Flavours and off-flavours in beer – Part 1

JOINT PROJECT | Between November 2012 and April 2013, a group of diploma master brewer students from two different brewing courses at the Scandinavian School of Brewing (SSB), Copenhagen, participated in a joint project aimed at investigating some of the most common flavours and off-flavours found in beer. BRAUWELT International will present the results in a two-part series.

THIS PAPER IS A SUMMARY of the efforts of all the students involved and is derived from the collective presentations given by each group, spanning two brewing courses. Unless stated otherwise, all material for this paper stems from the lectures and presentations from these courses.

Every single step in the brewing process is vital to flavour development. This installment in the series deals with flavour development during the first steps of the brewing process.

Raw materials

Malt

In brewing, decisions about raw materials go well beyond merely which type of malt to use. How the barley is stored prior to malting has a significant impact on both the

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quality of the malt and the flavour profile of the finished product. Improper storage of barley-largely relating to the humidity and temperature - can result in off-flavours and diminish the quality in a variety of ways, ranging from loss of germinative capacity to contamination with bacteria and fungus. As the barley kernels are still viable seeds at this stage, a moist environment can trigger germination in the kernels while they are in storage. If a kernel begins the germination process, it cannot be reinitiated once it is stopped. Figure 1 shows optimal storage conditions for barley and includes information for how to avoid germination losses, contamination by microorganisms, insects and mites.

It is well known that dimethyl sulphide (DMS), which lends a flavour most often described as sweet corn, cooked vegetables or ketchup to the finished beer, stems from the malting process. However, the precursor of DMS (S-methylmethionine or SMM) is already present in barley prior to malting. SMM levels are highly dependent on variety. There are a series of factors in the malting process which can increase the conversion of SMM to DMS. Low germination temperatures of 13-14°C, high moisture content of the barley (>47%) and a low temperature kilning profile (<90) are all factors that contribute to SMM conversion. A preventive strategy for avoiding the formation of DMS would be to choose varieties of barley with a relatively low SMM content or to ensure that optimal malting conditions are present, taking care to keep track of the moisture content and temperature, as mentioned above. Removing the DMS already present in the wort can be done quite

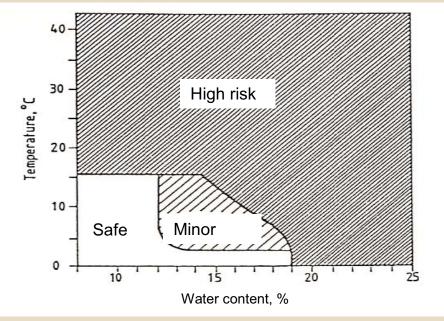


Fig. 1 Optimal storage conditions for barley [1]

Fig. 2 Chemical reaction mechanism of DMS

easily by boiling the wort for an adequate amount of time. In doing so, the DMS reacts with oxygen and is catalysed by heat, forming the compound dimethyl sulphoxide (DMSO). If this compound is not removed, it can impart a garlic-like flavour to the finished beer. Any DMS and DMSO in the wort evaporate over the duration of the boil, effectively removing them from the wort and the finished beer. The mechanism by which DMS is produced is shown in figure 2 [1].

Hop storage

After harvesting, it is imperative that hops be stabilised as quickly as possible to avoid spoilage. Hops can be stabilised through processes such as drying and pressing (to avoid oxidation by removing excess air from between the cones) as well as through further process steps, for example, pelletisation and/or packaging under a nitrogenrich atmosphere, in order to reduce contact with oxygen. The primary reason for stabilising hops is that both moisture and oxygen diminish their quality and bring about the slow degradation of the alpha-acids in the lupulin glands. Furthermore, the application of heat dramatically increases the oxidation rate in hops. One of the alpha acids, humulone, contains a side-group called isovaleryl. When this acid undergoes degradation, it loses its isovaleryl group, which then reacts with any oxygen that may be present, forming isovaleric acid. This compound imparts a cheese-like, sour odour and flavour to the beer, frequently described as "cheesy feet" - not particularly pleasant.

