

Effect of production and storage of beer on its sensory stability

Karel Štěrba^{*1}, Lucie Kyselová²

- ¹ Department of Chemistry, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 00 Prague, Czech Republic
- ² Research Institute of Brewing and Malting, Lípová 511/15, 120 00, Prague 2, Czech Republic

* corresponding author: sterba@af.czu.cz

Abstract

Freshly produced beer is in a state of chemical imbalance and its sensory characteristics change and deteriorate over time. The period when beer resists these undesirable changes is referred to as its shelf stability, which is precisely defined from a microbiological, colloidal and sensory point of view. The sensory stability of beer can be adversely affected by vibrations during transport and improper storage at elevated temperatures, the presence of oxygen and light. Sensory stability can be improved during production, in particular by selecting suitable raw materials, limiting the access of oxygen and reducing the heat load. Although this review is based on well-known and frequently discussed facts, it primarily presents the latest scientific results and theories concerning the sensory stability of beer, which have been published in recent years.

Keywords: beer stability, sensory evaluation, carbonyl compounds, aldehyde

1 Introduction

Beer has been one of the most popular drinks since ancient times. Along with its growing production and export opportunities all over the world, it has become necessary to ensure that beer will retain the properties of a fresh beverage for as long as possible, i.e. that it will keep the highest feasible microbiological, colloidal and sensory stability.

Historically, microbiological stability was the first to be addressed. Beer is one of the microbiologically relatively stable beverages due to the content of ethanol, bitter substances, carbon dioxide, low pH and low oxygen concentration. However, there are some microorganisms such as lactic acid bacteria or wild yeast, which are able to grow in beer (Suzuki, 2011). To prevent their growth, breweries use thermal pasteurisations or membrane filtration (Briggs et al., 2004).

If beer does not have a good colloidal stability, precipitate or turbidity of non-microbiological origin appears in it during storage. This is mostly caused by complexes of proteins with polyphenols, but other substances such as a higher content of β -glucans or oxalates may also appear. Their formation is supported by several factors such as improper storage, movement during transport and most frequently unsuitable temperature, e.i. either the temperature is too high or too low that it causes the beer to freeze. From the point of view of beer production, the choice of raw materials is vital, especially the choice of malt with a low content of β -glucans. Also, a higher content of calcium ions in the brewing water can prevent problems with precipitates caused by oxalates. Many breweries prevent formation of protein-polyphenolic turbidity by stabilization, which removes either proteins using silica gels or polyphenols using polyvinylpolypyrrolidone (Kosař and Procházka, 2000; Čejka et al., 2019; Olšovská et al., 2021).

A number of sensory changes, which are typically designated as the old taste of beer, occur during aging. The first general conception of sensory changes during

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beer aging (Dalgliesh, 1977) included an increase in sweet and toffee-like flavours, a sharp increase in the aroma of currant together with its subsequent continuous decrease, and also a gradual decrease in bitter taste. Development of cardboard flavour was manifested in later stages of aging. A similar trend was presented by Zufall et al. (2005), who observed an increase in cardboard flavour after about 2 weeks of beer aging, while its maximum intensity was reached after about 4 weeks. Then the cardboard flavour decreased until the end of the experiment.

The accurate sensory description of beer aging required a detailed and standardized vocabulary, thus in 2003 the EBC commission developed a descriptive system for assessing the old taste of beer based on the most frequently-used descriptors by professional tasters, see Table 1 (Hill, 2003). Although less detailed, an established EBC beer flavour wheel represents a valuable tool. This contains among others "Class 8 Oxidized, stale, musty" which comprises catty, papery, leather, mouldy, earthy and musty flavours (EBC 13.12, 1997; Olšovská et al., 2017a).

In addition to changes in taste and aroma, the colour also varies with beer aging. Vanderhaegen et al. (2003) found that when beer was aged at a temperature of 40 °C without access to air, there was a linear increase in colour during the entire aging period (5 EBC in 187 days). When oxygen was present, there was a sharp

increase in colour in the first days of aging (2.5 EBC in 12 days), however the next observed increase was slower.

The aim of this paper is to describe changes of carbonyl compounds in beer during its lifecycle, from raw materials to the end of beer storage. Special attention is given to factors influencing formation of aldehydes and their precursors and also to possibilities of reduction of aldehyde formation.

