On hops, filters and precious oils

UNIQUE CHARACTER | Volatile oils and aroma compounds in the hop umbels are responsible for lending beer its special and unique aromatic character. It is, therefore, an essential task of the brewing process to retain the concentration of the hop oils in the beer. This article examines the impact of sheet filtration on the concentration of hop oils.

HOPS, A PLANT OF THE HEMP FAMILY, have been one of the basic ingredients used in brewing beer for many centuries. They lend the "amber nectar" not only its special flavor but also its aroma. A variety of volatile oils and aroma compounds in the hop umbels are responsible for this – similar to those in flowers, perfumes and spices – providing the pleasant and "hoppy" scent. Although not all characteristics of hops have been analyzed, we know they cannot be replaced with chemical aromas. While the proportion of these oils is only around 0.5-3 %, they are still a defining factor in terms of aroma. We are capable of clearly smelling a concentration of as little as 10 ppm (0.001 %) in the finished beer. It is therefore important to preserve these precious aromas in the filtration stage.

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The character of hops

Hops are an important raw material for brewers, influencing the character of a beer depending on the amount, variety and region of origin [5]. This affects the bitterness of the beer, which is measured in "EBC bitterness units" (BU), or frequently on the basis of Iso-α-acids (the isomers of the main bitterness components of the hops, the α-acids). A second group of bitter acids, the β-acids, are almost insoluble under the conditions of the brewing process. However, their oxidation products, the β-soft resins, are soluble and, with their mild bitterness, also contribute to the bitter flavor of a beer [4]. When characterizing the bitter acids, the ratio of β:α-acids is an important indicator for describing a hop variety [3].

In addition to a beer's bitterness, its hop aroma is another important factor. These volatile substances are terpene hydrocarbons (mono- and sesquiterpenes) or belong to the oxygen group (alcohols, aldehydes, esters, ketones, etc.) and are, in turn, specific to the individual varieties. The terpenes myrcene, humulene, β-caryophyllene, farnesene, α- and β-selinene and selinadien allow hops to be grouped as follows: bitter and high-α varieties have significantly more than 40 % myrcene; the ester methylbutyl isobutyrate is also typical, at between 1.5 and 3.5 % myrcene. Aromatic hops have 30 % myrcene or less, farnesene is significant in the hops of the Saaz group of varieties and the "post-humulenes", such as selinene, etc., are found in Hersbrucker hops and their derivatives [5]. However, terpenes are only found in extremely small quantities after the standard brewing process. Evidence of the alcohols, such as linalool, terpineol, geraniol and some esters are found in more significant quantities [5].

Hop aromas are referred to as "volatile oils". This means that they tend to disappear from hops and beer over time, due partly to evaporation and partly to oxidation. To aid in combating both of these, the same methods used with the α-acids may be applied: storing in cool conditions and sealing the bags so that they are as airtight as possible and have low air content. The aromas may also be lost later, in the bottle, if they react with the residual oxygen. For this reason, efforts should be made during filtration and

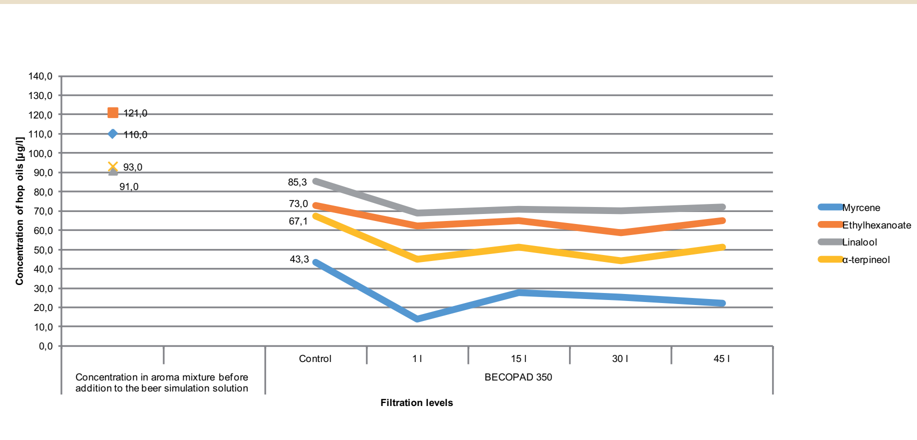

Fig. 1 Concentration trend of hop oil aromas in beer simulation model solution

THRESHOLDS OF SELECTED HOP AROMA COMPOUNDS [2]

