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Suppression of Gushing by Hop Constituents

Gushing is one of the most unsolved problems in brewing. This is a very severe quality defect. Efforts are being made to reveal the identity of gushing components. The beer defect of gushing is a temporary brewery problem that is primarily caused by fungi derived factors. In this work the influence of humulones, pure linalool and hop oils on natural occurring gushing and an activated carbon (AC) induced gushing of commercial brews was tested. The experiments proved that linalool significantly reduces the gushing volume. Hop oils (linalool) decreased the gushing tendency of beer. Gushing, induced by activated carbon, is suppressed by the addition of linalool and humulones. These results suggest that some of the properties of the hop constituents, humulones and linalool, prevent beer from gushing especially when hops are added at late stages of wort boiling.

Descriptors: Gushing, beer, hops, linalool, humulones, hop oils, *Humulus lupulus* L.

1 Introduction

Spontaneous and sometimes violent overfoaming of beer is known as gushing. In 1909, *Kastner* was the first to describe this phenomenon occurring in malt beer [1]. It is believed that his observation was due to biological reasons. Even though beer is very sensitive to gushing it is not the only beverage prone to it. Sparkling wines, champagne and lemonades can also show gushing [2, 3]. Red berry lemonades show a higher overfoaming tendency since many protein-polyphenol-complexes are present and these can act as condensation nuclei [3]. A number of factors is needed to generate gushing. *THORNE* published that excessive carbonisation is not the reason for spontaneous overfoaming [4]. However, the CO₂ content is a promoting force for gushing [5].

When a bottle is opened, pressure is released; for decarbonisation the presence of a nuclei is essential [2, 4–7]. According to *Thorne* [4] such nuclei can be formed by surface active compounds, such compounds can accumulate at bubble/liquid interface in the liquid because of their amphiphilic character. This theory is supported by *Christian et al.* who observed a gushing relevant particle formation with a size of several 100 nm when tensides are added [8]. They assumed also that a accumulation of tensides at the bubble/liquid interface cause gushing [9, 10]. When bubbles disappear (e.g. by pressure increase) surface active compounds can form micelles by hydrophobic interactions which can lead to stable nuclei [4]. This mechanism of nuclei formation by the disap-

pearance of bubbles was described by *Krause* [11]. A contraction of bubbles will compress the compounds which are accumulated at the bubble/liquid interface. If the gas is completely dissolved in the liquid it can leave a small compact particle of surfactants [11]. Beside the property to micellate tensides are also known to lower the surface tension. According to *Garbe* [12] a reduced surface tension gives more micro bubbles which are very unstable. Therefore this leads to a higher gushing tendency [12]. A detailed overview on the physics of bubble formation and stabilisation is given in literature [2, 5, 12, 13].

Gjertsen et al. divided gushing into two classes, primary and secondary gushing. This classification is based on the factors that cause overfoaming [14]. Primary gushing is caused by raw materials and occurs mostly in epidemic fashion [14, 15]. Secondary gushing is generated through mishandling of beer. This causes particles (i.e. kieselgur, tensides and others) to stay in solution and these act as active nucleation sites [5, 16]. In 1938 *Helm* and *Richardt* described that the primary source for overfoaming are different barley varieties and harvest years [15] which was confirmed by *Munekata et al.* [17] and *Gjertsen et al.* [14]. In the 1960s *Gjertsen et al.* found that weathered barley is the primary cause and they assumed that microorganisms, which grow in barley during storage, were the cause for primary gushing. Later it was discovered by *Sarlin et al.* [18] that barley infected with *Fusarium spp.* show higher gushing tendency [18]. Similar observations were made for fungi derived metabolites [19]. So-called hydrophobins are of special importance. Hydrophobins are small (ca. 100 amino acids) proteins produced by filamentous fungi. *Sarlin et al.* could show that small amounts of hydrophobins are sufficient to induce gushing [19]. As a result of their amphiphilic character they accumulate on hydrophobic/hydrophilic interfaces and micellization takes place [5]. These micelles can act as active nucleation sites for bubble formation. *Sarlin et al.* could confirm that hydrophobins are able to induce gushing [19]. Additionally, *Hippelli et al.* concluded that infected barley contains heat stable proteinases which degrade the LTP1. The reaction of the LTP1 degradation products with sugars increases their amphiphilic character and thus they can act as condensation nuclei [20].

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Figures see Appendix

Already in the first reference of “wild beer”, Kastner pointed out that an appropriate hop dosage would have suppressing effects [1]. Helm and Richardt [15] as well as Brenner [21] observed that lager beers are more prone to gushing than pilsner style beers. The observations of Curtis *et al.* further support this statement. They noticed that beer with lower hop concentrations showed a higher gushing tendency [6, 22]. All these observations suggest an inhibitory gushing effect of hops.

