Method for the treatment of the phenomenon gushing in beer and malt beverages

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Introduction

A high percentage of breweries worldwide had and still have problems with gushing. The phenomenon occurs in all brands and types of beer. Since gushing not only leads to a loss in reputation for the breweries but also indirectly affects all malthouses, brewing industry and malting industry alike are very interested in processes and methods to analyse and prevent gushing (Christian et al. 2011).

After more than 90 years of gushing research, many causes for this uncontrolled reaction in beer have meanwhile been identified. Particularly in focus are a high oxalate concentration as well as fungal proteins (surface-active hydrophobins and proteases), which migrate into the malt via mouldy cereals. The occurence of hydrophobins caused by, above all, species of *Fusarium* fungi strongly depends on weather conditions. Therefore in some years, the barley and thus malt crop is more affected than in other years (e. g. 2000, 2006, 2007 as well as 2010, 2011 and 2012). Despite new findings on the origin of gushing, so far, industries have not succeeded in controlling hydrophobin occurence.

Description of the problem and frequency of the phenomenon

Gushing is the uncontrolled, sudden escape of foam and beer when opening a beer bottle which is not caused by high temperatures or shaking.

As origin of gushing different factors are subject of the current discussion. On the one hand, especially poorly soluble calcium oxalate crystals at which CO_2 is liberated is considered to be the reason for gushing. On the other hand, gushing is caused by mould-infested and thus qualitatively modified malt, and here, in particular by surface-active proteins, so-called hydrophobins of class II from (*Fusarium*) fungi. Principally, one distinguishes between primary and secondary (technologically caused) gushing (Deckers et al. 2010):

According to the current state of research primary gushing is strongly induced by the fungi *Fusarium graminearum, F. culmorum, F. equiseti, F. sambucinum* (Zepf 1998, Sarlin et al. 2012).

Gushing is hereby triggered by hydrophobins and further fungal metabolites (polar lipides, proteolytic decomposition products of lipotransfer proteins (LPT)). Hydrophobins are small proteins (approx. 100 amino acids) which are mainly secreted by these filamentous fungi (Wösten et al. 1994; Sarlin et al. 2005; Zapf 2006).

Hydrophobins spontaneously adhere to all types of surfaces and migrate to the interface between phases modifying surface energy. This behaviour has an impact even on crystal growth. The adsorption reaction and the resulting changed surface properties of such particles may lead to the fact that the tendency towards aggregation is increased. (see fig.1).

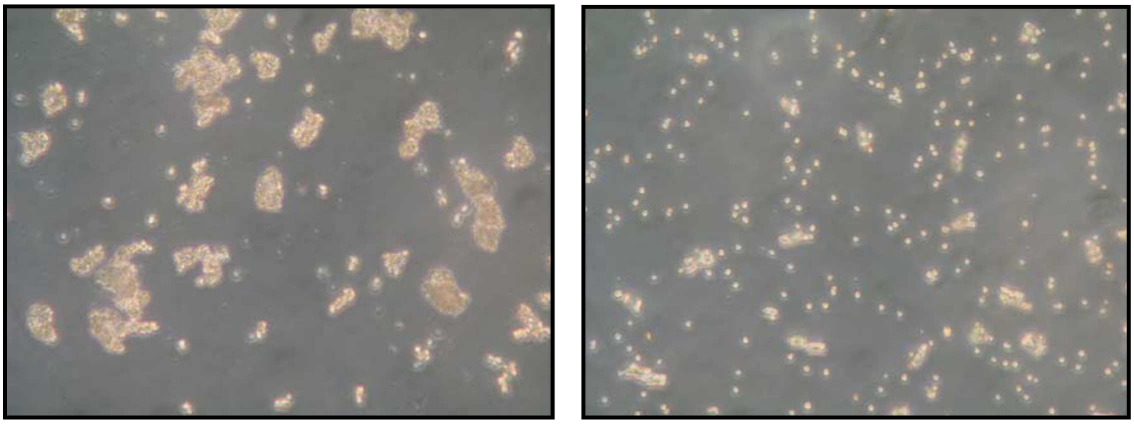

Figure 1: Impact of hydrophobin on crystallization behaviour, on the left: calcium oxalate with hydrophobin, on the right: calcium oxalate without hydrophobin

Oxalic acid present in beer, respectively the calcium salts of oxalic acid, are affected by hydrophobins leading to aggregated, amorphous calcium oxalate structures which constitute ideal bubble seeds. Thus hydrophobins affect in many respects the gushing tendency of the beer.

