P. C. Wietstock, F. Götz, R. Klie, F.-J. Methner and H. Scheuren

Feasibility Study using a Novel Desorption/ Absorption Process for Transferring Hop Volatiles to Beer

Specialty beers with distinct hop flavour profiles are becoming increasingly popular. To impart a 'hoppy' aroma, hops are commonly added as whole hops or as pellets during fermentation or maturation which can result in filtration/clarification problems. A separation of the aroma extraction process from the aroma insertion process is therefore advantageous.

In this study, a novel hopping technique with sequenced desorption and absorption process was used to transfer hop volatiles into beer. Hop volatile desorption from a hop-water-mixture is forced by a stripping gas with following transfer in the gas stream to an absorption medium. The system operates in a closed loop. The process was tested with water, a buffered model solution (pH 4.3, 5 % (v./v.) EtOH) and lager beer (11.8 °P, 4.8 % (v./v.) EtOH) as absorption media. The experimental data were furthermore compared to thermodynamically calculated data.

Outcomes from the study demonstrate that the process works and a maximum transfer was achieved after 24 hours desorption/absorption. The linalool transfer rate to beer was about 65 %. The thermodynamic approximation was deficient when working with water as absorption medium and was closer but still showed deviations to the experimental data when working in a beer system. Further terms are needed to optimize the model.

This novel method features an easy-to-implement and cost-effective method for transferring hop aroma compounds into beer without directly bringing the beer in contact with hop solids that e.g. may yield filtration/ clarification problems.

Descriptors: linalool, hop aroma, beer, desorption, absorption, hopping, dry hopping, stripping

1 Introduction

Within the last decade, the popularity of hop-rich beers has increased worldwide and hops have received much more attention among the circle of beer drinkers. Not only the bitterness meets with great acclaim, but especially the numerous aroma impressions evolving from the hops' essential oils raise the interest in late and dry hopped beers. This 'trend' is thought to be started in the United States' craft beer scene but now spread out to Europe where also craft beers with unique flavour profiles gain more and more interest [5, 6, 21, 30, 31].

Traditionally, hops are given in the hot section during beer production and its addition time depends on the desired bittering and aroma properties of the beer being produced. An early addition ensures long reaction times at high temperatures thus creating more isomerization products which are responsible for the beer bitterness [1, 20]. But exposing hops to high temperatures for a certain time consequently results in changes and losses of the volatile hop aroma compounds [26]. Thus, if a beer with enriched hop aroma and an unchanged hop aroma profile is desired, dry hopping is applied. The hops are given as pelletized hops or as whole cone hops in the cold section of the brewing process. Dependent on the applied dry hopping technique, the volatile hop oils survive more or less unchanged and to some degree till the finished beer and add significant flavours. Typically, whole cone or pelletized hops are put into a polymer bag before added to the beer tank, keg or cask. That way, the hop material can easily be removed again. The downside is, that the extraction process is not very effective and transfer rates for hop aroma compounds can be low [22]. The most common hop addition is performed into a cylindro-conical vessel (CCV) which is either already filled or about to be filled with beer. The yeast that has settled into the cone of the CCV is typically dumped prior to the hop addition. All methods used have in common that the hops are brought in direct contact with the beer and may result in a hard to clarify suspension. Furthermore, as the amount of hops used for dry-hopping is usually larger than when used for bittering purposes only, the beer quality can be compromised as also unwanted compounds, e.g. pesticides, are transferred in higher concentrations into the beer [17]. By separating the aroma extraction process from the aroma insertion process these problems can be avoided.

One possibility is to use hop aroma enriched oils which are added downstream. But the compositions of hop oils and aroma impressions are then always limited to the products available on the

Authors

Dipl.-Ing. Philip Ché Wietstock, Cand. Dipl.-Ing. Fabian Götz, Rüdiger Klie, Prof. Dr.-Ing. Frank-Jürgen Methner, Technische Universität Berlin, Institut für Lebensmitteltechnologie und Lebensmittelchemie, Fachgebiet Brauwesen, Berlin, Germany; Dr. Hans Scheuren, Ingenieurbüro Dr.-Ing. Hans Scheuren, Bad Kreuznach, Germany; corresponding author: philip.wietstock@tu-berlin.de

market, and this technique is not allowed when brewing according to the German purity law.

Since 2012, the addition of some hop products including whole cone hops and pellets, but not extracts in the cold section of the beer production is in Germany not legally banned anymore [24]. Dry-hopping is therefore also becoming increasingly popular in Germany and brewers have to challenge this process.

Thermodynamically seen, all methods for dosing hops are extraction processes. The desired aromatic components have to be transferred by mass transport from the hop particle into the liquid beer. For extraction processes, generally two process parameters have to be considered: temperature and time. A high temperature is important because it causes a high mass transport velocity as the diffusion properties of the aromatic components are increased with increasing temperatures [13] and sufficient time needs to be guaranteed for the extraction to occur.

