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The Influence of Hop Acid Components on the Phenomenon of Gushing in Various Standard and Non-Alcoholic Beers – Evaluation of Advanced Hop Products under Induced Gushing Conditions

Clearly the occurrence and control of gushing is a critically important quality factor for many brewers. A large number of studies, publications, and presentations have addressed this topic in the past. Efforts to identify gushing promoters have focused on species generated from barley degradation and infestation, and, to a lesser extent hop constituents, among others.

The use by brewers of pre-isomerized hop acid products, including isohumulones and reduced forms such as *di-*, *tetra-*, and *hexa-hydroisohumulones*, continues to increase. To date, a comprehensive study to evaluate the potential for these advanced hop products to either promote or suppress the gushing phenomenon has not been reported. We have undertaken a study to assess the potential impact on gushing for a variety of hop acid products. Research was conducted using forced testing conditions, which included direct dosing into beer with vigorous long-duration shaking. The influence of hop acid identity, hop processing conditions, and dosing levels were investigated. Other factors such as base beer type, alcohol level, and country of origin were also evaluated. It was determined that low- and non-alcoholic beers are particularly susceptible to induced gushing from hop acid components. Results from this work indicate that the formation of potential gushing initiators in advanced hop acid products can be effectively prevented.

Descriptors: hops, humulones, gushing, beer, isohumulones, oxidation

1 Introduction

Spontaneous overfoaming upon opening a carbonated beverage, often referred to as gushing, is a problem that continues to challenge beer and beverage manufacturers. [1] Gushing in beer has been traced to raw materials, particularly malt, which has been classified as 'primary' gushing. [2] Other potential sources of the gushing phenomenon, such as metal ion contamination, inadvertent kieselgur particulates, or calcium oxalate, are often regarded as 'secondary' promoters. [2]

The mechanism of gushing in carbonated solutions is generally accepted as involving surface-active substances that stabilize CO_2-bubbles through an agglomeration at the liquid-gas interface. [3–9] Micelle formation with amphiphilic surfactant-type molecules may also contribute to the stabilization and concentrating of CO_2 bubbles within the bulk media. A leading source of these surface-active condensation nuclei has been attributed to infestation of barley with *Fusarium spp.*. [10–12] Annual growing conditions in which *Fusarium* infection is widespread has been correlated with an increased occurrence of gushing in beer produced from these malted barleys.

Although the majority of research points towards barley as the major contributor to primary gushing, hops and hop constituents have been shown to both promote and suppress beer gushing. [13–18] In general, hop oils and fatty acids are regarded as agents that help to decrease or eliminate gushing in beer that is susceptible to this phenomenon, whereas hop acid degradation products have been implicated as gushing initiators. [19–21] For example, addition of hop oils or linalool to beer reduces the amount of gushing under controlled conditions. [14, 20] A reduction in gushing has also been observed when non-isomerized alpha acids were added to beer that was predisposed to gushing. [14, 15] By contrast, isohumulone degradation products such as dehydrated humulinic acid and oxidized hop resin species have been suggested as promoting the occurrence and extent of gushing in beer. [16] Given the potential for hop constituents to either accentuate or depress gushing, it is important to understand the critical factors and parameters necessary for eliminating any negative impact on beer quality.

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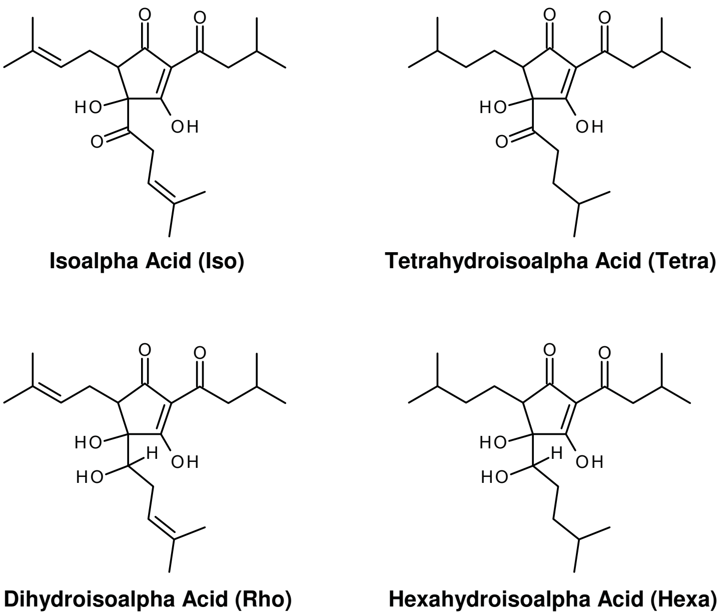