Secondary gushing is mostly caused by calcium oxalate precipitations and metal ions as for instance Fe^{3+}. The migration of iron ions into beer is due to the application of the filter aid kieselguhr (diatomaceous earth). Sometimes also rinsing agent residues or rough container or bottle surfaces cause gushing.

Oxalic acid is present in malt in high concentrations. In wort oxalic acid content is around 40 mg/L, in beer it still ranges between 10 to 25 mg/L. When this oxalic acid precipitates in the form of calcium oxalates, air bubble formation is very likely due to the high amount of existing crystallization seeds.

So far realized approaches for the prevention of gushing:

1. Hops shows a slightly gushing-suppressing effect. Thus a suitable hops technology in the brewing process could help to reduce the problem (addition of isomerized hops oils).

Restriction: Beer aroma is significantly affected when the hops proportion is increased and it is not allowed by German purity law.

2. Blending of different malt batches to minimize primary gushing.

   Restriction: Malt-houses are faced with the need for larger storage areas and higher storage costs for the blending of different malt batches from different crops with different gushing potential. In case of gushing years in succession there is not enough malt in good quality available which can be used without running the risk of gushing.

3. A CO_2-liberation at calcium oxalate precipitations can be prevented by the addition of soluble calcium salts with the brewing liquor. During the cold storage phase of the green beer poorly soluble calcium oxalate is precipitated before filtration, so that crystals during subsequent filtration are retained in the filter sheet. As preventive measure, so far $CaCl_2$ or $CaSO_4$ have been used. 1 kg $CaCl_2$ solution (34 %): 123 g calcium and 1 kg $CaSO_4$ * 2 H_2O (gypsum): 232 g calcium.

   Restriction: $CaSO_4$ in the presence of Mg^{2+} ions can cause hops-untypical bitter taste and thus alters beer aroma considerably (stronger, sharper, lacking noble hops flavour). $CaCl_2$ in higher concentrations equally causes a salty off-taste and heartburn and, if chloride concentration exceeds 70 mg/L, may corrode stainless steel.

   Both substances are however permitted by German purity lawn.

All in all can be stated: so far no safe and reliable proceeding exists which prevents gushing. The methods in use require an additional process step or significantly affect the aroma profile of the beer product.

Application and mode of action of AnGus1516® for the treatment of gushing

The newly developed AnGus1516® is a greyish-white solid and consists of a mixture of different calcium-enriched silicates. It is added during the mashing process in the same way calcium sulphate or calcium chloride are added which means, the brewer does not need to change his usual habit of proceeding. The product reacts with the oxalic acid and precipitates together with the mainly bound oxalate. Already during lautering a large proportion of the settled oxalate can be removed together with the spent grains. Furthermore hydrophobins (about 17 kD), equally acting as liberation seeds and also detrimental proteases and their decomposition products are reduced (Fröhlich et al. 2012). The hydrophobin binding activity of the product was tested by means of SDS-PAGE. With a dosage of 100 g/hL AnGus1516®, protein concentrations could hereby be reduced by about 30 % (see fig. 2).

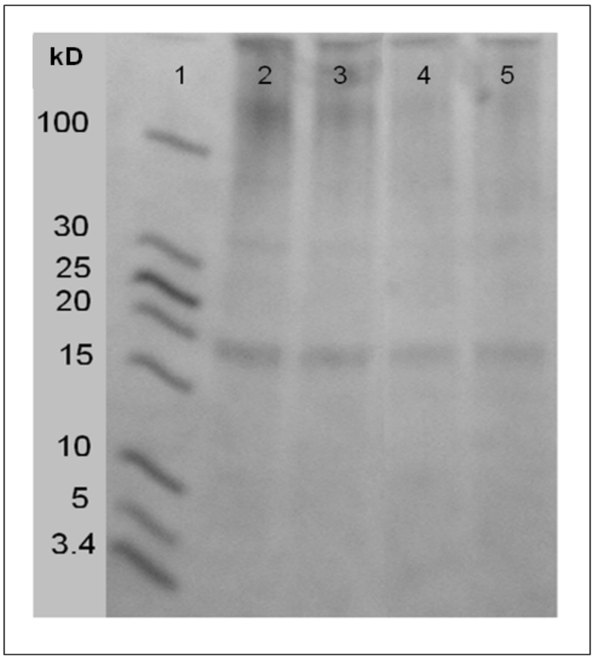

Figure 2: Hydrophobin analysis by SDS-PAGE:1) marker 5 µl, 2)+3) hydrophobin-containing beer, 4)+5) hydrophobin-containing beer whose mash was treated with AnGus1516®.

