartridge that contained activated carbon material. In the filter material the same eight hop oil components were quantified. For analyses and quantifications of hop oil substances an isotope dilution assay (SIDA) was used. Additionally water content and concentration of alpha- and beta-acids were determined in green and kilned hops.

Descriptors: hop, kilning, hop oil, energy recovery, condensate, exhaust air

1 Introduction

For more than 1000 years hops have been cultivated in central Europe [1]. Hops were one of the herbs that were added to beer. Originally the main reason for adding hops to beer was to increase the microbial stability of the beer. In 1516 the Bavarian purity law allowed only the use of water, barley and hops to produce beer. The rising demand for beer was followed by an increasing need for hops. Green hops as they are harvested cannot be stored because the high water content promotes microbial spoilage what decreases hop quality. To increase stability the water content of green hop cones is usually reduced from approx. 80 % after harvest to less than 12 % [2]. Until the 19th century hops were dried in layers of 3 to 5 cm for 2 to 10 days. The duration of the drying period was mainly dependant on weather conditions. Later, picking machines increased the amount of hops that had to be dried and consequently more efficient ways to dry hops evolved. During the last century several possibilities of hop drying have been developed [2]. In Europe mainly 3-floor kilns and belt driers are used, whereas in the United States of America 1-floor kilns are most common. In hop kilns hot and dry air is forced through the layers to more rapidly reduce the water content of the hops. Typical time periods for kilning hops range from 5 to 8 hours, depending on the hop variety and system in use. To heat fresh air to the usual kilning temperatures of 63 to 68 °C, high amounts of thermal energy are needed. Fuel oil or gas burners are most common in hop kilns. The warm exhaust air is typically released to the atmosphere.

Today the majority of harvested hops (> 90 %) are used for brewing. The major purpose of hop in brewing is to provide bitterness to the final beer. Beer bitterness mainly dependents on the concentrations of alpha-acids added during the wort boiling stage [e.g. 3–5]. Depending on the variety, type of hop products, and the way hop products are used in the brewing process hops do also contribute to beer flavour [e.g. 6–8, 10]. Hop essential oils play an important role in brewing which has made them the subject of several research projects [e.g. 7–9]. The composition and amount of oil in dry hops is, similar to alpha-acids, influenced by kilning conditions [2, 11–14]. The moist exhaust air of hop kilns does have a very typical aroma indicating the presence of several hop derived volatiles. In the Hallertau region it is even spoken of as a special “perfume” during the harvesting period of hops. *Forster* [15] indicates alpha-acid losses of 3.5 to 10 % during hop drying depending on the overall quality of the hop drying process. *Zeisig's* [2] results showed that increasing drying temperatures from 55 °C to 60 °C at an air velocity of 0.28 m/s already lowered the bitter substance concentration to 95 % compared to the reference drying procedure. The losses may be avoided by increasing the air velocity. The total loss of bitter substances cannot be interpreted in his study since Zeisig used a drying procedure with 55 °C at an air velocity of 0.28 m/s as reference [2]. *Kieninger* and Forster

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considered the influences of drying on hop quality as similar to ageing [13]. The presence of air leads to oxidation of alpha- and beta-acids whilst only alpha-acid losses were observed at ambient temperatures und under inert atmosphere [14–17]. Losses for total hop oil during hop drying were reported by several authors [2, 11–14]. Losses were observed between 10 % and 60 % depending on authors, drying conditions, physical properties of the substances and varieties used in the respective studies. Generally monoterpenes (e.g. myrcene) showed higher loss rates compared to sequiterpenes (e.g. α-humulene or β-caryophyllene) and terpene alcohols (e.g. linalool).

The aim of the present study was to evaluate the possibility of reducing the primary energy input during hop drying. In order to recover energy from exhaust air a heat exchange system was installed. The warm exhaust air should be used to heat up the fresh air needed for the kilning process. Since the exhaust air provides a pleasant aroma a strategy to recover hop oil components from the exhaust air should be developed. In a first stage the naturally occurring condensation during the heat exchange on the exhaust air side was used. Later in the project the possibility of directly filtering volatiles out of the air stream was tested. The influence and the efficiency in terms of preservation of hop components during the kilning process should be determined as well.

2 Materials and Methods

2.1 Probing of the hop kiln, condensate collection and installation of the activated carbon filter

The hop kiln (see Fig. 1) was equipped with temperature, humidity und air flow probes in order to control the kilning process. Temperature probes were positioned above every kiln floor. Above the top floor of the kiln a probe measure the relative humidity of the exhaust air was installed. All four air flows in the heat exchanger (exhaust air in (t_{11}) and out (t_{12}), fresh air in (t_{21}) and out (t_{22})) were equipped with probes for temperature, humidity and air flow measurement. The probes were positioned vertically inside the air ducts to or from the heat exchanger. Furthermore, the fresh air's humidity and temperature for the hot air supply fan were monitored as well as the air flow, temperature and humidity of hot air for distribution under the bottom floor of the kiln. The heat exchanger that was applied to recover thermal exhaust air energy leads to a condensation of considerable amounts of water. This vapour condensate is collected below the heat exchanger and pumped into a condensate collection vessel. In 2011 an activated carbon filter (CamCarb 2600; Camfil AG, Switzerland) was additionally installed in one of the eight suction pipes on top of the kiln (see Fig. 2). Activated carbon filter cartridges were kept in the air flow over differing time periods (from 6 to 50 hours).