Fig. 1 Chemical structures of n-Isoalpha acid and the corresponding reduced forms

The use of advanced hop products in brewing continues to increase. [22] These include pre-isomerized extracts and pellets as well as solutions of isohumulones and the dihydro(rho)-, tetrahydro-, and hexahydro-isohumulones reduced forms, which are often added post-fermentation (Fig. 1). Many of these advanced products provide unique properties, for instance light-stability and foam enhancement, that are difficult to achieve by other means. Greater hop acid utilization and the corresponding potential for cost savings are also driving the increased use of these hop forms. While the use of these isomerized products was estimated at 5 % of the hops used in brewing in 1994, the estimated usage increased to 18 % of the worldwide hops market by 2009. This trend is predicted to continue. Given the increased reliance on pre-isomerized advanced hops, it is imperative to recognize all of the impacts these products may have on beer quality. Until now, their potential role in beer gushing has been largely ignored. [21, 23]

In this study various hop acid products were evaluated for their impact on the gushing phenomenon in beer under controlled induced conditions. The products examined were generated via different processes in order to assess the impact of processing conditions on the formation of gushing promoters. Different beer types, including non-alcoholic varieties, were examined to help establish the general range of gushing that can result and the impact of beer base and other beer components on gushing. The use of hop oil component linalool to suppress hop acid induced gushing was also examined. It has been discovered that correct selection of the downstream hop processing method and/or careful control of processing conditions can eliminate the formation of gushing promoters in advanced hop products.

2 Materials and Methods

Materials

All of the hop acids evaluated were standardized aqueous solutions of the corresponding potassium salts, as supplied by several advanced hop product manufacturers. The solutions examined included:

- *Isoalpha Acids* – Iso, 30 % (m/m) – Kalsec® Isolone® product codes 46-22 and 46-122 as well as similar commercial products supplied by two additional manufacturers
- Tetrahydroisoalpha Acids – Tetra, 9–10 % (m/m) – Kalsec® Tetralone® product code 46-12 and similar commercial products from three additional manufacturers
- Dihydroisoalpha Acids – Rho, 30 % (m/m) – Kalsec® Reduced Isolone® product code 46-09 as well as similar commercial products supplied by two additional manufacturers
- Hexahydroisoalpha Acids – Hexa, 20 % (m/m) – Kalsec® Hexalone® product code 46-05 as well as a similar commercial product from another manufacturer.

A high sales volume American-style "light" lager beer, purchased locally, was used to investigate the impact of added hop acids on gushing. In over 50 individual trials, this beer never demonstrated gushing in the experimental negative control samples (zero added hop acids). In order to assess the universality of gushing produced by added hop acids as well as the impact of beer base, seven additional standard alcohol beers were also used in gushing trials. These included a Pale Ale (United Kingdom), three Pilsners (Germany), and Amber, Brown, and Pale Ales from US micro/craft brewers. The impact of hop acids on gushing in non-alcoholic beers (0.5 and 0.0 % alcohol by volume) was assessed with nine different beers from the United States (3), Germany (3), Netherlands (1), United Kingdom (1), and Canada (1). All alternate beers were as available in the United States. Pure (±)-Linalool (> 95 %, GC) was purchased from Sigma-Aldrich (USA, Fluka brand) and used as received.

2.1 Evaluation of Gushing Potential

Equipment

A New Brunswick Scientific (Model 76) shaker bath with a maximum output of 400 revolutions per minute (rpm) was converted into a platform shaker capable of accepting a 24-bottle crate in the vertical position, with bottles thus horizontal relative to the ground. A foam-padded cover was secured in place to prevent any bottle motion independent of the shaker platform.