Substances	Thresholds* in µg/l	Fluctuation margins** in µg/l
Linalool	27.1	5; 27; 80; 100
α-terpineol	1075.6	2000
Myrcene	118.8	10; 30; 125
Ethylhexanoate	1.5	

** Values calculated as part of PhD thesis* *** Values from the specialist literature*

Table 1

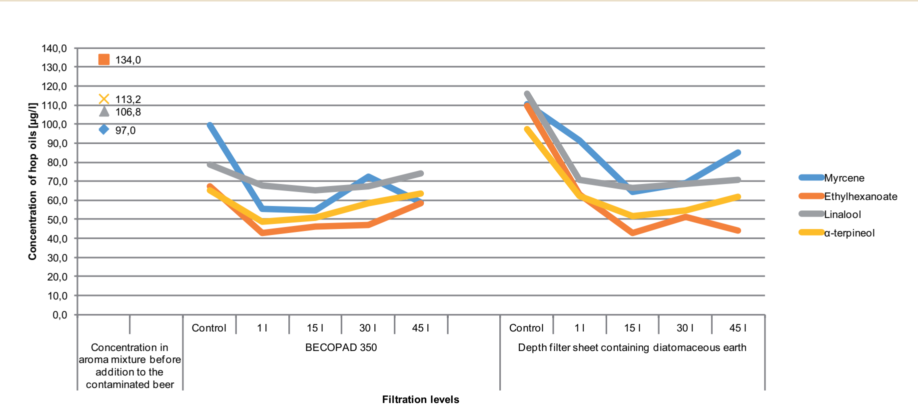

Fig. 2 Concentration trend of hop oil aromas in contaminated beer filtered with Becopad 350 depth filter sheets

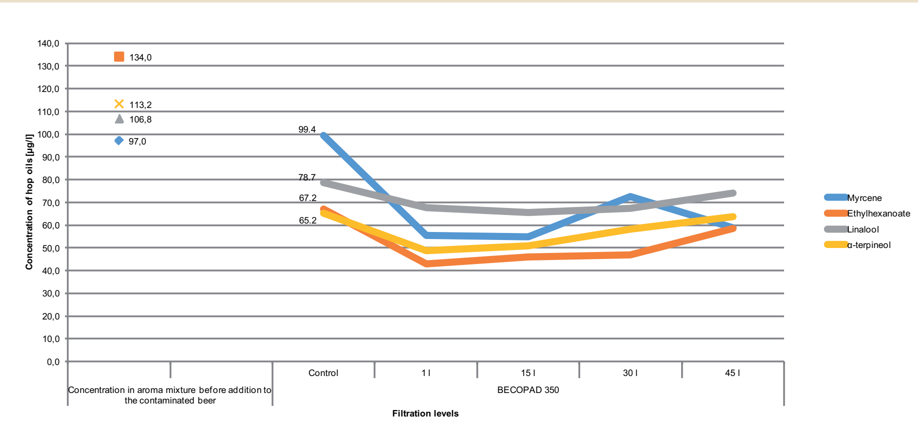

Fig. 3 Concentration trend of hop oil aromas in contaminated beer filtered with Becopad 350 depth filter sheets and a depth filter sheet containing diatomaceous earth

bottling to ensure that as little oxygen as possible finds its way into the beer.

Individual hop aromas

Myrcene is the most important ingredient of hop oil in terms of quantity and is found in almost every variety of hops. The content can vary from 20 to 70 % of the total oil. Myrcene is highly volatile and therefore very ineffective in wort brewing because it completely evaporates within a few minutes. As a result of its high volatility, as well as its low solubility, it is present in trace quantities of a few µg/l in beers with normal hop content. In dry-hopped beers, however, quantities of 20 to 200 µg/l can be detected, depending on the variety and quantity of hops used. The flavor threshold of myrcene is between 30 and 100 µg/l. The aroma description is extremely broad, with notes ranging from resin, pine, herbal, green and aromatic to citrus and floral [1].