Unsaturated fatty acids were also claimed to have inhibitory properties [23]. Gardner *et al.* determined that a hop oil concentration of 1 ppm in beer is a very good gushing inhibitor [24]. Among oil constituents, the terpene fraction proved to be more suppressive than the oxygenated fraction. β -caryophyllene, a hop essential oil constituent, was described by Gardner as a good inhibitor [24]. Curtis *et al.* found that malt derived gushing factors are removed when hops are added to the wort [22]. In literature it is suggested that humulones possess inhibitory properties [17, 25–28]. However, it is not specified if this effect is due to the humulones or to the iso- α -acids isomerized during wort boiling from the α -acids. Hulupones and iso- α -acids are also known to inhibit gushing [17, 26, 28].

Although it has been proven that many hop constituents have suppressing effects, many authors consider that some hop compounds, like the polyphenols, promote gushing [17, 29, 30]. Hildebrand *et al.* ascribed saturated hop lipids to have weak inducing properties [23]. However, Carrington *et al.* did not find such effects for saturated lipids [26]. When humulones are externally isomerized into isohumulones, a powerful gushing promoter can be formed [26]. This explains the gushing properties caused by isomerized hop extract (isoextract) [7]. Humulinic acid can be formed during isoextract production and under strong alkaline conditions dehydrated humulinic acid (DHA) can be formed. The latter is known to be a very strong gushing promoter [24, 28–31]. In addition to dehydrated humulinic acid, several α - and iso- α -acid derived oxidation products can be responsible for gushing [24, 29]. Beers bittered with reduced hop extracts also show a higher gushing potential [26, 29]. Outtrup assumed that the β -tricarbonsystem of the bitter compounds is important for protein interaction. He asserted that a missing hydrophilic hydroxy group at the C-5 atom is the difference between promoting and non-promoting compounds [31].

Based on the information found, it can be asserted that high, yet not excessive, hop doses produce beers with a lower gushing sensitivity [1, 14, 17, 22, 29]. Gjertsen *et al.* could inhibit gushing by a content of 24 mg/l isohumulones [14]. The objective of this study was to confirm the influence of hop constituents on the overfoaming properties of beer.

2 Experimental

A commercial German lager beer (original gravity 12.2 %mas, 21 IBU), showing spontaneous overfoaming, was used to investigate the influence of different hop constituents on gushing. Because of limited amount of sample material only a small range of concentrations could be investigated. All additives were dis-

solved in ethanol and 1 ml of the solution was dosed to a 500 ml bottle at 0 °C. After dosing, the samples were immediately re-capped, mixed (3 times by inversion) and stored for 15 hours at room temperature. Bottles were opened without prior shaking. After opening the overfoaming volume was measured with a graduated cylinder.

Pure linalool was purchased from Sigma-Aldrich (Germany). Hop extract “G” and hop oil samples were commercial products provided by Hopsteiner (Germany). Hop extract G contains iso- α -acids (30 %) and a gushing reducing additive. No data about the nature of the additive were available. The main constituent of the used hop oil samples is linalool (25 %). Other compounds are present in smaller amounts. The myrcene content is below 5 % and the β -caryophyllene, humulene and farnesene content are below 1 %. The tested α -acids (alphahop) were samples from Haas Hop Products (USA). This product contains also trace amounts of iso- α -acids and β -acids.

In the second phase of this study, attempts were made to decrease induced gushing. To induce gushing, activated carbon (AC) was added to a commercial German lager beer (original gravity 11.6 %mas, 21 IBU) that showed no gushing. AC was dosed as powder. The tested compounds were added in solution as described for the natural gushing trials.

All trials were done with 5 bottles. Confidence intervals ($n = 5$, $\alpha = 0.05$) were calculated and are shown in the figures.

3 Results

3.1 Trials with gushing beer

The reference beer was a German lager with an overfoaming volume of 132 ml. Preliminary tests were done to evaluate the effect of the added solvent would have when opening the bottles (all compounds were added in 1 ml of ethanol). The difference was 2.5 ml and therefore negligible. This beer was the basis for the spiking tests.

The hop extract G is a commercial product which is distributed as gushing inhibitor. In our experiments we tested the influence of this special hop extract on the gushing behaviour of the lager beer. The dosage was done according to manufacturer’s instructions for weak and strong gushing. In figure 1 it can be seen that a concentration of 5 mg/l is sufficient to significantly reduce gushing. A higher addition shows no further reduction. This bitter acid and hop oil based extract is able to reduce the overfoaming. Because of an unknown additive in the hop product the reason for reduction cannot be identified clearly.