2.2 Hop (oil) analysis from cones, condensate and activated carbon filter material

Hop drying trials were carried out during the harvesting periods of the crops 2010 and 2011. Samples of fresh hop cones were withdrawn after picking and cleaning of the industrial scale harvest. Samples of dried cones were collected after kilning of the respective hop batch. Standard kilning conditions of the hop farm are displayed in Tab. 1. The hop sampling included the following Hallertau varieties:

- Hersbrucker (2010 and 2011)
- Merkur (2010)

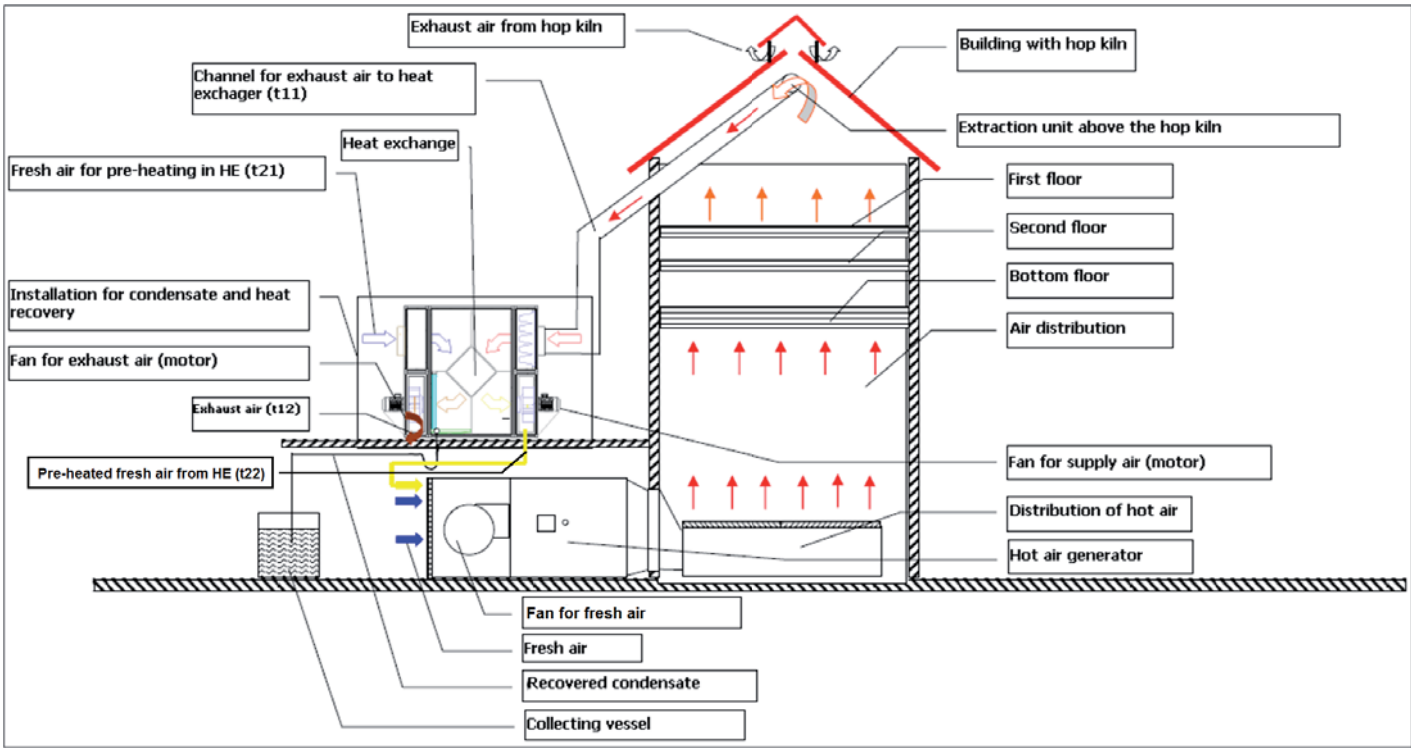

Fig. 1 Scheme of the hop kiln with condensate and heat recovery

Table 1 Average hop kilning conditions during tests

Measurement position	Temperature [°C]
Fresh air	15.0
Hot air underneath bottom floor	64.0
Between bottom and second floor	57.6
Between second and first floor	52.6
Temperature of top layer (IR)	30.7
Exhaust air above kiln	32.1

- Taurus (2010)
- Magnum (2010 and 2011)

The water content of green and dried hops was determined according to Analytica-EBC (7.2). Alpha- and beta-acids were separated by reversed phase – liquid chromatography (RP-HPLC) and quantified according to Analytica-EBC (7.7). For essential oil analysis hop samples (fresh and kilned cones) were stored under vacuum conditions at –23 °C.

Analysis of selected hop essential oil constituents from hops, vapour condensate and activated carbon filter material was performed by gas chromatography – mass spectrometry (GC-MS) in combination with a stable isotope dilution assay (SIDA). Internal standards (IS) were 2-Octanol and deuterium labelled linalool (d_5-linalool).