Induced Gushing Method

The protocol employed was a modification of the 'box shaker' method first introduced by Laws and McGuinness. [23] Using volumetric glassware, a 0.10 % (m/v) solution of the hop acid (HA) of interest was generated by dilution with demineralized water that had been previously adjusted to a pH of 10.5 with aqueous KOH. The resulting hop acid solution (3.5 mL) was then added directly to bottled beer (355 mL or 0.3 L, depending on beer type and brand) that had been chilled to 0 °C prior to dosing in order to minimize CO_2 loss. The addition of HA therefore equals approximately 10 ppm in each beer sample. A negative control, with dosing of 3.5 mL of the pH 10.5 dilution water, was performed for every trial in duplicate. Each dosed beer was subjected to foam-in-bottle air expulsion, via sharp contact of the bottle lip with a solid object, and quickly recapped. Care was taken to ensure that no beer or dosed hop acid solution was lost during this procedure. Bottles were subsequently placed in random positions of a 24-bottle crate, loaded into the modified platform shaker, and agitation at approximately 280 rpm (70 % of shaker maximum) was initiated and maintained for a period of 18 hours. Bottles were then removed, weighed, and allowed to stand undisturbed for a period of 30 minutes. Each bottle was then opened rapidly and assessed for gushing. If gushing occurred, as defined as any beer loss over the top of the bottle, the mass of beer lost was determined by reweighing the bottle with cap followed by a mass difference calculation. Every hop acid solution was evaluated in a minimum of 5 replicate analyses (individual bottle dosing) and the results were averaged. For some hop acids, significantly more replicate analyses were performed (up to 30) in order to better assess the absolute standard deviation of the measurements. While methods exist to test barley for the presence gushing initiators, a standard method of assessing other gushing potential has not been approved. This is likely due to the well-recognized intrinsic variability of different assessment techniques. Different samples of a standard American-style "light" lager beer were utilized in order to evaluate any impact of batch-to-batch beer variability. A consistent result for both replicate tests of hop acid addition as well as blank trials across different beer batches indicates that any potential beer variability does not impact our test. For example, gushing was never observed in the negative control samples (0 g added hop acid) despite using over 40 different cases of this purchased beer.

3 Results and Discussion

Hop Acid Induced Gushing

In initial studies, different advanced hop products from a single manufacturer were evaluated for the presence of gushing promoting or initiating species using a forced 'shaker box' methodology. This test protocol was chosen to differentiate gushing potential since it is a common technique employed by both advanced hop acid producers as well as major breweries to screen these incoming raw materials prior to use. Commercially available isoalpha acids (Iso), tetrahydroisoalpha acids (Tetra), dihydro-ρ-isoalpha acids (Rho), and hexahydroisoalpha acids (Hexa) solutions (Fig. 1) were examined. The results of this testing, with 10 ppm added hop acid to an American-style "light" lager beer, are depicted in figure 2. As can be observed, all four advanced hop products from this particular manufacturing process produced beer gushing under these forced conditions. The amount of beer loss ranged from a low of 33 g (9.3 % of total volume) for the Iso product up to 61 g (17 % of total volume) for the Tetra product. The Hexa and Rho products had similar forced gushing response, initiating beer loss of approximately 46–47 g each. Negative control samples, with zero added hop acids, did not display any gushing. This clearly indicates that the species responsible for initiating gushing following an 18 h agitation are present in these advanced hop acid samples and introduced during direct dosing. The fact that all products from the same manufacturer afford similar gushing amounts suggests a common process intermediate and source of molecular gushing initiators in their commercial practices.

The extent and range of gushing possible from direct dosing of advanced hop acid solutions into beer was investigated using different hop products from several different manufacturers (Fig. 3). It was found that high-purity solutions of isoalpha acids (Iso) are particularly susceptible to the formation of active gushing initiators, especially when these alkaline solutions of isoalpha acids are stored in the presence of air for prolonged periods of time. For example, an aged "degraded" Iso solution was found to cause a loss of 170 g of beer (48 % of the total volume) under the induced gushing conditions. In order to determine if species responsible for gushing in isoalpha acid solutions carry forward in subsequent processing, tetrahydroisoalpha acid (Tetra) solutions were produced via standard hydrogenation of isoalpha acids that had been exposed to aerobic conditions (Fig. 3). These solutions were also found to generate relatively large volumes of beer loss through gushing (60–100 g). By contrast, other solutions of the four advanced hop acids evaluated in this study did not generate any gushing using the induced shaking method.