So for hop aroma transfer into wort or beer, it is obvious that dosing hops at the end of wort production has the advantage of a high temperature but the disadvantage of a short process time. Extending the extraction time by an earlier addition would result in too high losses and changes of hop aroma volatiles during boiling. By dry hopping in the cold section a long enough extraction time is ensured but the predominant low temperatures counteract a maximal extraction. When summarising hot and cold hopping, the technologies used nowadays are effective but not always efficient.

The basic hop aroma components consist of terpene oils, sulfur compounds and their derivatives [1]. They attribute a variety of aromas and odours to the beer, i. e. piney, tropical, flowery or citrucy notes [1]. While hop oils are claimed to be primarily responsible for those aroma impressions, there is evidence that also water soluble substances from hops such as hop polyphenols contribute to the flavour impression of a dry hopped beer to some degree [11]. But this may also be traced back to glycosidically bound hop aroma compounds which are released in the finished beer [3, 18, 33].

There are several methods for quantifying hop aroma in beer. Solid phase micro extraction (SPME) may be the most flexible method for capturing volatiles that also has the advantage of a simple sample preparation. It is generally used to assess volatiles in the sample's headspace (HS). After the needle of the SPME fibre is pierced through a septum into the headspace of the sample vial, the volatiles are adsorbed on a coated silica fiber and can be subsequently determined via GC analysis coupled with a flame ionization detectoion or, preferably, with a mass spectrometer. Various sorptive materials can be used to change the volatile/fiber interactions thus enabling the analysis of a wide variety of compounds [2, 15, 32]. By adding a salt to the sample, the volatility of those compounds is increased [34]. The extraction selectivity is dependent on the polarity of the analytes and it was found that less polar compounds are absorbed faster by the fiber [2].

In this article, the idea of a novel hopping technique is presented. In opposite to the extraction methods which are commonly used, a combined desorption/absorption process was applied. The experimental design used is described and the mass transport is predicted thermodynamically and is ultimately compared to the experimental data. These data give an important screening in which quantity different flavour components can be transferred from hops to beer.

2 Materials and methods

2.1 Chemicals

Ethanol was obtained from Merck KgaA, Darmstadt, Germany. The hop aroma standards α-humulene, α-terpineol and trans-caryophyllene as well as sodium acetate trihydrate and acetic acid (glacial) were purchased from Sigma Aldrich (Sigma-Aldrich Laborchemikalien GmbH, Seelzen, Germany). Limonene, linalool, and myrcene were purchased from Fluka (Fluka Chemia AG, Buchs, Switzerland). All reagents were from analytical grade or higher.

1.2 Beer production

The base beer used for the trials was produced in the Technische Universität Berlin's 1.2 hL research pilote plant. The beer was brewed using 100 % Pilsner malt and dosing 125 mg hop CO_2 extract (Hallertauer Magnum, 47.9 % (wt./wt.) α-acid) per liter wort for bittering at the beginning of kettle boil. The pitching wort was fermented at 12 °C using the lager yeast strain 'RH', maturated for 2 weeks and stored at 0 °C after bulk yeast removal until it was used.

1.3 Quantification of hop volatiles

Myrcene, limonene, linalool, trans-caryophyllene, α-humulene, and α-terpineol were measured by headspace (HS)-SPME-GC/FID and using a Gerstel MultiPurposeSampler MPS (GERSTEL GmbH & Co.KG, Mülheim an der Ruhr, Germany) for sampling.

5 mL sample was filled in a 15 mL glass vial and hop volatiles were adsorbed to a 2 cm tri-phase fiber (PDMS/CAR/DVB) with a

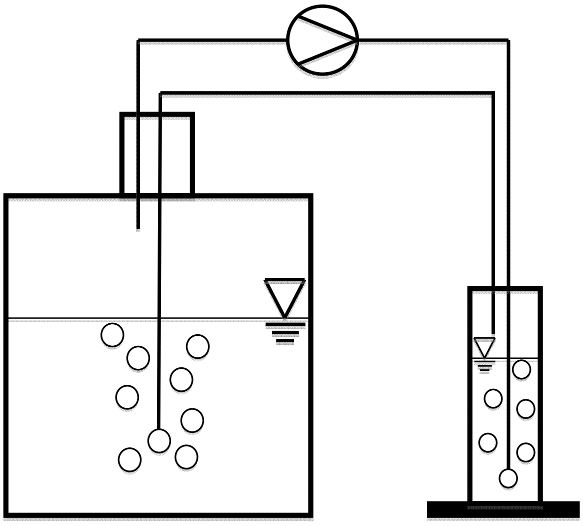

Fig. 1 **Experimental set-up with absorption-vessel (left), desorption-vessel (right) and pump (top)**

50/30 µm coating thickness for 40 minutes at 40 °C under constant stirring. The volatiles were desorbed in the GC port at 240 °C (splitless) and were separated on a DB-WAX column (60 m, 0.50 µm, 240/250; Agilent Technologies, St. Clara, USA) by using constant pressure mode and following the temperature program: 40 °C for 3 min, heating to 200 °C at 4 °C/min, in 2 min to 220 °C and holding for 15 minutes. Quantification was done using standard addition in water, buffer, or beer, and a 6 point calibration.