The product shall be added with the aim to induce the formation of calcium oxalate crystals as crysallization seeds. Oxalate crystals grow best on the granulates, since these have a large surface (300-800 m^2/g). Scanning electron microscopy proves that oxalate crystals grow very well and quickly on the calcium-activated silicate (see fig. 3). In addition the added AnGus1516® increases the pH-value of the brewing liquor and in this way decreases calcium oxalate solubility, thus favouring its precipitation. With a dosage of 100 g/hL to the mash, stability values of the Ca-sulphate/Ca-oxalate ratio of 16.9 could be obtained in the wort. Normally the brewing liquor used for the mash is within the pH-range of 5.2 to 5.4. With the process proposed and the addition the pH-value of the brewing liquor is raised to approx. pH 5.8. Moreover the pH-shift also has an impact on the aggregation of the 17 kD hydrophobin. It is reduced together with the gushing potential.

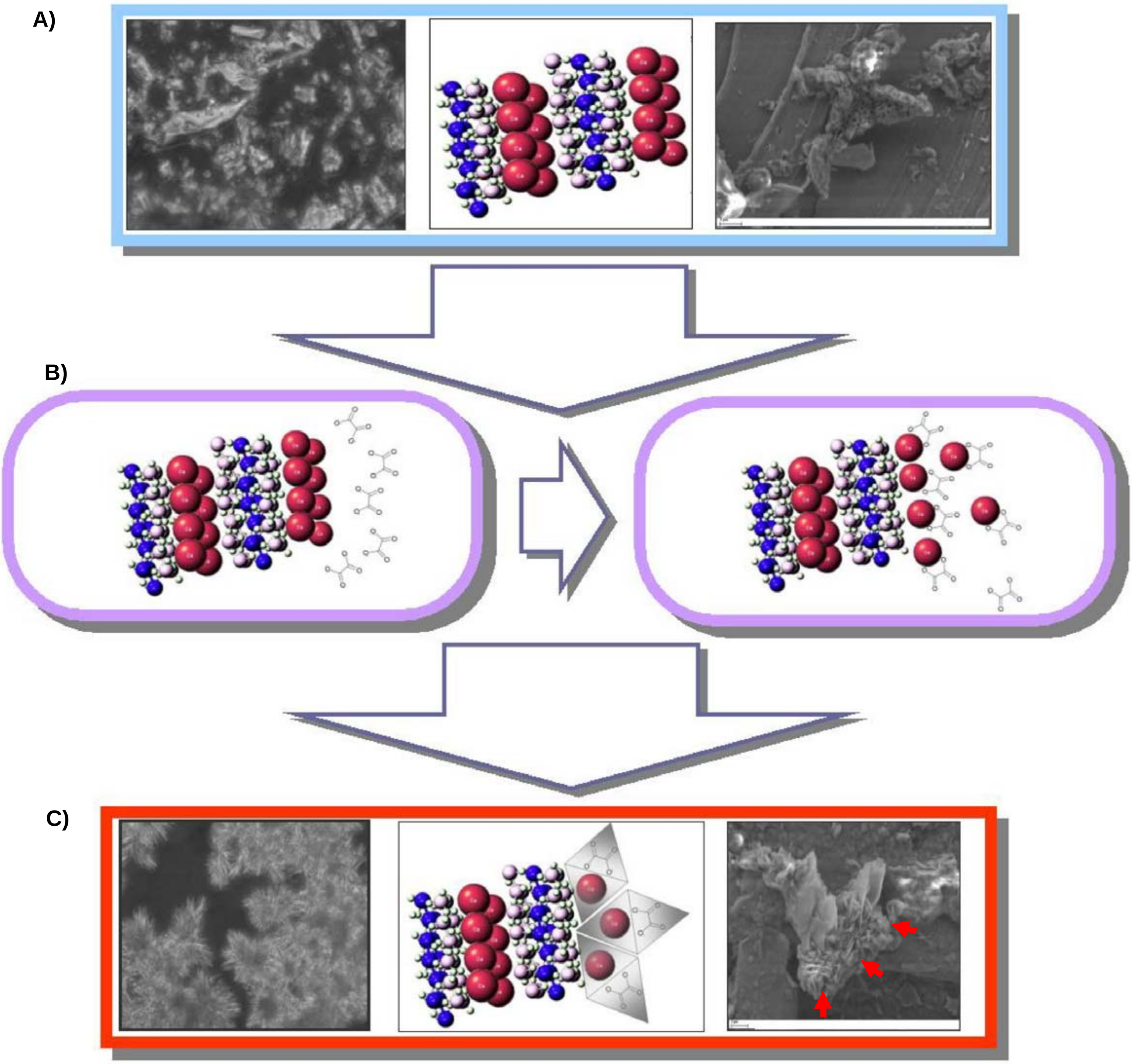

Figure 3: Appearance and mode of action of AnGus1516® in oxalate-containing beverages.