2 Chemical changes during beer aging

The old taste of beer and the substances that cause it have been the subject of many studies in recent decades. Carbonyl compounds were identified to be a likely source of old taste as early as in 1966 (Vanderhae-

| Table 1 | Descriptors for the evaluation of the old taste of beer (Hill, 2003) |
|---------|----------------------------------------------------------------------|
|---------|----------------------------------------------------------------------|

| Group | Descriptors |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| Vinous | Sherry, madeira, whisky, rum, wine-like, fusels |
| Bready | Bread, bread crust, dough, biscuits |
| Fruity | Cherry, plum, berries, overripe fruit, blackcurrant leaves, ribes, catty, jam-like, cooked, stewed fruit, dried fruit, tropical fruit, green apple |
| Caramel | Toffee, molasses, treacle |
| Cereal | Grainy, husky, dusty, straw |
| Resinous | Woody, nutty, spicy, clove |
| Honey | Honey |
| Fatty | Soapy, waxy, cheesy, sweaty, rancid |
| Smoky | Smoked bacon, kippers, cigarette ash |
| Sulphury | Lightstruck, skunky, meaty, drains, cooked vegetables |
| Roasted | Liquorice, toast, roasted malt |
| Papery | Paper, cardboard |
| Mouldy | Musty, earthy, leathery |
| Acidic | Sour, vinegar, acetic |
| Bitterness | Lingering afterbitterness, harsh bitterness |
| Sweet | Sweet |
| Mouthfeel | Wide, broad mouthfeel, viscous, chewy, sticky, cloying, astringent, drying, metallic, rusty |

 Table 2
 Selected formation mechanisms of substances responsible for the old taste of beer (Vanderhaegen et al., 2006)

| Mechanism | Reaction products |
|----------------------------|--------------------------------------------------------------------------------------|
| Strecker degradation | 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, methional, phenylacetaldehyde |
| Oxidation of fatty acids | hexanal, trans-2-nonenal |
| Maillard reactions | furfural, 5-hydroxymethylfurfural, 2-furfurylethylether, γ-nonalakton |
| Degradation of carotenoids | β-damascenone |

gen et al., 2006). Their concentration in fresh beer is very low, however they gradually increase during aging. And just these changes of carbonyl compounds are considered as the main reason of the old taste (Malfliet et al., 2008; Baert et al., 2012). Also, other substances that may be involved in the development of old taste have been gradually identified (Vanderhaegen et al., 2006), for example, esters, furans, furanones, cyclic acetals, pyrazines, sulphur compounds or lactones. The mechanism of formation of many of them is not fully elucidated, but it is generally agreed that oxidative processes are involved. The mechanisms of some substance formation are given in Table 2 (Vanderhaegen et al., 2006) and in Figures 1 to 4 as examples. Other mechanisms include, for instance, the formation of carbonyls from bitter hop substances, but the effect of

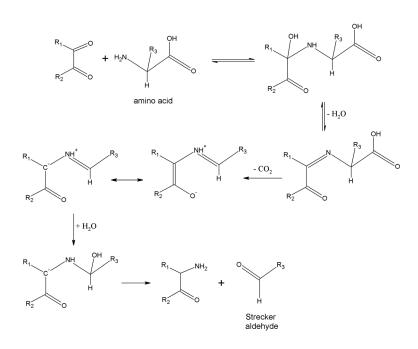


Figure 1 Mechanism of Strecker degradation of amino acids forming Strecker aldehyde (Baert et al., 2012)

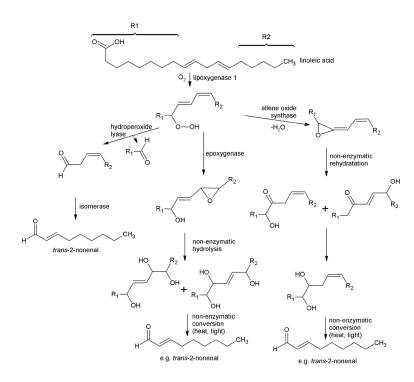


Figure 2a Enzymatic oxidation of fatty acids (Baert et al., 2012)

this degradation on sensory stability is thought to be negligible compared to the above mentioned reactions (De Clippeleer et al., 2010).