1.4 Experimental part

The desorption/absorption process of hop volatiles was tested with water, a buffered model solution and the base beer. The experimental set-up is depicted in figure 1.

The principle and implementation were similar for all trials. The set-up consisted of a ‘desorption-vessel’ and an ‘absorption-vessel’ which were connected in a closed loop (Fig. 1). A peristaltic pump at a velocity of ca. 600 mL/min was used for gas transport between the two vessels.

20 g of hops (Huell Melon, pellets type 90, crop 2013, 2 mg/100 g linalool, measured by EBC analytica 7.10 [7]) were firstly solved in distilled water in the ‘desorption-vessel’ which was placed then in a water bath at 50 °C. The amount of water used varied and is stated in the respective trials. Then, the pump was switched on and gas from the ‘absorption-vessel’s’ headspace was bubbled through the hop-water mixture consequently getting enriched with hop volatiles as defined by the temperature dependent vapour-liquid-equilibrium (VLE). The gas was subsequently transferred to the ‘absorption-vessel’ and bubbled through the sample thereby releasing the hop volatiles into the sample solution. As the system was a closed looped only the included gas was used for desorption/absorption process.

1.5 Pre-trial using water as absorption medium

In a preliminary trial, the process was tested using water as absorption medium. A gas wash bottle was used as ‘desorption-vessel’ and 20 g hop pellets were solved in 260 mL distilled water under atmospheric conditions. The hop volatiles were transferred and captured in 5 L of distilled water which was held at room temperature (20–22 °C). The process time was 12 hours and the experiment was performed in triplicate. The contents of hop volatiles in the absorption-vessel were quantified by HS-SPME-GC/FID. The results are presented as the arithmetic mean with a confidence interval of 95 %.

1.6 Investigation of the effect of process time

The effect of process time on extraction of hop volatiles was subsequently tested in a buffered model solution (acetate buffer; pH 4.3, 5 % (v./v.) etOH). A gas wash bottle was used again as ‘desorption-vessel’ and 20 g hop pellets were solved in 260 mL distilled water under atmospheric conditions. The hop volatiles were transferred and captured to 5 L of the buffered model solution at room temperature (20–22 °C). 144 hours of circulation were realized and sampling took place in a 3 hour-period within 0–15 h and every 24 hours within 24–144 h. The experiment was conducted under atmospheric conditions not excluding oxygen ingress. All samples were frozen until analysis by HS-SPME-GC/FID.

1.7 Trials with beer as absorption medium

Finally, the experiment design was also tested with beer. For the beer trials, the hop volatiles were desorbed in a reactor-chamber with a stirring device. 20 g of hops were solved in 1 L degassed distilled water and the whole system was purged with carbon dioxide before the process was started to prevent oxidation reactions. A 15.5 L keg was used as the ‘absorption-vessel’ and was filled with 10 L of the same base beer (lager beer, 11.8 °P, 4.8 % (v./v.) EtOH; 5.5 g/L CO_2) for each trial. The beer was cooled to 4 °C during the whole process and the time of desorption/absorption was 24 hours. The system operated under a pressure of 0.6 bars and oxygen ingress was prevented as good as possible at all times. After finishing the experiments, the content of hop volatiles in the beer container were quantified by HS-SPME-GC/FID. The experiments were perfomed in triplicate. The results are presented as the arithmetic mean with a confidence interval of 95 %.

1.8 Thermodynamic approximation of the desorption/absorption process

The process was calculated for linalool using thermodynamic equations. Linalool was used because it is a well-studied hop volatile, the volatility data in the temperature range from 72 to 100 °C is known, and because it is one of the most potent odorants in hops [9, 16]. The calculations and assumptions are shown in the results and discussion section.

2 Results and discussion

This article features a novel method for transferring hop volatiles to beer, ultimately aiming to enrich beers with hop volatiles. Desorption and absorption of hop volatiles can be regarded as vaporisation and condensation processes. Calculating these processes enables a high process control and the possibility of e.g. react to natural fluctuations in the hop quality. In particular, the scale-up to new container dimensions and process parameters are facilitated.