The dramatic differences observed between various hop acid products, and between samples of the same hop acids from different manufacturers, clearly suggests that significant material compositional differences exist. It is therefore reasonable to

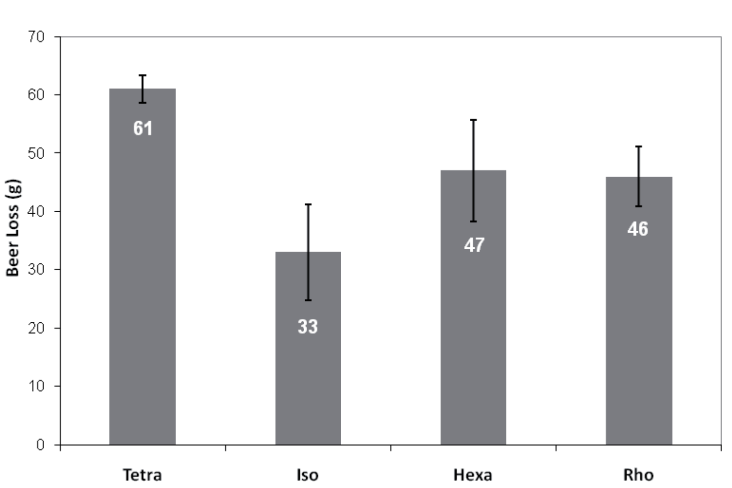

Fig. 2 Hop acid induced gushing in "Light" Lager Beer – common downstream hop product manufacturing process