The concentration of carbonyl compounds in beer is mostly below their sensory threshold. Nevertheless, these substances can be sensory active (Table 3) even at lower concentrations due to interactions and syner-

gic effect of individual carbonyl compounds. When the sensory thresholds of pure substances and mixtures of 2-methylbutanal, methional and phenylacetaldehyde were compared, an additive effect (lower sensory threshold) for a mixture of methional and phenylacetaldehyde and an antagonistic effect (higher sensory threshold) for a mixture of 2-methylbutanal and phenylacetaldehyde was observed. Although the mixture of 2-methylbutanal and methional displayed no effect on sensory threshold of these aldehydes, mixture of all three aldehydes already showed an additive effect. In Figure 5, sensory thresholds values of individual mixtures are depicted as a percentage against the sensory thresholds of pure substances (Saison et al., 2009).

Bitterness decreases and changes the character of bitterness during beer aging (Pangborn et al., 1977). This is mainly due to the degradation of transiso- α -bitter acids to tri- and tetracyclic compounds responsible for the harsh, lingering bitterness (Intelmann et al., 2011). On the contrary, *cis*-iso- α -bitter acids are stable and their content did not undergo significant changes even after 582 days of aging at 28 °C (Intelmann et al., 2011). An extreme case in terms of bitterness degradation was described in the analysis of a beer approximately 100 years old, which was sensorially completely free of bitterness, although 22 IBUs were analytically determined (Olšovská et al., 2017b).

Four types of substances mainly contributing to the colour of beer are listed in Table 4 (Hughes and Baxter, 2001). Two mechanisms are supposed to be responsible for colour changes of beer during aging. The principle of the first mechanism is the formation of new products,

i.e. the Maillard reaction producing melanoidins, the rate of which depends on storage temperature. The others are oxidation, subsequent degradation of polyphenols based on a sharp increase in colour during beer aging in the presence of oxygen and decrease in flavanoid concentration at a constant content of total polyphenols (Vanderhaegen et al., 2003).

3 Overview of aldehyde formation and their changes during beer production

The aldehyde concentration in fresh beer is usually negligible and eventually increases during time according to storage conditions. However, the beer production process is also considered as an important factor of beer aging. When isotopically labelled amino acids were added prior to the wort boiling process, it was found that 85% of Strecker's aldehydes come just from the brewing process (Suda et al., 2007). It is assumed that the increase in aldehydes during aging occurs mainly due to their gradual release from adducts formed during fermentation (Baert et al., 2012).

Therefore, in the following text are listed the main known trends of aldehyde formation and changes during the whole beer production process and the possibilities how to influence them.

3.1 Effect of malting process on the formation of aldehydes and their precursors

The malting process can be divided into three basic operations – steeping, germination and kilning – and each of them affects the formation of aldehydes in a different way.

During steeping, water is absorbed by grain. Enzymes catalysing the formation of aldehyde precursors are activated after reaching at least 32% of the water content in grain (Briggs, 1998). The content of total polyphenols decreases during steeping, thus the content of substances capable to act against the formation of aldehydes is reduced (Filipowska et al., 2021).

During germination, the enzymatic activity of malt reaches maximum values. The activity of lipoxygenases, i.e. enzymes responsible for the formation of aldehyde precursors (see Figure 2a), increases twice to five-fold (Yang and Schwarz, 1995). At the same time, the content of free amino acids rises. These serve, among others, as precursors of Strecker aldehydes (Filipowska et al., 2021). A significant increase in

Table 3 Correlation of the old taste intensity and concentration of selected aldehydes (Olšovská et al., 2016)

| Compound | Correlation coefficient ^a |
|--------------------|--------------------------------------|
| 2-methylpropanal | 0.96 - 0.98 |
| 2-methylbutanal | 0.91 - 0.96 |
| 3-methylbutanal | 0.91 - 0.95 |
| furfural | 0.87 - 0.96 |
| phenylacetaldehyde | 0.85 - 0.93 |

^a range of correlation coefficients for four different Czech lagers

Table 4 Main contributors to beer colour and their origin in brewing process (Hughes and Baxter, 2001)

| Compounds | Origin | Colour |
|----------------------|--------------------------------------|---------------|
| melanoidins | malt, special malts, wort boiling | yellow, amber |
| oxidised polyphenols | malt, hop, oxidation, pasteurisation | red, brown |
| copper, iron | water, malt | |
| riboflavin | malt, yeast | yellow |