Therefore, the temperature dependent vapour-liquid equilibrium (VLE) of the compound of interest in water (binary mixture of water and aroma compound) has to be considered. It describes the correlation between liquid and gas phase concentration. The parameter volatility K_i is defined as follows:

$$K_i = \frac{y_i}{x_i} \qquad \text{(Eq. 1)}$$

with

y_i = concentration of a component *i* in the gas phase.

x_i = concentration of a component i in the liquid phase.

As gas molecules do not influence the volatility of linalool in water in infinite dilution (no interactions of linalool molecules, assumption of single molecules in an infinite amount of solvent-water), only the ratio of linalool in the liquid and in the vapour phase has to be taken into account. In dependence to volatility of linalool in water, three possible scenarios have to be considered:

- If water vaporises in higher quantity than linalool ($K_i<1$) the process is not very efficient because too much water has to be vaporised. The process needs too much time and too much vaporisation energy for the hop aroma transfer. Furthermore, the beer gets diluted and in the worst case, water has to be vaporised again.
- If linalool and water vaporises in the same ratio ($K_i=1$), it is important to have a very high concentration of linalool in water. Unfortunately, this is not possible without an additional extraction medium because the solubility of linalool in water is considerably low [14].
- If the volatility is higher than 1 ($K_i>1$), more linalool than water is vaporising and can be condensed in the absorption medium. The concentration of linalool is increased and the proposed method is working. So for calculating the desorption/absorption process the temperature dependent VLE is needed. These data can be found in the literature [14].

By being able to calculate a thermodynamic process, the experimental results can be predicted. Therefore, the process can be controlled most efficiently and the effect of process parameter changes can be foreseen. Furthermore, the calculations can be used for a scale-up and allow an optimal design and pre-set of process parameters.

Vaporisation processes of binary mixtures like linalool in water in infinite solution at very low concentrations of $x_i<10^{-6}$ can be calculated with high accuracy [14, 27]. For the calculation of the described process following simplifications have to be made:

- linalool in water is highly diluted (infinite dilution) [14]. Molecular interactions only occur between water and linalool molecules, the volatility is independent from other solved substances [19, 23, 27];
- as linalool is highly diluted the volatility is not dependent on pressure and only influenced by temperature [25, 29];
- the vaporised linalool is nearly totally condensed in the absorption medium because of the higher sample volume compared to the volume of the desorption medium (water-hop-mixture) and because of the temperature difference of both (higher solubility at lower temperatures): Linalool is transferred into the absorption-vessel and not vice versa.
- the gas flow is constant.

The time dependent enrichment $\frac{dx_i^B}{dt}$ of an aromatic component *i* in the absorption-vessel can then be described by following equation:

$$\frac{dx_i^B}{dt} = \frac{\dot{n}_i}{V_B} \qquad \text{(Eq. 2)}$$

with

V_B = liquid volume in the absorption-vessel

$\dot{n}_i$ = molecule flow of a volatile in the gas phase

Furthermore, the molecule flow $\dot{n}_i$ of an aromatic component i in the gas phase is described by the equation:

$$\dot{n}_i = \dot{n} \cdot y_i \qquad \text{(Eq. 3)}$$

with

$\dot{n}_j$ = flow of all water molecules

$\dot{n}_i$ = flow of all volatile molecules

As the component *i* is in liquid and vapour phase in infinite dilution, the parameter $\dot{n}$ can be substituted by the parameter $\dot{n}_j$ which can be calculated by a modified form of the ideal gas law:

$$\dot{n}_j = \frac{p_j^S}{R \cdot T} \cdot \frac{V}{t} \qquad \text{(Eq. 4)}$$

with

p_j^S = vapour pressure water

R = universal gas constant

T = temperature

V = volume

t = time

Considering the mentioned simplifications and combining eq. 1, 2, 3 and 4 is leading to the following differential equation:

$$\frac{dx_i^B}{dt} = \frac{\frac{p_j^S}{R \cdot T} \cdot \frac{V}{t} \cdot x_i \cdot K_i}{V_B} \qquad \text{(Eq. 5)}$$

Using integration leads to the final equation:

$$x_i^B = \frac{\frac{p_j^S}{R \cdot T} \cdot \frac{V}{t} \cdot x_i \cdot K_i}{V_B} \cdot t \qquad \text{(Eq. 6)}$$

The integration constant is 0, as the initial conditions are 0, too. The values of the different parameters are summarised in table 1.