The isolation of hop oil constituents from fresh and dried hop cones was carried out as follows: 15 medium sized hop cones (dry matter approx. 2.5 g) were mixed with 500 mL deionized water drawn from a Merck Millipore Synergy® UV ultrapure water purification system. (Merck Millipore, D-64293) After addition of the IS the mixture was homogenized using an Ultra-Turrax® T18 Basic (IKA, D-79219 Staufen) and transferred into a 1l round bottom flask. Simultaneous distillation extraction (SDE) was carried out according to the method of *Likens* and *Nickerson* [18] using 200 mL pentane/diethylether (1:1). After 2 hours of SDE the organic phase was filtered and dried over anhydrous Na_2SO_4. Solvent was removed by Vigreux distillation, for analysis the dry residue was resolved in 1 mL of ethylacetate. Each sample (green and kilned hops) was extracted and analysed in repeat determination. Solvents (n-pentane, diethylehter) as well as anhydrous Na_2SO_4 were purchased from Carl Roth GmbH + Co. KG (D-76185 Karlsruhe).

For the analysis of hop oil constituents from exhaust air condensate, condensate samples (200 mL) were collected from the pipe between condensate pump and the condensate collection vessel. Samples were spiked with IS in 250 mL Duran® screw cap bottles (Schott AG, D- 55122 Mainz), shaken and allow to stand in order to reach equilibration of analytes and IS. Condensates were extracted trice with each 50 mL of tert-butylmethylether (MTBE, Carl Roth GmbH + Co. KG, D-76185 Karlsruhe). The combined organic phase was filtered and dried over anhydrous Na_2SO_4. Solvent removal was carried out as described for the hop samples. Condensate extraction and analysis was carried out in triplicate.

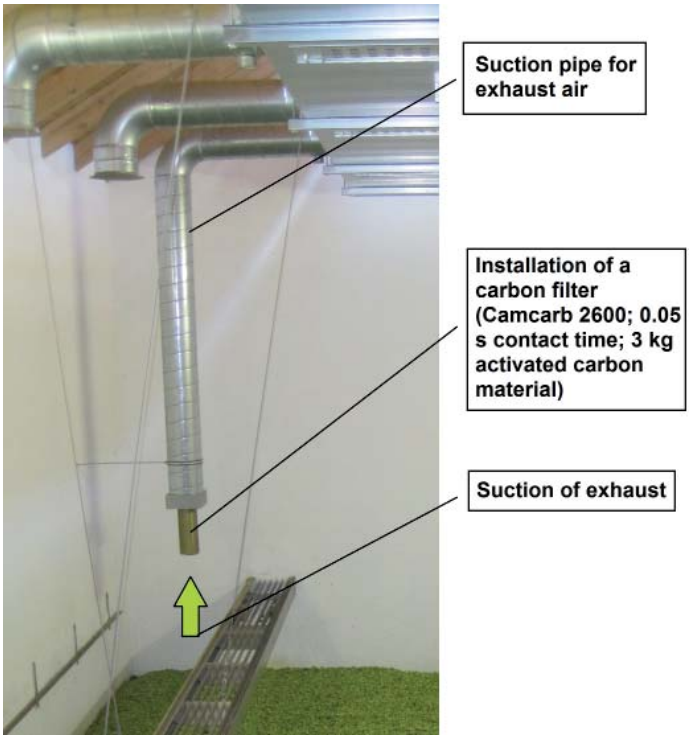

Fig. 2 Installation of additional carbon filter to trap hop oils in the exhaust air

The extraction of volatiles trapped on the activated carbon filter was carried out as follows: The total mass of the activated carbon filter material (approx. 3 kg) was homogenised. Aliquots of 15 g were transferred into 250 mL Duran® screw cap bottles (Schott AG, D- 55122 Mainz), and solved in 100 mL of MTBE. After addition of IS the filter material was extracted (shaking 15 hours at room temperature). Afterwards the MTBE extract was filtered and dried as described before. Each activated carbon filter material was prepared and analysed in repeat determination.

2.3 GC-MS analysis

Hops contain several hundred volatile constituents [6]. To keep the analytical examination in a reasonable scope the quantitative analysis focussed on the following hop oil constituents:

- Myrcene
- Linalool
- Nerol
- α-Terpineol
- Geraniol
- α-Humulene
- β-Caryophyllene
- Farnesol

Table 2 GC/MS parameters for the determination of hop oils

Gas chromatography	Column	DB-5ms UI (30 m/25 µm film/0.25 inner diameter)
	Carrier gas	Helium, linear velocity (40 cm/sec)
	Injection	1 µL, split ratio of 10, 240 °C, 79.5 kPa head pressure
	Oven	40 °C (3 min), rate 10 °C to 300 °C, hold (10 min)
Mass spectrometry		EI ionization (70 eV) Scan MS (m/z = 29–600)

GC-MS analysis was performed on a Shimadzu GCMS-QP2010 Plus applying a non-polar DB-5 UI column (Agilent Technologies, D-71034 Böblingen). This non-polar phase showed very suitable performance to separate above listed target compounds. Analyte ionization was reached by electron impact ionization (EI). For data acquisition QP-MS was operated in scan mode (m/z = 29–600). Compound identity was ascertained by comparison of retention times and mass spectra with analytical standards (purity > 97%, Sigma-Aldrich, D-89555 Steinheim). A detailed overview on the GC-MS parameters is given in table 2.