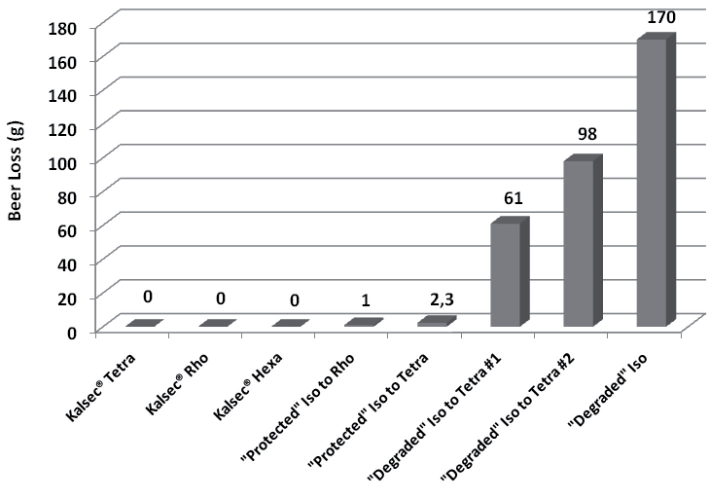

Fig. 3 Range of gushing from various hop acid components in "Light" Lager Beer

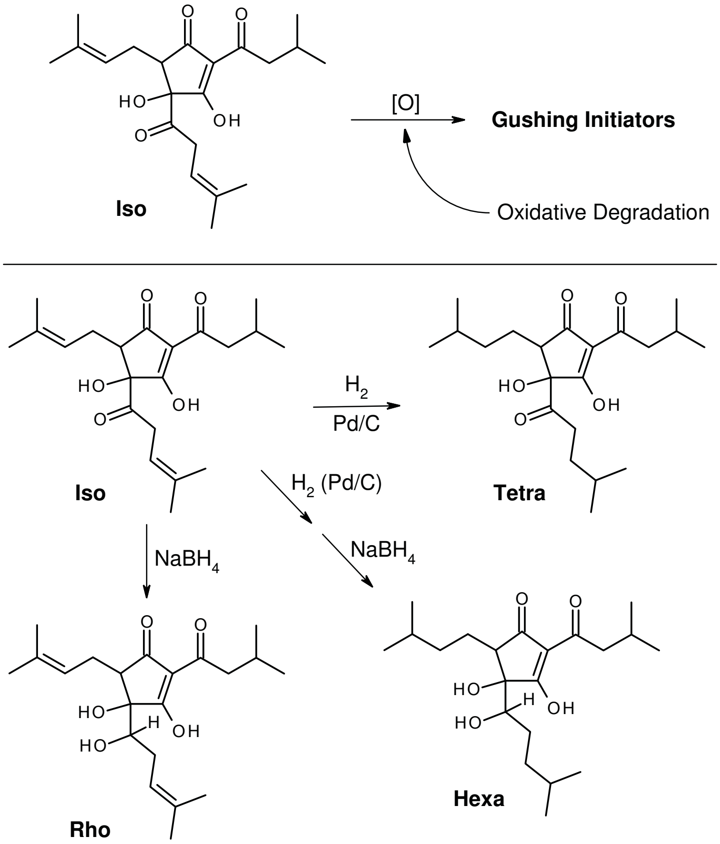

Fig. 4 **Initiators of gushing via oxidative degradation of isoalpha acids and common routes to downstream products**

hypothesize that hop acid solutions that cause gushing under induced conditions must contain chemical species that serve as gushing "initiators". Hop acid solutions that do not promote gushing under these conditions either lack these initiating species or have additional compounds present in solution that either mask or quench the propensity of these compounds to initiate gushing. While the hop degradation byproduct dehydrated humulinic acid has been previously reported as promoting gushing, [16] this species was not detected in any of the hop acid products evaluated in this study. Isoalpha acid oxidation products, particularly those with an abeo-isohumulone structure, [24] have also been implicated in previous studies as contributing to the promotion of gushing. This has been confirmed in our study, where chromatographic analysis coupled with mass spectral characterization has iden-tified several isohumulone oxidation compounds in all of the hop acid products that were found to promote induced gushing. While not definitively identified, the molecular masses and fragmentation pattern are consistent with abeo-isohumulone species. Hop acid solutions that promote gushing were found to contain relatively high amounts of certain of these compounds. Thus, oxidative degradation of isoalpha acids in solution affords powerful gushing initiators that are not destroyed during subsequent hydrogenation or reduction. Any advanced hop acid products such as Tetra, Hexa, or Rho derived from isoalpha acids (Fig. 4) have the potential of causing gushing under induced conditions.

In order to eliminate the formation of gushing initiators in advanced hop products, extreme care must be taken to avoid oxidative degradation of isoalpha acids, which is reported to occur via humulinone intermediates, olefin epoxidation, and ring closure. [24] Alternatively, the process route employed could avoid isoalpha acid intermediates entirely. For example, hydrogenation of alpha acids to tetrahydroisoalpha acids prior to isomerization eliminates the possibility of forming cyclic oxidation products of isohumulones since the ring-contracting isomerization, which brings the side chains into reactive proximity, is not performed until after olefin hydrogenation has occurred. Thus, the formation of gushing initiators is bypassed when tetrahydroalpha acids are intermediates on the route to Tetra or Hexa (Fig. 5). The impact is clearly evidenced in figure 3, where Kalsec® Tetra, Hexa, and Rho samples did not promote gushing and afforded zero grams of beer loss following forced condition testing. It is well documented that the Kalsec® routes to advanced hop products avoid isoalpha acid intermediates. [25–27]