Table 1 Parameters for water experiment

Parameter	Symbol	Value	Unit
content i absorption-container	X_B^i	calculated	[ppb]
time	t	43200	[s]
vapour pressure j (water)	p_B^S	2400	[Pa]
ideal gas constant	R	8.314	[J/ (mol*K)]
temperature	T	323	[K]
volume flow	V/T	0.15	[L/min]
volatility	K_i	37.2	[–]
liquid volume absorption-container	V_B	5000	[mL]

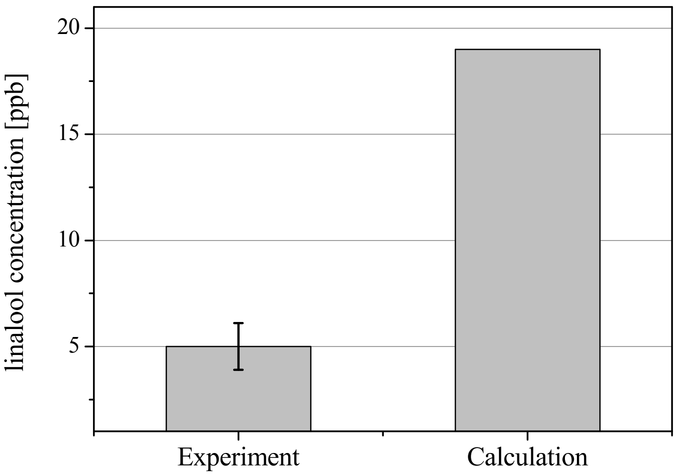

Fig. 2 **Comparison of measurement (left column) and calculation (right column). Error bars represent the confidence interval (95 %, n = 3)**

The volatility of the compounds is from major importance. The volatility of linalool in water in infinite dilution at 100 °C is 35.6 [14] and the volatility at 72 °C can be calculated using a published flash vaporisation result of linalool out of wort and thus is 37.2 [14]. Because there are no relevant volatility data of linalool in water in infinite dilution at 50 °C available, the volatility of 72 °C was used for calculating the desorption/absorption processes. As the change of volatility between 100 and 72 °C is low [13], it can be expected that the deviation of the volatility between 72 and 50 °C is negligible.

In a preliminary trial, the design was tested with water as the absorption medium. The result from the experiment is presented in figure 2.

Linalool was clearly very low and the calculated data showed a deviation of 100 % as compared to the experimental data. However, the trial suggested that the idea of using a desorption/absorption process worked and the process was thus further investigated.

In a subsequent trial, the buffer model solution containing 5 % (v./v.) ethanol was used as absorption medium. This new matrix is closer to the matrix beer. With respect to the volatility, it has to be considered that this matrix is not a binary mixture anymore. The volatility of linalool (in the beer container) is now influenced by the ethanol concentration. Linalool has an increased solubility in a water-ethanol mixture than in water with the consequence that the last mentioned simplifications must be reinforced. It can be considered advantageous for the process that the hop container still contains a binary mixture and the linalool's volatility remains unchanged and high (the transport of ethanol during the process from beer to hop container is negligible as the volatility of ethanol in water is only in the range of 2–5).

The influence of the process time on the concentration of the hop volatiles in the absorption medium was assessed. The results are depicted in figure 3.

It can be seen that all measured hop volatiles with the exception of myrcene reached their maximum concentration after 24 hours or earlier and remained unchanged or slightly decreased again. Myrcene was highest at the first sampling point (after 3 hours) and then decreased tremendously up to 24 hours to a final concentration of 17 ppb. Linalool increased the slowest as compared to the other compounds and was highest after 24 to 48 hours. The decrease of myrcene and (potentially) reciprocal increase of linalool may be explained by the oxygen-induced transformation of myrcene to linalool. The transfer rate of linalool was 180 % which is another indication that linalool was formed 'de novo' during the experiment. The concentrations of trans-caryophyllene, α-humulene and α-terpineol remained very low. Limonene reached its maximum concentration after 9 hours desorption/absorption and then also decreased again. This may also be traced back to oxidation reactions. Based on this trial, the process time for the subsequent trials was set to 24 hours.

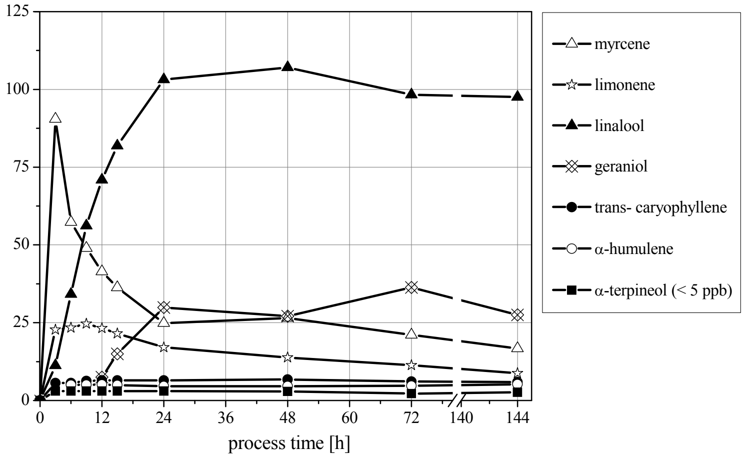

Fig. 3 **Time-dependent increase of hop volatiles in buffered model solutions with 4 g/L hops**

Finally, beer was used as the absorption medium and oxygen ingress was prevented as good as possible at all times. The result is demonstrated in figure 4.