3 Results

An example for a typical temperature and humidity development in the course of one day is shown in figure 3. The data points were collected in 5-minute intervals. The volumetric air flows for exhaust and fresh air were always kept equal to each other. A direct correlation of the air mass flows was not possible due to permanent changes in temperature and relative humidity. The green lines show the temperature and humidity (t_{21}) of the fresh air for the respective day. The day started with 16 °C and a 90 %rH (relative humidity). During the day temperature increased up to 24 °C and dropped towards the evening down to 20 °C. In the same time the relative humidity decreased to a minimum of 57 %rH around 3 pm and increased again to 78 %rH at the end of the day. The temperature and humidity curves reflect a typical day in the Hallertau region during mid of September when hops are harvested. The red lines (t_{11}) show the temperature and relative humidity of the exhaust air from the hop kiln. When picked and cleaned hops were filled onto the top floor of the kiln the humidity was highest with 90 to 100 %rH and the temperature was lowest with approx. 28 °C. During the kilning process the temperature increased to approx. 40 °C and the relative humidity decreased to approx. 40 %rH until the top layer was transferred to the second floor and the top floor was filled with fresh green hops. Fig. 3 shows that nine loads of the top floor have been monitored for the heat exchanging process on the respective day. After heat exchange the exhaust air (blue lines; t_{12}) was cooled down to 25 to 30 °C and subsequently the relative humidity increased in comparison to t_{11}. The relative humidity was kept at a level of 100 %rH during the first phase of the kilning and with the falling relative humidity of t_{11} dropped to approx. 70 %rH until a new batch of green hops was filled onto the top layer of the kiln. The heat transfer led to an increase of temperature and a decrease of relative humidity in the fresh air (yellow lines; t_{22}). The fresh air was heated up to 27 to 34 °C while the relative humidity was lowered to less than 40 %rH. The data from the heat exchanging process was collected for several days during the crop. In 5 minute intervals temperature, humidity and air flow data were recorded. After all trials were finished the data (in sum more than 2,000 data points per crop) was analysed and mean values for the total run time of the heat exchanger could be calculated. Tab. 3 shows the mean results for heat recovery with the installed system during the crops 2010 and 2011. Indeed, means do not represent the situation in the heat exchanger at every stage of the process (as Fig. 3 demonstrates) but help to bring the total data to a number of figures that further calculations may be based on. Since daily weather conditions influenced the heat exchange process it was more representative to look at the total harvest time and not at selected days or moments only. In the mean the exhaust air of the hop kiln was cooled down 8 K while the fresh air was heated up 9 K. The transferred heat may also be expressed as an increase of the enthalpy h of the fresh air of more than 9 KJ/kg. The temperature and relative humidity dependent mass flow differences compared to volumetric flows are not considered. Generally the cooler fresh air has an about 6 % (relative) higher density (and mass) while the increased humidity for exhaust air increases the mass by approx. 2 % (20 g water per kg air).

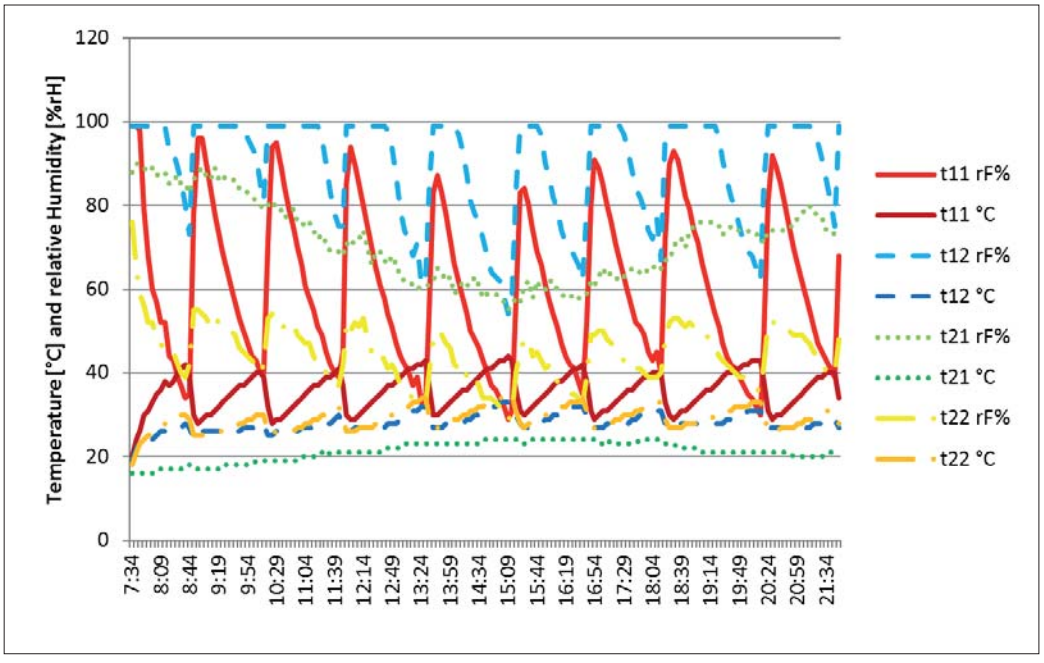

Fig. 3 Temperature and humidity in the heat exchanger on September 17th 2010

Table 3 Energy recovery in the heat exchanger

	2010	2011	Ø
Time of operation [h]	153.1	186.2	169.7
Temperature of exhaust air (t_{11}) before heat exchanger [°C]	31.3	33.8	32.5
Temperature of exhaust air (t_{12}) after heat exchanger [°C]	23.2	26.1	24.6
Temperature of fresh air (t_{21}) before heat exchanger [°C]	15.0	18.7	16.9
Temperature of fresh air (t_{22}) after heat exchanger [°C]	24.4	27.2	25.8
Calculated heat recovery efficiency exhaust air	49.8 %	50.9 %	50.3 %
Calculated heat recovery efficiency fresh air	57.8 %	56.3 %	57.1 %
Air flow exhaust air [m³/h]	11880	15283	13582
Air flow fresh air [m³/h]	12031	15279	13655
Recovered thermal energy per hour [kWh/h]	38.0	46.8	42.4
Recovered thermal energy per hour as fuel oil with η = 0.9 [L/h]	4.2	5.2	4.7