3.2 Effect of hop oils

Gardner [24] described hop oils as effective gushing inhibitors. The mentioned concentration (1 ppm) is not applicable because consumers would decline a beer with such a high oil concentration. In this paper the influence of lower oil concentrations was evaluated.

It could be shown that pure linalool, at all added concentrations, reduced the overfoaming volume more than the hop oil sample. Figure 2 compares the reduction potential of pure linalool and hop oil, and as it can be seen, the difference between these is not significant. A 50 µg/l dose of linalool or hop oil is enough to reduce gushing significantly. A higher oil concentration marginally reduces the overfoaming volume. Because of the difference in the added amounts of linalool (hop oil max 25 % linalool) and the similar reduction potential other oil constituents must have reducing effects too. These results agree with those published by Gardner et al. [24] but it was shown that 0.1 ppm is sufficient to reduce gushing.

3.3 Effect of humulones

Humulones are known to have good inhibitory properties [17, 26–28]. Figure 3 shows the gushing reduction with humulone additions of up to 5 mg/l. Although overfoaming was reduced, this is not as significant as the hop oil reduction. These results coincide with Carrington et al. [26] who observed that artificial gushing is decreased by adding humulones. In contrast to our findings *Laws et al.* [29] found complete gushing inhibition with humulone concentrations of 5 mg/l. This proves once more that gushing is a very complex phenomenon and that reduction possibilities are to some extent beer dependent.

3.4 Trials with induced gushing

To investigate the influence of hop constituents on induced gushing, activated carbon was added to a non-gushing beer. At higher AC concentrations linalool showed a significant reduction of the overfoaming volume (see Fig. 4). Doubling the dose concentration did not result in a further decrease of the gushing volume.

As a result of the low reduction potential of humulones in the ‘existing gushing’ tests only a 10 mg/l dose was tested. This concentration showed an effective inhibition of gushing. None of the tested bottles showed overfoaming.

4 Discussion

It was shown that the tested hop constituents have gushing reducing properties. *Krause* [11] assumed that surfactants accumulate on bubble/liquid interface and can form stable nuclei when gas dissolves in the liquid. Because of the hydrophobic character of hop oil constituents it is possible that they accumulate on hydrophobic/hydrophilic interfaces. This would lead to gaps between the molecules of gushing promoting surfactants and they cannot form stable nuclei. It can be assumed that such a competition for the surface results in lower amounts of stable nuclei and therefore the gushing tendency is reduced. This goes along with the results of Gardner [28] who described the influence of DHA and other hop constituents as a competition of these surfactants for the surface as well. Humulones can act in a way similar to hop oils.

Unisomerized humulones were effective against induced gushing but showed minor effects on existing gushing. By comparing the results of figure 3 and the effect of humulones in the AC trials

it is likely that the mechanism for the different gushing types (endogenous vs. induced gushing esp. primary vs. secondary gushing) has a different physiochemical basis. The induced gushing is completely inhibited by humulones therefore it seems that humulones can cause a reduction of foaming of the treated beer. *Klopper* reported an unfavourable effect of humulones on the foam time of a peptone solution [32]. This could be one explanation for the inhibitory effect of humulones. Otherwise they are known to be positive for the head retention and therefore they are known as foam stabilizers [33, 34]. Beer foam is formed by interactions between hop bitter acids and proteins [35]. If added to an unhopped beer the foaming was enhanced by this humulone product (data not shown). So the gushing reducing effect was not due to anti foaming properties of the product. The influence on foaming by the other products was not tested.

Fischer [13] found that residual gas which is enclosed in cavities of particles can act as active nuclei when the pressure is released after opening the bottle. Humulones can accumulate at the hydrophobic interface and so they would inactivate this potential active nuclei.

5 Conclusion

The occurrence of gushing is a problem for breweries since consumers classify this as a product defect. There is substantial research running to inhibit or reduce the gushing tendency of beer by technological means. A trivial way is using healthy non-infected malt and avoid particle uptake during the production process. In addition to malt, hops are also a raw material which can influence the gushing potential of beer. The current study tested the influence of different hop constituents on gushing. It was shown that addition of linalool and hop oil significantly reduce the overfoaming volume. Humulones also lower the gushing in beer.

Furthermore the influence of linalool and humulones on activated carbon derived gushing was tested. This secondary gushing was effectively inhibited by humulones and significantly reduced by linalool. These results confirm the possibility to influence the gushing tendency of beer through selected hopping technologies. Higher hop additions at the end of wort boiling are appropriate to maximize the linalool transfer into the wort [36] and the gushing tendency can be reduced by means that comply with the German purity law.