The data show distinct increases in hop volatiles from the base beer to the beer after desorption/absorption for 24 hours and linalool showed a transfer rate of about 65 %. The hop volatile concentrations in the base beer (reference) were below the limit

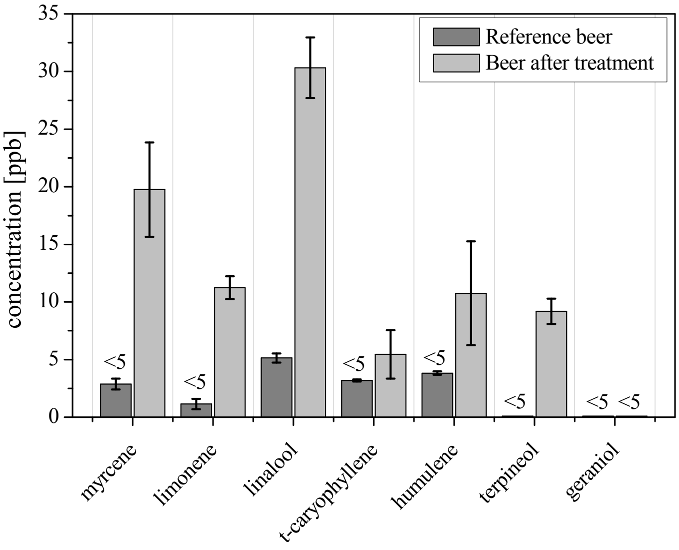

Fig. 4 **Hop volatiles in beer after 24 h desorption/absorption with 2 g/L hops. Error bars represent the confidence interval (95 %, n = 3)**

Table 2 **Parameters for beer experiment.**

Parameter	Symbol	Value	Unit
content i absorption-container	X^i_B	calculated	[ppb]
time	t	86 400	[s]
vapour pressure j (water)	p^S_B	2400	[Pa]
ideal gas constant	R	8.314	[J/ (mol*K)]
temperature	T	323	[K]
volume flow	V/T	0.6	[L/min]
volatility	K_i	37.2	[–]
liquid volume absorption-container	V_B	10 000	[mL]

of quantitation (< 5 ppb) with the exception of linalool which was 5 ppb. The treatment had a clear impact on the concentration of hop volatiles and yielded a general increase with the exception of geraniol which was not found in the beer after treatment. Forster and Gahr [8] achieved a 100 % transfer rate when working with the same hop cultivar and doing 'conventional' dry-hopping during maturation. However, as related to the short process time of 24 hours and the other advantages, like omitting additional hop particle dependent clarification steps or pesticide ingress from the hops, the result achieved here can still be considered satisfying.

Again, the experimental data was compared to calculated data for linalool (Fig. 5). The parameters used for the calculation are depicted in table 2. In contrast to the experiments which were done using water as the absorption medium, in this trial, the calculated data was closer to the experimental data. Interestingly, the experimental data even exceeded the calculated data which cannot be explained by the volatility. The volatility of linalool in a mixture of water and ethanol reinforces the enrichment of linalool in the beer container because it is assumed that all linalool molecules solve in this mixture. That the measured value is higher than calculated may be explained that still little oxidation of myrcene to linalool and a 'de novo' formation of linalool occurred during the experiments.

Taken together, these data implicate that the current calculation model for the process still needs optimization and is not capable of accurately displaying the correct linalool concentration because it lacks two potential influencing factors: the solubility of linalool in water or a water-ethanol mixture, respectively, and potential chemical conversion reactions yielding a 'de novo' formation of linalool in the solutions. Using beer as the absorption medium yielded a better result which is a indication that mixture properties and the solubility of linalool in the absorption medium may influence the process. A first explanation may be given here: linalool solves only in low concentration in water and the corresponding volatility is therefore high. Linalool in a water-ethanol mixture (as beer is) has a much higher solubility and the volatility must therefore be low. The difference between water and beer experiments may be traced back to the fact that the final concentration of linalool in water is lower than the concentration of linalool in beer. Water as a solvent cannot 'hold back' linalool molecules. Taking that into consideration, the above mentioned simplification of the total condensation of linalool in beer is not valid for water because of this special mixture property.