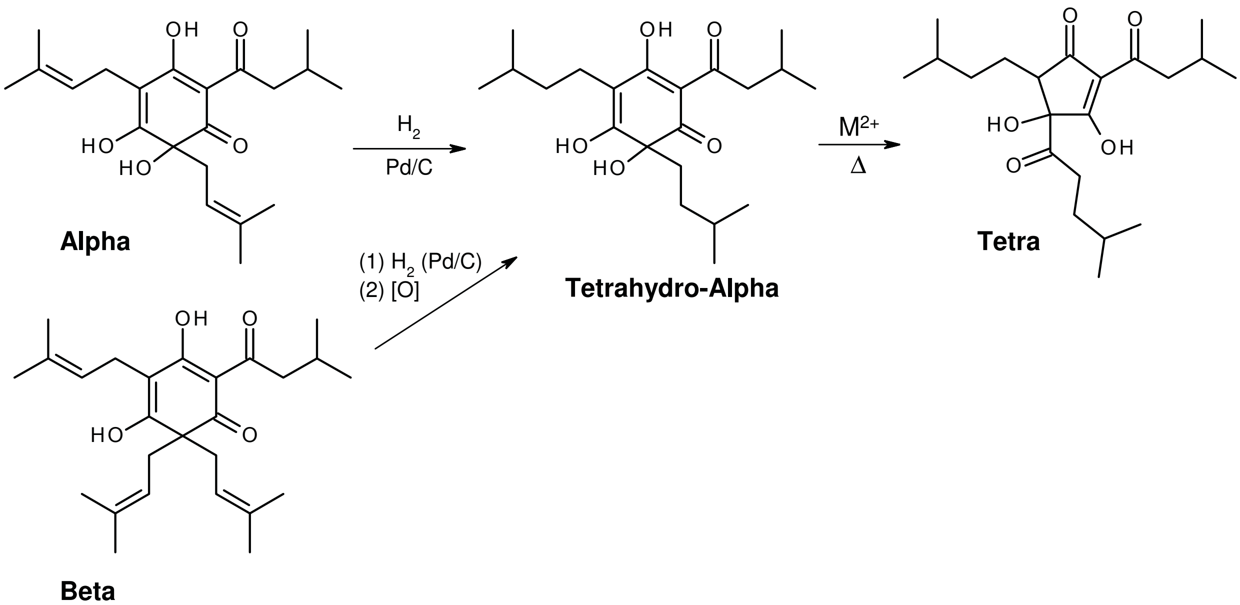

Fig. 5 **Tetrahydroalpha acid (TH-Alpha) route to Tetra and Hexa – avoids oxidative formation of gushing initiator species**

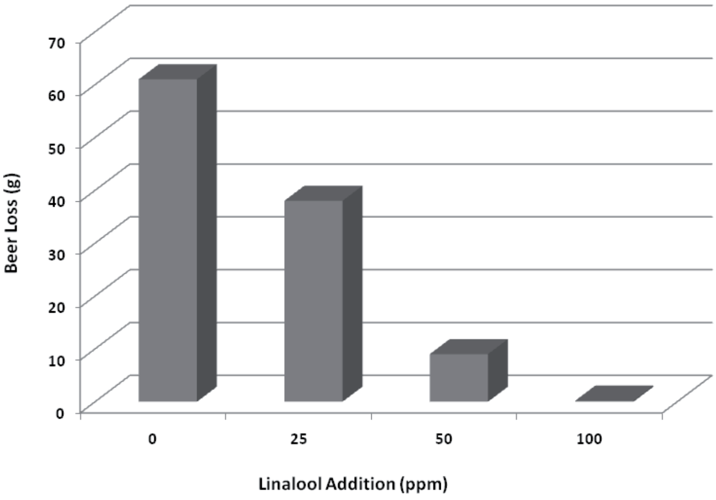

Fig. 6 Impact of linalool on hop acid induced gushing

Impact of a Hop Oil Component on Gushing

Hops have traditionally been viewed by brewers as gushing suppressors, where the practice of adding high hop amounts has been shown to afford beer with a reduced predisposition towards gushing. The use of hops or hop components to control or reduce gushing has also been demonstrated in numerous studies, [14, 15] where hop oils have been shown to suppress both primary gushing as well as secondary gushing induced by activated carbon. Further confirmation of the role specific hop derived compounds play in reducing gushing in beverages has also recently been reported. [13, 14, 19, 20] In order to ascertain the impact of a hop oil component on gushing that is induced by other hop compounds, namely oxidized hop acids under forced conditions, experiments were conducted where varying amounts of linalool were added to the beer prior to shaking. The results are given in figure 6. As can be observed in this data, the addition of the hop oil linalool can dramatically influence the extent of gushing in beer containing gushing promoting tetrahydroisoalpha acid components. Addition of 25 ppm of linalool decreases the amount of beer loss in gushing by approximately 40 %. Adding 100 ppm of linalool essentially pacifies the gushing initiators, where the amount of beer loss was insignificant. However, these relatively high levels of hop oil would render the resulting beer largely undrinkable. As in previous studies, it is proposed that the largely hydrophobic properties of linalool interact at the hydrophobic/hydrophilic interface of gushing initiators and effectively disrupt the formation of CO_2 nucleation sites.