In 2011 tests were carried out with the Hallertau grown varieties of Hersbrucker and Magnum. After picking and cleaning the Hersbrucker hop samples had an average moisture content of 80.6 % and were dried to 8.0 %. The Magnum hop samples were in the mean dried from a moisture content of 73.6 % to 10.6 %. Referring to 1 kg dry hop material for Hersbrucker hops 4.1 kg water were lost while for Magnum hops 2.7 kg water reduction resulted per kg dry hop material. Using Analytica-EBC method 7.7 the aroma variety Hersbrucker had alpha-acid concentrations of 4.6 % dry matter (d.m.) and beta-acid contents of 8.3 % d.m. after harvest. The measured bitter acid contents decreased during kilning to 3.9 % d.m. for alpha-acids and 7.5 % d.m. for beta-acids. Thus, a relative loss of 15.4 % alpha-acids and 9.9 % beta-acids was calculated. For Magnum hops the alpha-acid content according to EBC 7.7 were 20.2 % d.m. after harvest and 18.8 % d.m. after drying. The results for beta-acid contents were 8.8 % d.m. green and 8.6 % d.m. dried. In terms of losses this would mean 6.9 % relative for alpha-acids and 2.9 % relative for beta-acids.

For the (monitored) hop essential oils the Magnum hops showed significantly higher amounts in total (see table 4). The sum of hop oils reveals that Magnum hops contained approx. twice as much hop oils per g dry hop material compared to Herbrucker hops. The highest concentrations were measured for myrcene in both Magnum (more than 9 mg/g d.m.) and Hersbrucker hops (more than 4.5 mg/g d.m.). Approx. 50 % of the myrcene concentration could be found for α-humulene and 40 % for β-caryophyllene. Furthermore, the Magnum hops were higher in concentrations of Terpineol and Nerol. Nevertheless, the concentrations of linalool and farnesol were higher in Hersbrucker hops compared to Magnum hops.

The exhaust air from the hop kiln that was high in its moisture content produced significant amounts of condensate during the heat exchanging process. Between 40 and 350 litres of condensate were collected per day. The condensate volume depended mainly on fresh air temperature and water content of the green hops. The condensate had a strong aroma and taste that can be described as the typical harvesting aroma of hops. Compared to the original hop material the concentrations of the eight targeted hop oils were fairly low. The highest concentrations were found for linalool and farnesol. In the condensate of Hersbrucker hops also geraniol was found in relatively high concentrations. Nerol and β-caryophyllene were present only in traces for both Hersbrucker and Magnum hops.

The concentrations of the eight studied hop essential oils in the activated carbon filter material differed considerably between the single substances. The relations between concentrations of the single substances correlated to those found in green and dried hops. For both hop varieties the concentrations detected for myrcene, α-humulene and β-caryophyllene were highest by far. Linalool and terpineol were present in slightly higher concentrations for the Magnum hops while Nerol was only present in Magnum hops. For both varieties farnesol and geraniol were detected only in traces. The data for activated carbon filter material that is shown in table 4 was achieved with carbon filters that were kept in the kiln for 6 hours.

4 Discussion

With the help of the temperature and humidity figures the efficiency of the heat exchanging process can be calculated using the fol-

Table 4 Results of the hop oils analysis for Hersbrucker and Magnum hops in ppm resp. µg/g or ml (2011)

	Hersbrucker				Magnum			
	Green hops	Kilned hops	Condensate	Filter material	Green hops	Kilned hops	Condensate	Filter material
	[µg/g d.m.]	[µg/g d.m.]	[µg/ml]	[µg/g]	[µg/g d.m.]	[µg/g d.m.]	[µg/ml]	[µg/g]
Myrcene	>4000	>4000	0.020	>1000	>9000	>9000	0.027	>1500
Linalool	184.5	159.7	0.084	24.28	164.4	148.0	0.079	36.87
Terpineol	3.14	2.74	0.016	0.19	7.16	6.63	0.028	0.29
Nerol-1	11.10	9.25	0.004	<0.1	49.73	49.95	0.005	0.42
Geraniol	0.98	0.85	0.047	<0.1	3.28	3.00	0.004	<0.1
Caryo-phyllene, β-	1497	1315	0.004	683.2	3977	3732	0.004	1233
Humulene, α-	>2000	>2000	0.016	>1000	>4500	>4500	0.016	>1500
Farnesol	8.86	8.73	0.114	n.q.	3.22	2.85	0.099	n.q.

lowing formula:

$$Heating\ of\ fresh\ air\colon\ \phi_1 = \frac{t_{22} - t_{21}}{t_{11} - t_{21}}$$

$$Cooling\ of\ exhaust\ air\colon\ \phi_2 = \frac{t_{11} - t_{12}}{t_{11} - t_{21}}$$