Ethylhexanoate can be found in fresh cut pineapple and is therefore classified in the fruit esters group. At 1.5 µg/l, the flavor threshold is very low, and notes of tropical fruit and floral aromas can be detected [2].

Linalool is regarded as a key component and indicator substance for the hop aroma. Linalool has a direct influence on the beer aroma. If the odor threshold of 8 to 80 µg/l is exceeded, citrus notes and a floral/fruity flavor can be detected [2].

The α-terpineol alone makes no direct contribution to the hop aroma. It is only in combination with other hop aroma compounds, such as β-caryophyllene or humulene, that it contributes to an intensification of the hop aroma. The aroma of α-terpineol is described as floral and citrusy [2].

Influence of sheet filtration

The volatile and aromatic oils must remain preserved as effectively as possible in order to lend the beer its special flavor. All process steps should therefore be optimized for maximum aroma preservation. Filtration is an important process step. In order to calculate the extent to which sheet filtration influences the concentration of hop oils in beer simulation model solution and in beer, an investigation was carried out at the Research and Teaching Institute for Brewing (Versuchs- und Lehranstalt für Brauerei in Berlin, VLB) in Berlin.

The tests were carried out with a Beco Compact® Plate 200 plate and frame filter (20x20 cm) with Becopad® 350 depth filter sheets (see fig. 1 - 3) and a depth filter sheet containing diatomaceous earth (see fig. 3) at a filtration rate of 200 l/m²/h. The filtration throughput was 13.6 l/m². The filtrate samples were analyzed via fluid extraction (three times in each case) using $^2H_3$-myrcene, $^2H_5$-linalool und 1-^{13}C-ethyloctanoate as internal standards. The extracts were analyzed using GC-MS/MS in multiple reaction monitoring mode.

The aroma mixture was composed as follows: 100 µg/l each of the substances linalool, α-terpineol, myrcene und ethylhexanoate were added to a beer simulation model solution (95 % water, 5 % ethanol and phosphate buffer at pH 4.3) and to a beer.

A sample was first taken before the filtration process, which was designated as the control, and subsequently after the following filtration levels: 1 liter of filtrate, 15 liters of filtrate, 30 liters of filtrate and 45 liters of filtrate.

Figure 1 shows that the recovery rates are very different in the beer simulation model, depending on the hop aroma under investigation. In the control, they are at around the same level for ethylhexanoate (60.3 %), linalool (93.7 %) and α-terpineol (72.2 %) The recovery rate of myrcene is, at 39.4 %, significantly lower, which can be attributed to the poor water solubility of the substance.

The analysis of the filtrate samples resulted in a slight reduction in the aroma components linalool and ethylhexanoate after the first liter and a rapid stabilization of the concentration in the remaining filtration process. The reduction of myrcene and α-terpineol was more pronounced. After the stabilization phase, the concentrations of hop oil measured fluctuated between 5 and 10 μg/l.

In order to analyze the influence and the interaction between the aromas of the hops and the beer ingredients, the same test process was carried out with contaminated beer. The same aroma mixture was added to beer and then filtered with Becopad 350 depth filter sheets.

The concentration trends of the aromas added to the contaminated beer are illustrated in figure 2. The recovery rates for the individual hop aromas are different from those in the beer simulation model solution. Myrcene was found at 102.5 % in relation to the initial concentration. The recovery rate was 50.1 % for ethylhexanoate, 73.7 % for linalool and 57.6 % for α-terpineol.

The picture of the concentration trend during the filtration process is a consistent one. After the 1-liter filtrate sample, the concentration of the aroma compounds ethylhexanoate, linalool and α-terpineol stabilizes and then rises again slowly. The concentration trend for myrcene is characterized by a significant decrease from 102.5 μ/l to 57.3 μ/l, with the trend stabilizing in the remainder of the filtration process.