Induced Gushing in Various Standard and Non-Alcoholic Beers

The ability of hop acid components to initiate gushing in different base beers, other than a "light" lager, was also investigated to determine the impact beer style or other beer constituents may have on the gushing phenomenon. [28] Seven different standard alcohol beers from the United States and Europe were dosed with tetrahydroisoalpha acids (Tetra, 10 or 20 ppm), which had been previously shown to initiate gushing in the "light" lager. All beers were analyzed in triplicate, and the averages of these results are depicted in figure 7 along with the result for the "light" lager for comparison.

The first set of samples, from relatively large USA craft brewers, includes an amber ale, a brown ale, and a pale ale. As can be seen, the amount of gushing induced by the added hop acid was highly dependent upon the beer type. The pale ale displayed zero gushing whereas almost 60 g of brown ale was lost to gushing with the same hop acid addition. Gushing induced in the amber ale was approximately half of that observed for the brown ale. Consistent with the result for the USA pale ale, a similar style beer from the United Kingdom also displayed minimal gushing. Pilsner style beers from Germany were also evaluated for Tetra induced gushing, where the amount of beer loss observed ranged from 2 g up to 44 g. As can be seen in figure 7, all of the different beer bases/styles had lower beer loss than the "light" lager initially evaluated. It is proposed that overall higher levels of hop oil and other beer constituents, relative to the lager, work to diminish the extent of induced gushing in these beers.

Given the impact of different beer styles and hop oil components as discussed above, it was decided to evaluate induced gushing in non-alcoholic beers, which is a growing market segment in

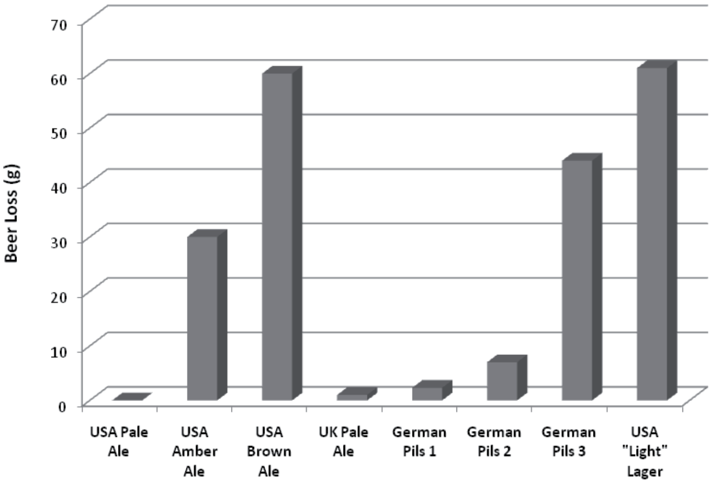

Fig. 7 Induced gushing from tetrahydroisoalpha acids, common manufacturing route with initiators, in different beer styles

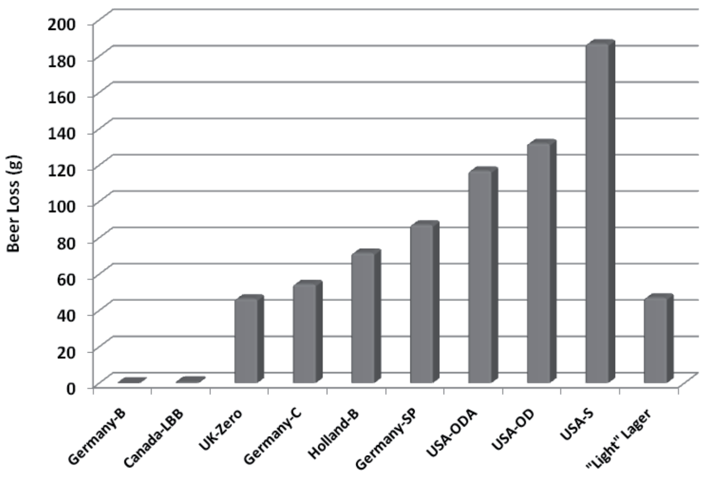

Fig. 8 Induced gushing from hexahydroisoalpha acids, common manufacturing route with initiators, in various non-alcoholic beers