A) AnGus1516® on the left: phase-contrast microphotograph (200x), in the middle: lattice model, on the right: scanning electron microscopy of the honeycombed structure

B) Reaction of oxalate with the strongly calcium-charged surface of the product

C) Growing of calcium oxalate crystals on the left: phase-contrast microphotograph (200x), in the middle: lattice model, on the right: SEM red arrows illustrate calcium oxalate formation.

Results in comparison with standard methods of water hardening

In comparison with the AnGus1516®-treated beers, parallel tests with calcium chloride were conducted in beer (control) and analysed. Most of the tests were performed by accredited service laboratories of the Versuchs- und Lehranstalt Berlin (VLB) and of the Technische Universität München (technical university Munich); Forschungszentrum Weihenstephan für Brau- und Lebensmittelqualität (TUM) (research center Weihenstephan for brewing and food quality).

Normally, the compounds calcium chloride and calcium sulphate applied as precipitating agents are acidic salts and lower the wort pH-value. This pH-reduction also leads to an increase in calcium oxalate solubility, whereas by the application of AnGus1516® the pH-value is slightly increased, the calcium oxalate solubility decreases respectively, i.e., compared to the so far used methods, precipitation conditions are much more favourable. The slight pH-shift takes place within the optimal range of activity of the α-amylases. A decrease in yield due to the somewhat increased pH of the mash was not ascertainable, neither in the laboratory test series nor during application in the breweries. With both comparison variants conducted at three breweries, yields ranged between 79-81 % (extract; MEBAK II (4th edition) 2.33.3). Equally affected by the process was the hops yield. Compared to this of the standard beers, the yield was by around 8-10 % higher when beers were treated with AnGus1516® (see table 1).

By the poor solubility of the silicate mixture, the beer almost not at all undergoes mineral change which means, the sensory profile remains unaffected contrary to the treatment with calcium chloride or calcium sulphate. Also tested was the impact on beer taste in comparison with calcium chloride-treated beers. By expert tastings according to DLG scheme (Mebak II 3.17) could be proved that beers treated by the new method were assessed to have a higher drinkability than the conventionally treated beers. For the evaluation according to DLG-scheme as example Hefeweizen (Bavarian wheat beer) was chosen: O-beer (control) / AnGus1516® 4,2 : 4,7. During these comparison tests also no deterioration of the chemical-physical storability (shelf life) of the beers could be ascertained (see table 1). The equally analysed foam stability was always better than this of the comparing variant with calcium chloride (see table 1).

Foam values according to NIBEM in [s], MEBAK II (4th edition) 2.23.3		
Breweries	**O-beer (control)**	**AnGus1516® treated**
Brewery A	297-299	333-335
Brewery B	246-248	275-277
Brewery C	264-266	280-282

Forcing test (40°C/0°C) in [WT], MEBAK II (4th edition) 2.15.2.1		
Breweries	**O-beer (control)**	**AnGus1516® treated**
Brewery A	15.0	15.3
Brewery B	10.8	10.5
Brewery C	14.8	15.0

Bitter units in [BE], MEBAK II (4th edition) 2.18.1		
Beer type	**O-beer (control)**	**AnGus1516® treated**
Pils	28	30
Export	22	24
Kölsch	15	17
Weizen (wheat beer)	11	13

Table 1: Forcing tests, foam values and bitter units according to MEBAK II (4th edition), 2002

Remarks on the application of the AnGus1516® method:

Despite many advantages of AnGus1516®, gushing can be triggered by substances or conditions against which the product helps only in a limited way or not at all, as for instance, in case of residues of surfactants or a rough inner bottle surface. Proteins such as hydrophobins or proteases are reduced by AnGus1516®, yet not entirely removed. So, the impact of a primary gushing is indeed reduced but not completely prevented. In practical tests at several breweries that have used AnGus1516® already for more than one year, an increase of hops yield was noticeable. When adding the hops, this must be taken into account to avoid increased bitterness of the beers.

The use of AnGus1516® is in conformance with the requirements of the German purity law for the recommended application. To confirm this fact the Erbslöh Geisenheim AG has currently ordered an expertise. All ingredients of AnGus1516® are permitted according to European law for the use in feedstuffs. Therefore brewers' grains can be used in animal feed also after the application of AnGus1516®.

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Acknowledgement

Gefördert durch:

Bundesministerium für Wirtschaft und Technologie

aufgrund eines Beschlusses des Deutschen Bundestages