These results agree with observations from the brewing industry who state that beers with higher hop additions (pilsner style) are not that affected by gushing in the severity seen in beers with lower hop concentrations. Adaption of the hop dosing technology to achieve a hoppy flavour is an elegant tool to reduce the gushing tendency of beer.

6 References

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Appendix

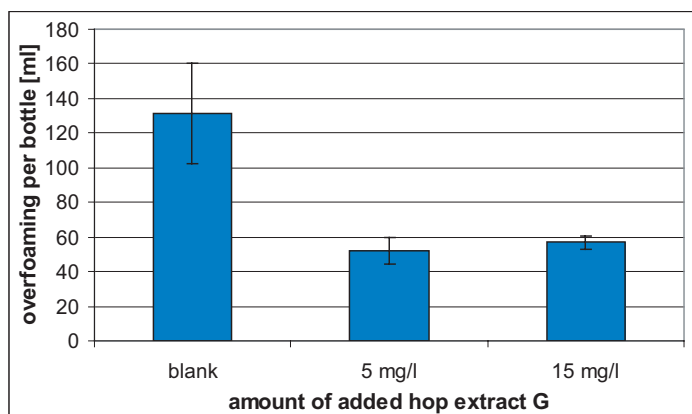


Fig. 1 Reduction of overfoaming volume by addition of hop extract G

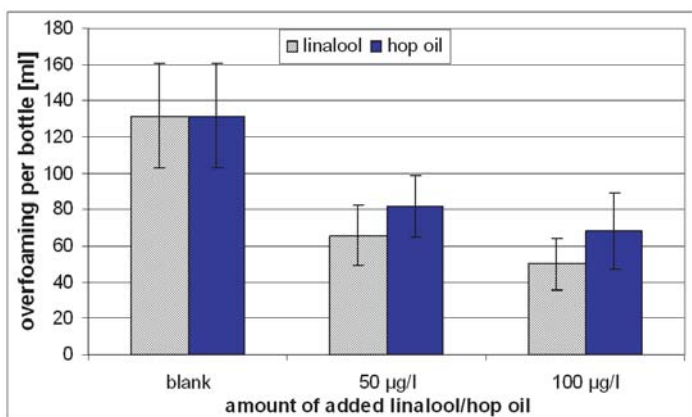


Fig. 2 Reduction of overfoaming volume by addition of pure linalool and hop oil

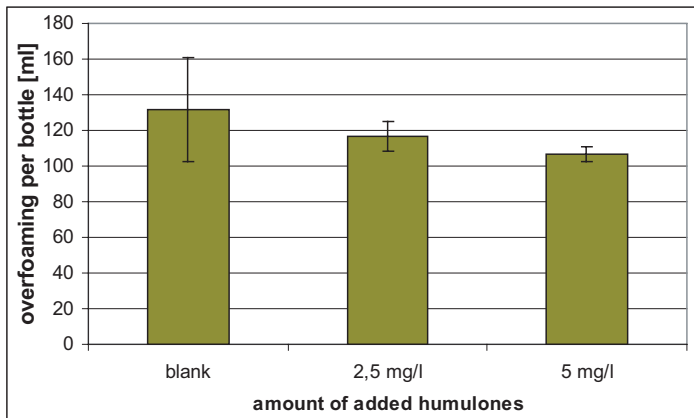


Fig. 3 Reduction of overfoaming volume by addition of humulones

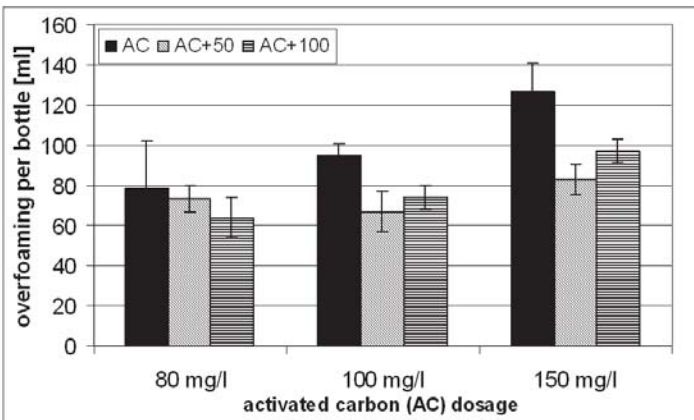


Fig. 4 Reduction of induced gushing by addition of linalool (AC = activated carbon; AC + 50/100 = dosage of 50/100 µg/l linalool)