many parts of the world. Results of hexahydroisoalpha acid (Hexa, 10 ppm) induced gushing for eight different non-alcoholic beers (< 0.5 ABV) and one alcohol-free "zero" (0.0 ABV) beer are displayed in figure 8 along with the result for the standard alcohol "light" lager for comparison. The amount of induced gushing in these beers ranged from a low of 0 g for a German non-alcoholic beer up to approximately 190 g (over 50 % of the bottle contents) for a USA product. In general, non-alcoholic beers from the United States were more susceptible to Hexa-induced gushing than related beers from Europe (Fig. 8). It is worth noting that 7 of the 9 non-alcoholic beers had gushing equal or greater than that of the standard alcohol "light" lager. In separate studies with alcohol-free beers, it was observed for the first time that hexahydroiso-alpha acids at levels between 10 and 20 ppm, from any manufacturing process, could induce significant gushing even in the absence of shaking. In these solutions, molecules of hexahydro-isoalpha acids are thus gushing initiators that stabilize regions of CO_2 saturation and leads to significant gushing. Hexahydroiso-alpha acids are known to be strong foam stabilizers, a property that may be related to the propensity towards gushing in alcohol-free beers. This finding, coupled with the results given in figure 8, clearly suggests that non-alcoholic beers are far more susceptible to hop acid induced gushing than standard beers. Further studies are being undertaken to better determine the root cause of elevated hop-acid promoted gushing in alcohol-free beers.

4 Conclusion

Beer gushing is an important quality parameter for breweries. While hops have traditionally been viewed as an essential ingredient capable of mitigating the occurrence of gushing, this research clearly demonstrates that advanced hop acids such as pre-isomerized isoalpha acid solutions as well as the reduced dihydroisoalpha acids (Rho), tetrahydroisoalpha acids, and hexahydroisoalpha acids can promote beer gushing under forced conditions. The propensity of these hop acid products to promote gushing is directly connected to the process by which the modified hops were generated as well as the care with which the isoalpha acids were handled. In general, oxidation of isoalpha acids prior to carbonyl or olefin reduction leads to undesirable byproducts capable of initiating localized CO_2 concentration and gradient release in the form of gushing. This phenomenon can be eliminated by rigorously protecting the isoalpha acids from oxygen prior to reduction or by a process route wherein the active olefinic groups are reduced prior to isomerization, for tetrahydroisoalpha acids and hexahydroisoalpha acids, or where the carbonyl is effectively reduced concurrent with its formation, for dihydroisoalpha acids (Rho).

This research has also shown that the hop oil component linalool is capable of disrupting the gushing phenomenon induced by advanced hop products under forced conditions. This is consistent with other work that has shown linalool to be an effective agent against other secondary gushing.

Hop acid induced gushing is highly dependent on the type of beer and other constituents present in the solution. For example, the exact same dosing of tetrahydroisoalpha acids that resulted in approximately 60 g of beer loss in a standard American lager generated over 180 g of beer loss in a non-alcoholic beer and zero gushing in an American pale ale. Overall, more complex beers such as pilsners and pale ales appear to have compounds present that help mitigate the gushing potential of beer while "light" and non-alcoholic beers are far more susceptible to hop acid induced gushing.

While the direct hop acid injection and forced initiation utilized in this research does not directly compare to conditions in a brewery, where beer is often dosed upstream of filtration and subsequent other processing, the results clearly indicate that species can be present in advanced hop products that promote beer gushing. A brewer that is utilizing these hops products and is concerned about any components that may promote gushing could institute a testing regimen to screen for the presence of these oxidized hops acid species.

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