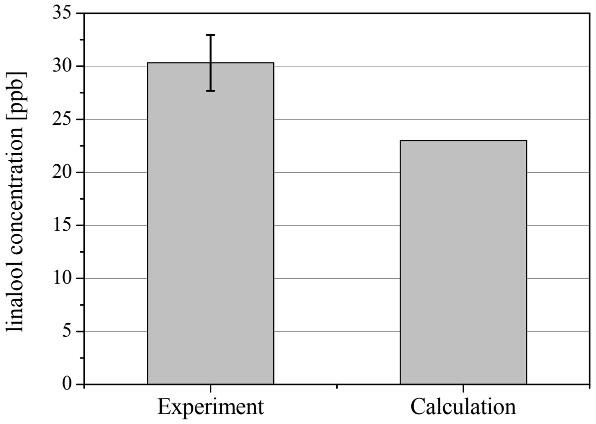

Fig. 5 **Comparison of experimental data (left column) and calculated data (right column) for the experiment using beer as the absorption medium. Error bars represent the confidence interval (95 %, n = 3)**

For optimising the model, additional terms need to be inserted which describe the enrichment of linalool in water or beer and furthermore comprise potential chemical conversions. Future research is needed here in which the temperature-dependent volatility of linalool in water and in different mixtures of ethanol and water is investigated.

3 Summary and Perspectives

In this article, a method for hop aroma insertion into beer which is based on a sequenced desorption and absorption process is presented. The method was tested and validated in laboratory scale by transferring hop volatiles from a hop-water-mixture into water, a buffered model solutions, and beer. This novel method features an easy-to-implement and cost-effective method for transferring hop aroma compounds into beer without directly bringing the beer in contact with hop solids that e.g. may yield filtration/clarification problems.

The prediction of the linalool enrichment in water or beer by thermodynamic calculation needs further model optimization because solubility properties of linalool in water/beer and chemical conversions were not considered. The calculations and assumptions made here are a first approach to predict a very complex process with the final goal to accurately calculate the process thereby easing complete process control. Further research is needed here. The next steps consist of a scale-up and following sensorial validation of the resulting beer. Eventually, it can be concluded that applying 'desorption/absorption processes for transferring hop volatiles to beer' are feasible.

4 Literature

1. Briggs, D. E.: Brewing science and practice, CRC Press; Woodhead Pub., Boca Raton, Cambridge, England, 2004.
2. Charry-Parra, G.; De Jesus-Echevarria, M. and Perez, F. J.: Beer volatile analysis: optimization of HS/SPME coupled to GC/MS/FID, Journal of Food Science, **76** (2011), no. 2, pp. 205-211.