Theoretically the temperatures of exhaust air and fresh air could have been changed with a maximum of approx. 16 K. For cooling of the exhaust air 8 K were achieved, thus the efficiency was 50 %. The fresh air was heated 9 K, resulting in an efficiency of 57 %. The heat exchanger was planned with an efficiency of 50 % on the heating side. Thus, the results for heat exchange were within the expectations. Generally the efficiency, but especially the amount of transferred heat, primarily depended on the daily weather conditions. Cold and rainy days lead to high moisture contents in the hops. Thus, the exhaust air showed high water contents and subsequently more condensation energy set free in the heat exchanger. Colder fresh air increases the temperature difference between the two inlet air streams in the heat exchanger and obviously has a positive effect on the maximum heat that can be exchanged. If the recovered energy is compared to the total energy that is necessary to heat the fresh air for the kilning process approx. 20 % of the primary energy can be saved. The value of 20 % is based on a calculation of transferred heat compared to typical fuel oil consumptions. Since the heat exchanger used about 20 % of the total air flow in the kiln, a direct correlation with the consumed fuel oil of the kiln was not possible. The heat exchange process results in a pressure drop in the system that has to be compensated. Electric energy is necessary and its consumption negatively affects the total energy balance. Up to 10 % of the recovered energy has to be supplied as electric energy to overcome the resistance to air flow in the heat exchange system.

The RP-HPLC analysis of green and dried hop samples revealed a certain loss of bitter substances during kilning. The water content of green hops seems to correlate with the loss of valuable (bitter) substances. On the one hand higher water losses of hop cones may lead to higher losses of water soluble volatiles (mainly hop oils). On the other hand higher water contents will lead to a prolonged kilning time which may increase the negative influences of heat on the composition of bitter substances. The hop material was not analysed for oxidation products of alpha- or beta-acids but it is most likely that a certain amount of alpha- and beta-acids was oxidized during drying when the hop cones were treated with an excessive supply of hot air. In former research [10] little amounts of bitter substances were detected in the distillate after water steam distilling hops for more than two hours. These results suggest that despite their molecule size bitter substances may be lost with water vapour too. According to Forster [15] the 5 % relative loss for Herbrucker would be within the specification for a good drying process while losses of 10 % relative and more would indicate insufficient preservation of the hop quality. The results of Zeisig's study [2] showed a relative decrease of bitter substances (approx. 5 %) that was accompanied by an increase of hard resin when the air temperature was increased from 55 °C to 60 °C at an air velocity of 0.28 m/s. Although neither the decrease of bitter substances nor the increase of hard resin could be determined as statistically significant the study supports the findings presented in this document. Especially with regard to the fact that the Wöllmer method to quantify bitter substances and alpha-acids as used in earlier studies [2, 12] is less selective for determining the concentrations of hop alpha-acids and beta-acids when comparing the method to RP-HPLC according to EBC 7.7. Nevertheless, the method used for determination of bitter substances (EBC 7.7) is designed for dried hop products. When 10 g of green hops are used, the dry matter that gets extracted is approx. 2 g instead of approx. 9 g dry matter when dry hops (10 g air-dry) are used. It is most likely that the relative ether extraction rate during sample preparation according to EBC 7.7 is increasing with less dry matter. The effect may be stronger with higher contents of bitter substances. Laboratory results showed that the inaccuracy may contribute to up to 5 % relative higher alpha- or beta-acid contents. With respect to the inaccuracy of method EBC 7.7 – when reduced dry matter mass is used – the relative losses of alpha- and beta acids were (according to Forster [15]) in an acceptable range for a good hop drying process.

The calculable losses of hop oils during the kilning process (5 to 15 % relative) seemed to be in a comparable range to the losses of bitter substances. A direct correlation between the losses of bitter substances and hop oils was not observed. The hot and dry air that passes the hop cones takes up water from the hop cones. Together with water vapour volatile substances are stripped out of the hop material. The more water the hop cones lose the more volatiles may be lost as well. Compared to former studies [11–14] the loss rates were lower than expected. An explanation maybe the shorter drying time of 4 to 5 hours compared to the 6 hours in formerly published research [11, 12, 14] or the lower temperature [13].

Since the concentrations for the single substances differ by a factor of more than 1000 in the respective hop cones the addition of only one concentration for all three internal standards (ISTD) was not ideal. Especially for the very high concentrated hop oils as myrcene or β-caryophyllene quantification may be less accurate. For future analyses of hop oils in various hop materials the addition of varying concentrations of ISTD is the preferable solution. Today several internal standards are added in varying concentrations, thus a more accurate quantification of all analytes is possible. Therefore, results may become better to interpret.

The amount of condensate that could be collected depended very much on the conditions of the green hops and the fresh air temperature. The higher the moisture content of the green hops the longer exhaust air with a humidity level of more than 80 % was available. Thus, for a longer time the exhaust air left the heat exchanger with 100 % moisture content and subsequently water condensed in the heat exchanger. The colder the fresh air the lower temperatures could be achieved during cooling of the exhaust air. The capacity of air to carry water is dependent on its temperature. The more the exhaust air was cooled the more water the air was losing due to condensation in the heat exchanger. Differences in concentrations of hop oils in the condensate could not be directly correlated to weather conditions or actions during kilning like loading the top floor with green hops or highest humidity above the top floor. The concentrations of hop oils that were found in the condensate did also not correlate with the concentrations of the

respective substances in the original hop material. The influence of water solubility but also the general presence in the hop variety was more important for the detected concentrations of the targeted hop oils. The concentrations of the tested hop oil substances in the condensate are too low to distillate pure oil from the condensate. An alternative use of the condensate may be the collection for humidifying air during conditioning of the hops after kilning. Fresh water may be saved and a small amount of hop volatiles recovered.