Brewing liquor

As water makes up the vast majority of beer, it is important to ensure that the brewing liquor is of a sufficient quality. For instance, metallic, salty, alkaline, and chlorophenol-

ic off-flavours are all caused by contamination of the brewing liquor in some part of the process. A metallic flavour is usually caused by contamination with iron, which may be attributable to rusting equipment (poor quality), additives, water with a high iron content, low quality kieselguhr, etc. However, in some cases, a metallic flavour may also be caused by improperly stored grain. Alkaline and chlorophenolic offflavours are slightly more critical in terms of detection, as these are often caused by residues of CIP-detergents from cleaning. To avoid these issues, chemical analysis of brewing liquor should be performed at regular intervals, along with adequate rinsing with pure water after cleaning.

Milling, mashing, lautering and boiling

In order for the malt enzymes to come into contact with the starchy endosperm of the malt, the malt must be milled. The degree of milling required depends on the malt quality. Less well-modified malts, in which the protein matrix retaining the starch gran-

ules has not been fully degraded, require finer milling so that the enzymes can reach the starch granules in order to break them down into sugars. However, in the lautering process, it is important that a portion of the husks remain whole to create the filter bed through which the wort can be clarified. Apart from the risk of clogging the filter bed, finely milled malt particles also increase the amount of tannins in the wort. The subject of tannins and their relationship to the size of malt particles and issues during lautering will be addressed in a later article.

During mashing, the malt enzymes degrade the long-chain starch granules into fermentable sugars and non-fermentable sugars, called limit dextrins, which are created as a result of branching in starch molecules. The malt enzymes α - and β -amylase are incapable of degrading the starch at these branch points and are therefore unable to cleave entire starch molecules into fermentable short-chain sugars. These non-fermentable limit dextrins pose a potential problem for any brewer since they affect the final sweetness and mouthfeel of the finished beer, which in some cases may be considered undesirable. One way to eliminate or reduce the amount of limit dextrins, and thereby increase the quantity of fermentable sugars, is to employ limit dextrinase - an enzyme that is entirely capable of cleaving the branch points of starch and limit dextrins, thus allowing these to be further degraded by the malt enzymes α - and β -amylase. However, the quantity of limit dextrins is usually so small that not much can be gained in terms of fermentable extract. Degrading the limit dextrins into fermentable sugars means that a brewer achieves greater control over his



Fig. 3 Hop cone with abundant lupulin glands (the author's photo from a tour to Hopsteiner's hop fields in Yakima, CA, USA)

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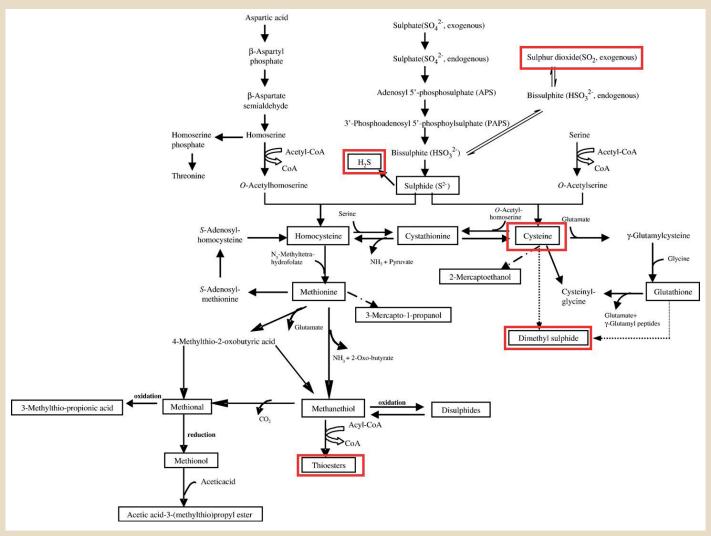


Fig. 4 Metabolic pathways of sulphur compounds in yeast

product, since brewers regulate the quantity of residual sweetness based on the real degree of attenuation (RDA) which serves as an indication of how much of the sugars originally present in the wort have been fermented. After mashing, the fermentable sugars along with the other wort constituents must be separated from the spent grains.