3. Daenen, L.; Saison, D.; De Cooman, L.; Derdelinckx, G.; Verachtert, H. and Delvaux, F.: Flavour enhancement in beer: hydrolysis of hop glycosides by yeast beta-glucosidase, Cerevisia: Belgian Journal of Brewing and Biotechnology, **32** (2007), no.1, pp. 24-36.
4. Dieckmann R. H. and Palamand S. R.: Autoxidation of some constituents of hops. I, The monoterpene hydrocarbon myrcene, Journal of Agricultural and Food Chemistry, **22** (1974), no. 3, pp. 498-503.
5. Dornbusch, H.: Hopfenstopfen: Eine neue Aromawelt auch für deutsche Biere!, Brauindustrie, (2012), no. 3. p. 33.
6. Dornbusch, H.: Bier ist eine „neue Religion" in den USA, Brauindustrie, (2010), no. 2, p. 37.
7. European Brewery Convention, 7.10: Hop Oil Content of Hops and Hop Products. In Analytica-EBC, Verlag Hans Carl Getränke Fachverlag: Nürnberg, Germany, 2002.
8. Forster, A. and Gahr, A.: On the fate of certain hop substances during dry hopping, BrewingScience – Monatsschrift für Brauwissenschaft, **66** (2013), no 7/8, pp. 93-103.
9. Fritsch, H. T.: Einfluß des Hopfens auf wertgebende Aromastoffe in Pilsener-Bieren sowie in Zwischenstufen des Brauprozesses, dissertation, TU München, 2001.
10. Godshall, A.: How Carbohydrates Influence Food Flavour, Food Technology, **51** (1997), no 1, pp. 63-67.
11. Goiris, K.; Jaskula-Goiris, B.; Syryn, E.; Van Opstaele, F.; De Rouck, G.; Aerts, G. and De Cooman, L.: The Flavoring Potential of Hop Polyphenols in Beer, Journal of the American Society of Brewing Chemists, **72** (2014), no. 2, pp. 135-142.
12. Hansson, A.; Andersson, J. and Leufven, A.: The effect of sugars and pectin on flavour release from a soft drink-related model systems. Food Chemistry, **72** (2001), no. 3, p. 363.
13. Hertel, M.: Verfahren und Vorrichtung zur Bierbereitung, Deutsches Patent- und Markenamt (DPMA), DE102010023886A1, 2009.
14. Hertel, M.: Das Ausdampfverhalten von Aromastoffen während der Würzekochung, dissertation, TU München, 2007.
15. IOFI Working Group on Methods of Analysis: Guidelines for solid-phase micro-extraction (SPME) of volatile flavour compounds for gas-chromatographic analysis, from the working group on methods of analysis of the international organization of the flavor industry (IOFI), Journal of Flavour Fragrance, **25 (**2010), no. 6, pp. 404-406.
16. Kaltner, D.: Untersuchungen zur Ausbildung des Hopfenaromas und technologische Maßnahmen zur Erzeugung hopfenaromatischer Biere, dissertation, TU München, 2000.
17. Kippenberger, M.; Hanke, S.; Biendl, M.; Stettner G.; and Lagemann, A.: Transfer of Nitrate and various Pesticides into Beer during Dry Hopping, BrewingScience – Monatsschrift für Brauwissenschaft, **67** (2014), no. 1/2, pp. 1-9.
18. Kollmannsberger, H.; Biendl, M. and Nitz, S.: Occurrence of glycosidically bound flavour compounds in hops, hop products and beer, BrewingScience – Monatsschrift für Brauwissenschaft, **59** (2006), no. 5/6, pp. 83-89.
19. Lubbers, S.; Landy, P. and Voilley, A.: Retention and Release of Aroma Compounds; Containing Proteins, Food Technology, **52** (1998), no. 5, pp. 68-74.
20. Malowicki, M. G. and Shellhammer, T. H.: Isomerization and Degradation Kinetics of Hop (*Humulus lupulus*) Acids in a Model Wort-Boiling System, Journal of Agricultural and Food Chemistry, **53** (2005), no. 11, pp. 4434-4439.
21. Mitter, W. and Cocuzza, S.: Wiederbelebtes Verfahren, Brauindustrie, (2012), no. 4, pp. 10-12.
22. Mitter, W. and Cocuzza, S.: Dry Hopping – a Study of Various Parameters. Brewing and Beverage Industry International (2013), no. 4, pp. 70-74.
23. Nahon, D. F.; Navarro y Koren, P. A.; Roozen J. P. and Posthumus, M. A.: Flavor Release from Mixtures of Sodium Cyclamate, Sucrose, and an Orange Aroma, Journal of Agricultural and Food Chemistry, **46** (1998), no. 12, pp. 4963-4968.
24. o.V.: Ist Hopfenstopfen zulässig? Brauindustrie, (2012), no. 3, p. 6.
25. Philippe, E.; Seuvre, A.; Colas, B.; Langendorf, V.; Schippa, C. and Voilley, A.: Behaviour of Flavour Compounds in Model Food Systems: A Thermodynamic Study, Journal of Agricultural and Food Chemistry, **51** (2003), no. 5, pp. 1393-1398.
26. Rettberg, N.; Thörner, S. and Garbe, L.-A.: Bugging Hop Analysis – on the Isomerization and Oxidation of Terpene Alcohols during Steam Distillation, BrewingScience – Monatsschrift für Brauwissenschaft, **65** (2012), no. 7/8, pp.112-117.
27. Scheuren, H.: Modellierung gekoppelter Austreibungs- und Nachbildungsprozesse aromatischer Komponenten in der Lebensmittelindustrie am Beispiel der Würzebereitung, dissertation, TU München, 2011.
28. Scheuren, H.; Methner, F.-J.; Sommer, K. and Dillenburger, M.: Thermodynamic Validation of Wort Boiling Systems, BrewingScience – Monatsschrift für Brauwissenschaft, **67** (2014), no.7/8, pp. 96-100.
29. Scheuren, H.; Dillenburger, M.; Tippmann, J.; Methner, F.-J. and Sommer, K.: The volatility of Dimethyl Sulfide Measured by Flash Distillation, BrewingScience – Monatsschrift für Brauwissenschaft, **67** (2014), no. 5/6, pp. 69-71.
30. Schönberger, C.: Hopfenstopfen – gut gestopft ist halb gewonnen, BRAUWELT **152** (2010), no. 9-10, 251-254.
31. Toft. E.: Adventures in dry-hopping with German aroma varieties, BRAUWELT International **28** (2010), no. 1, pp. 14-16.
32. Van Opstaele, F.; De Causmaecker, B.; Aerts, G. and De Cooman, L.: Characterization of novel varietal floral hop aromas by headspace solid phase microextraction and gas chromatography-mass spectrometry/olfactometry. Journal of Agricultural and Food Chemistry, **60** (2012), no. 50, pp. 12270-12281.
33. Winterhalter, P. and Skouroumounis, G. K.: Glycoconjugated aroma compounds: occurrence, role and biotechnological transformation, Advances in Biochemical Engineering/Biotechnology, **55** (1997), pp. 73-105.
34. Zuba, D.; Paczewski, A. and Rózanska, M.: Application of headspace solid-phase microextraction for determination of chloro-orgacompounds in sewage samples, 39th Meeting of The International Association of Forensic Toxicologists, 2001.

Received 30 September 2014, accepted 8 January, 2015