Most of the volatiles that are lost with the exhaust air of the hop kiln were not found in the condensate. Therefore, a carbon filter was installed in one of the air flow pipes over the top floor of the hop kiln. The relative concentrations of the targeted hop oil substances highly correlated with the concentrations of the respective substances in the green and kilned hop cones (Fig. 4 to Fig. 6). It was not possible to calculate a mass balance for the substances because of the many variables which could not be monitored in the trial setup, e.g. mass of hop cones in the kiln, total air flow in the kiln etc. If the single substances are summed up a total of at least 0.4 mg hop oils were trapped per g activated carbon filter material and hour. Taking into account that the air flow for one pipe can be assumed as 1,500 m^3/h and a cartridge contained approx. 3,000 g activated carbon filter material potentially more than 0.8 mg hop oils may be recovered from 1 m^3 exhaust air.

The considerations do not include the presence of other volatiles in the exhaust air. Both exhaust air and condensate exhibit a green and grassy aroma. Especially in the United States of America there is a certain trend towards the use of green hops in the Craft Brewing scene. These green hopped beers show a similar aroma to the one that was present in the exhaust air of the kiln and the condensate. It seems very likely that extremely volatile substances such as aldehydes and sulphur-containing substances are involved. These substances are probably lost to significantly higher relative amounts than the ones that were tested in this study. To be able to monitor “green hop” substances further knowledge about their nature as well as suitable analytical assays are necessary.

5 Summary

In 2010 the company Wolf Anlagen-Technik GmbH & Co. KG (Geisenfeld) and the VLB Berlin started a two year project focusing on energy recovery during hop kilning. Special attention was paid to a possible increase of hop quality and the recovery of volatiles during hop kilning. Integrated into an industrial scale hop kiln a heat exchanger was installed to recover energy from the exhaust air. The condensate that was produced in the heat exchanging process was collected and analysed regarding the presence of selected hop oil components. For green and kilned hops the water content, alpha- and beta-acids as well as the same hop oil components as for condensate were determined. The results of the year 2010 showed that only parts of the volatiles could be recovered in the condensate. This led to the installation of an activated carbon filter into the air flow of the exhaust air.

The heat recovery ran with approx. 57 % efficiency and was able to increase the fresh air temperature by 9 K. During the kilning process between 5 and 15 % were lost for selected hop oil components. In

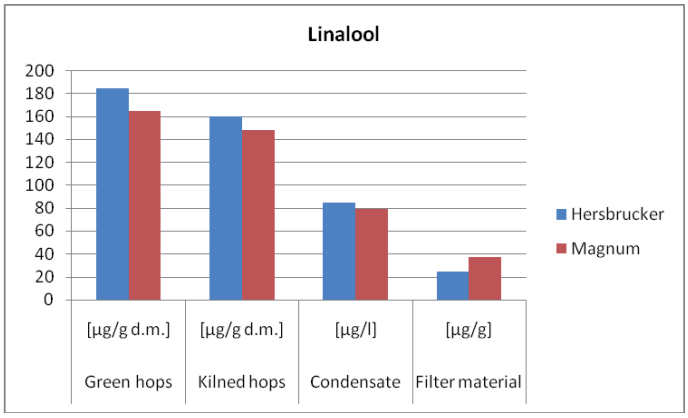

Fig. 4 **inalool concentrations in green hops, kilned hops, condensate and activated carbon filter material for Hersbrucker and Magnum hops (2011)**

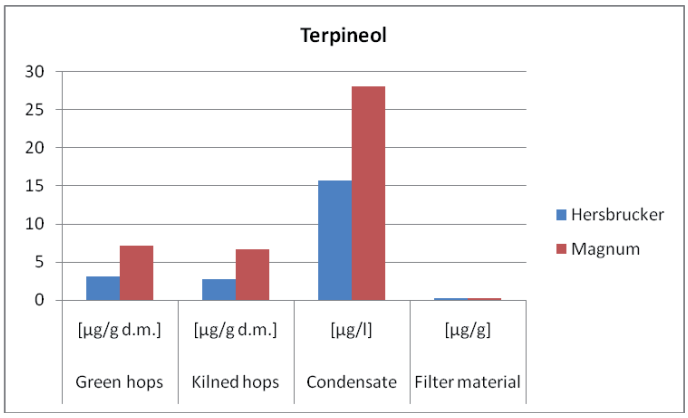

Fig. 5 **Terpineol concentrations in green hops, kilned hops, condensate and activated carbon filter material for Hersbrucker and Magnum hops (2011)**

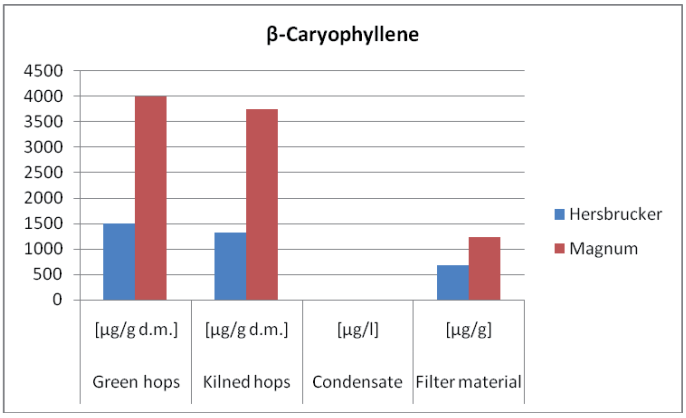

Fig. 6 **β-Caryophyllene concentrations in green hops, kilned hops, condensate and activated carbon filter material for Hersbrucker and Magnum hops (2011)**

the condensate of the exhaust air all tested hop oil components were detected in low concentrations, mainly depending on their water solubility. The analyses of activated carbon material to filter the exhaust air showed relative concentrations of all tested hop oil components that were similar to the relative concentrations in the original hop cone material. For recovery of volatiles the adsorption to activated carbon seems to be the more efficient possibility. Using the condensate or the cooled exhaust air for conditioning of hops after the kilning process may provide a possibility to recover some of the lost volatiles.