Figure 3 shows a direct comparison between filtration with a Becopad depth filter sheet and a conventional depth filter sheet with diatomaceous earth. Although the same aroma mixture concentration was added to the beer, the controls, and therefore the recovery rates, are different.

When filtering with a depth filter sheet containing diatomaceous earth, despite the higher initial concentration of the aroma compound ethylhexanoate of 109.6 μg/l in the 15-liter filtrate sample, a drop of 43.0 μg/l was observed. This drop was also observed for linalool – from 115.9 μg/l to 66.6 μg/l – and for α-terpineol, from 67.2 μg/l to 51.6 μg/l. Myrcene was the exception, with a drop from 110.6 μg/l to 64.3 μg/l.

The test results prove that the concentration of hop oils is slightly reduced by filtration with BECOPAD 350 depth filter sheets after the first liter. This reduction can be attributed to the adsorption capacity of the depth filter sheet. Because this depth filter sheet is exclusively composed of high-purity cellulose and has only a weak adsorptive effect, the adsorption saturation, and therefore the stabilization phase, starts very rapidly, and no other valuable aromas, such as linalool, the most effective aroma, are withheld.

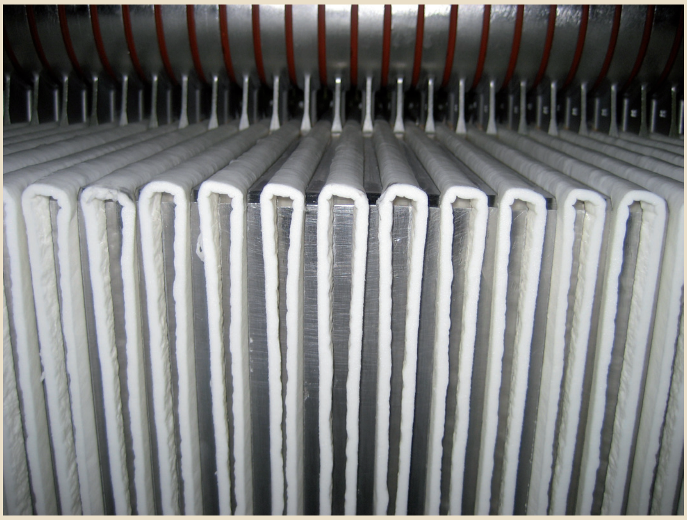

Fig. 4 Becopad depth filter sheets in practice *All images © Eaton*

The filter sheet containing diatomaceous earth reduces the concentration of hop oils to far beyond the 1-liter filtrate sample and up to the 15-liter sample. These results can be attributed to the higher adsorption capacity of the mineral components added to the filter sheets. The stronger adsorptive capacity means that the stabilization phase starts much later and results in greater aroma losses. The test results also show that the losses are primarily influenced by molecular properties (molecule size, polarity). Because myrcene is a pure hydrocarbon, its hydrophobic character is a possible explanation. The differences regarding the absolute values are not significant in the oxygen-containing ester (ethylhexanoate) and the terpene alcohols (linalool, α-terpineol). The extent to which the addition of the aroma mixture partially results in reactions with the beer ingredients and thus, potentially, in analytical markers, has not been looked at by this investigation.

Summary

A saying along the lines of "the aromas in hops make a tasty drop" would be appropriate in this case. The fact is that the precious hop oils lend the beer its characteristic aroma and bitterness, meaning that they should remain present in the greatest possible concentration after the filtration process. This can be achieved, for instance, by the Becopad depth filter sheets, because they are characterized by a significantly lower adsorption capacity, only absorbing a small concentration of the aroma compounds at the start of the filtration process and enabling stable filtration after only a short period.

This not only means that a high concentration of aroma is retained, but also the risk that a value decreases during an excessively long adsorption phase to such an extent that it drops below the odor threshold is reduced. If this happens, the beer's aroma is lost. This is because, as mentioned at the start of this article, the aromas cannot be replaced chemically or added artificially. Therefore, the most important thing is a filter sheet that retains the concentration of the hop oils as effectively as possible. ■

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