The filter bed consists of three different layers; fine particles form a loose dough on top, medium heavy particles and husk fragments occupy the middle, and the bottom layer consists of whole husks, larger particles, unmodified starch and proteins. The wort consists mainly of fermentable sugars, amino acids and proteins. As the wort seeps through the various layers of the filter bed, small particles are physically retained in these layers, resulting in a very clear liquid. The application of sparge water serves to extract the sugars and amino acids that may still remain in the filter

bed until the desired parameters are met. Although extraction of as much sugar as possible is desired, particularly with high gravity brewing, over-sparging may lead to a variety of flavour-related problems downstream in the brewing process. Oversparging, along with elevated tempera-

tures (> $80-82\,^{\circ}$ C) and a low pH during the lautering process, may cause an increase in the "grainy" flavour. This flavour is derived from the extraction of tannins accompanied by increased astringency from the extraction of polyphenols and anthocyanogens from the malt husks. These same





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factors may also increase the degradation of ferulic acid, and therefore increase extraction of its products, which include 4-vinyl guaiacol (4VG) and other phenolic compounds. It is possible to avoid the excessive extraction of tannins by adding mineral salts to the mash prior to lautering, which also improves protein precipitation in the whirlpool. However, in order to avoid over-sparging, there is a general "rule of thumb" which recommends sparging to no lower than $1-2\,^{\circ}\text{P}$, in order to avoid the extraction of compounds which will have a negative impact on the beer [1].

■Fermentation

Primary fermentation contributes more to the development of flavour in beer—whether it is considered good or bad—than any other part of in the brewing process. The yeast's ability to metabolise various fermentable sugars, amino acids and proteins into a wide array of compounds, such as esters, can produce a bouquet of delicious aromas and flavours even in the most basic wort. However, there are other aspects of yeast metabolism which have a much less pleasant effect. The sulphur metabolism of yeast is

an example of a biochemical process, which can impart a variety of highly unwelcome characteristics to the beer. Figure 4 provides an overview of the metabolic pathway for compounds containing sulphur with some of the by-products discussed in this paper indicated with a red box.

One of the worst offenders with regard to sulphur off-flavours is hydrogen sulphide (H₂S), which has an odour similar to that of rotten eggs. H₃S is caused by the degradation of the amino acid cysteine and the reduction of sulphur, sulphite and sulphate. The amount of H,S produced depends heavily on both yeast growth and wort composition, i.e. H₂S increases with low free amino nitrogen and high cysteine concentrations, along with other factors such as a high level of oxygen in the wort and high fermentation temperatures. However, the quantity of H₂S produced will decrease if the amino acid methionine and zinc are present at high levels [2, 3].

Also linked to the degradation of the sulphur-containing amino acids cysteine and methionine are mercaptans, thioesters and DMS. Synthesis of these sulphur compounds increases with deficiencies in yeast

nutrients, exposure to UV light, the Maillard reaction (browning) and high concentrations of H,S and alcohol [4].

■Literature

- 1. SSB Lecture presentations and in-class notes from the Diploma Master Brewer Class 2012/2013.
- 2. Moreira, N.; Mendes, F.; de Guedes Pinho, P.; Hogg, T.; Vasconcelos, I.: "Heavy sulphur compounds, higher alcohols and ester production profile of *Hanseniaspora uvarium* and *Hanseniaspora guilliermondii* grown as pure and mixed cultures in grape must", International Journal of Food Microbiology, 2008, 124(3), pp. 231-238.
- 3. Landaud, S.; Helinck, S.; Bonnarme, P.: "Formation of volatile sulfur compounds and metabolism of methionine and other sulfur compounds in fermented food", Applied Microbiology and Biotechnology, January 2008, volume 77, issue 6, pp. 1191-1205.
- 4. Vermeulen, C.; Lejeune, I.; Tran, T. T. H.; Collin, S.: "Occurrence of polyfunctional thiols in fresh lager beers". J. Agric. Food Chem., 54, 2006, pp. 5061-5068.