Outlook

With the trials of 2011 the research project was successfully finished. A heat recovery system was successfully implemented in an industrial hop kiln and the potentials of hop oil recovery from the exhaust air were shown. Based on the results of 2010 and 2011 a new research project was launched in 2012. Aim is to get a deeper insight in the basics of the kilning process. It is planned to collect further data of hops for all three floors of the kiln. Therefore, a pilot scale hop dryer (floor size: 1 m^2) was constructed and successfully tested in 2012. Variations in temperatures and air flows for the three floors of the pilot scale hop kiln shall reveal potentials to better control the process with special regards to a gentler kilning. In addition hop essential oil analysis has been optimized and expanded to a broader range of analytical targets. Also an analytical assay to determine extremely volatile and low concentrated hop oil constituents (such as aldehydes) is currently under investigation.

6 References

1. Linke, W. and Rebl, A.: Der Hopfenbau; 2nd edition, Fachverlag Hans Carl, Nürnberg, Germany, (1950).
2. Zeisig, H.-D.: Die Trocknung des Hopfens mit erhöhten Heißlufttemperaturen unter der Berücksichtigung ihrer Anwendung in der Darre und im Bandtrockner, dissertation, Technische Hochschule München, 1970.
3. Kolbach, P.: Die Ausnutzung des Hopfenbitterstoffes bei der Herstellung des Bieres, Monatsschrift für Brauwissenschaft, 15 (1961), pp. 61-66.
4. Narziss, L.: Technological aspects of the use of hop preparations, MBAA Technical Quarterly, **7** (1970), pp. 5-10.
5. Wilson, J. H.; Roberts, T.; Smith, R.J. and Biendl, M.: Improving hop utilization and flavor control through the use of pre-isomerized products in the brewery kettle, MBAA Technical Quarterly, **38** (2001), pp. 11-21.
6. Tressl, R. and Friese, L.: Gaschromatographisch-massenspektrometrische Untersuchung der Aromastoffe von Spalter Hopfen, Zeitschrift für Lebensmittel-Untersuchung und -Forschung, **166** (1978), pp. 350-354.
7. Kaltner, D.: Untersuchungen zur Ausbildung des Hopfenaromas und technologische Maßnahmen zur Erzeugung hopfenaromatischer Biere, dissertation, TU München, 2000.
8. Hanke, S.: Untersuchungen zum Einfluss der Hopfungstechnologie auf die Geschmacksstabilität und Harmonie untergäriger Biere, dissertation, TU München, 2010.
9. Kaltner, D.; Steinhaus, M.; Mitter, W.; Biendl and M., Schieberle, P.: (R)-Linalool als Schlüsselaromastoff für das Hopfenaroma in Bier und sein Verhalten während der Bieralterung, Monatsschrift für Brauwissenschaft, **57** (2003), pp. 192-196.
10. Sharpe, F. R. and Laws, D. R. J.: The essential oil of hops – A review, Journal of the Institute of Brewing, **87** (1986), pp. 96-107.
11. Narziss, L. and Forster, A.: Gaschromatographische Untersuchungen zur Bestimmung der Aromastoffe in Hopfen und Hopfenverarbeitungsprodukten (2. Mitteilung), Brauwiss. **24** (1971), pp. 145-151.
12. Narziss, L. and Forster, A.: Gaschromatographische Untersuchungen zur Bestimmung der Aromastoffe in Hopfen und Hopfenverarbeitungsprodukten (5. Mitteilung), Brauwiss. **25** (1972), pp. 239-244.
13. Kieninger, H. and Forster, A.: Der Einfluß der "Übertrocknung" von Hopfen auf die Aromazusammensetzung und den Geschmack des Bieres, Brauwiss. **26** (1973), pp. 214-217.
14. Narziss, L., Miedaner, H. and Gresser, A.: Technologische Maßnahmen zur Werterhaltung des Hopfens, Monatsschrift für Brauwissenschaft **38** (1985), pp. 360-366.
15. Forster, A.: So wie man ihn behandelt… Die Qualitätskette vom Hopfen bis zum Hopfenprodukt, Brauindustrie **86** (2001), pp. 14-20.
16. Forster, A. and Beck, B.: Der Einfluss von Licht auf den Abbau von Hopfenbitterstoffen bei der Lagerung von Pellets, Monatsschrift für Brauwissenschaft **38** (1985), pp. 372-375.
17. Forster, A.: Zum Abbauverhalten von Hopfenpellets in inerter Atmosphäre mit möglichen Auswirkungen durch ungewöhnliche Warmphasen, Brauerei- und Getränke-Rundschau **107** (1996), pp. 231-237.
18. Likens, S. T. and Nickerson G. B.: Determination of certain hop oil constituents in brewing products, Proc. Am. Soc. Brew. Chem. (1964), pp. 5-13.

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