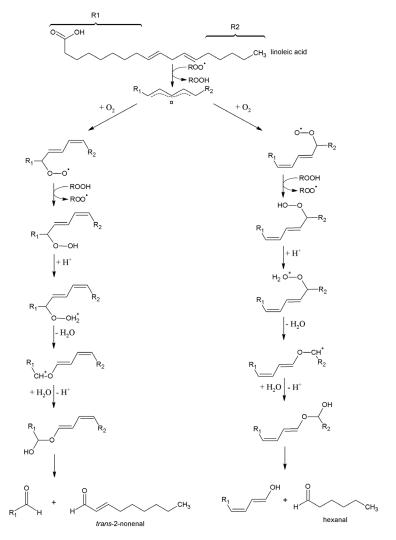


Figure 2b Autooxidation of fatty acids (Baert et al., 2012)

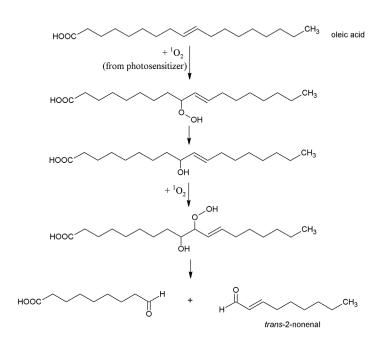


Figure 2c Photooxidation of fatty acids (Baert et al., 2012)

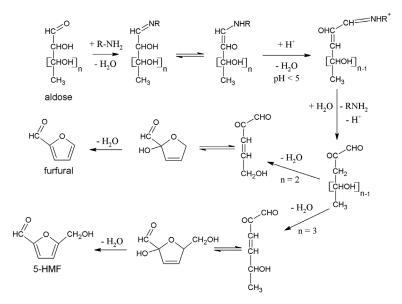


Figure 3 Formation of furfural and 5-hydroxymethylfurfural (5-HMF) by mechanism of Maillard reaction (Baert et al., 2012)

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are required for their formation at a low water activity (Filipowska et al., 2021). Furthermore, the activity of lipoxygenases significantly decreases during the kilning process (Yang and Schwarz, 1995), and the formation of polyphenolic compounds occurs (Inns et al., 2007). At high temperatures, especially at the end of kilning, radicals are formed, which can negatively affect beer stability (Cortés et al., 2010).

3.2 Changes in aldehyde content during wort production and fermentation

Figure 6 shows concentrations of aldehydes found at different stages of beer brewing process (Ditrych et al., 2019) for selected representatives of the aldehyde groups listed in Table 1. During mashing, there was a significant decrease in trans-2-nonenal, which supports the hypothesis that only a small amount of fatty acid oxidation occurs in a brewhouse (Bamforth, 1999). A significant decrease of Strecker aldehydes was observed during wort filtration, which according to the authors, was due to their higher volatility and adsorption to malt. In contrast, there was an increase in trans-2-nonenal content during wort filtration. This increase probably caused a release from the bounds with insoluble compounds during sparging (Ditrych et al., 2019).

Although Strecker aldehydes are formed at higher temperatures, their total content decreases during wort boiling. This is caused by faster evaporation against the formation of new molecules (De Schutter et al., 2008). The effect of volatility of individual compounds (see Table 5) is demonstrated by a comparison with a mere 5% decrease in pheny-

2-methylbutanal, pentanal, hexanal and *trans*-2-nonenal concentrations was observed in malts contaminated with fungus *Fusarium* (Chen et al., 2017).

High temperatures during kilning cause an increase in the concentration of furfural. However, the concentration of Strecker aldehydes changes only minimally. They are formed mainly in humid conditions, and temperatures above 130 °C

| lable 5 | Distribution of aldehydes according to their volatility |
|---------|---------------------------------------------------------|
| | (De Schutter et al., 2008) |

| Volatility | Aldehydes |
|------------|-----------------------------------------------------------------------|
| high | 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, pentanal, hexanal |
| medium | methional, phenylacetaldehyde, benzaldehyde |
| low | furfural |

lacetaldehyde concentration contrasted to a 86% decrease of 2-methylpropanal (Ditrych et al., 2019). In contrast to Strecker aldehydes, the furfural content increased. This is due to both its significantly lower volatility and the different reaction kinetics of its formation (De Schutter et al., 2008). For all compounds, an increase in concentration occurs during separation of the hot trub in the whirlpool, which has been attributed to a reduction in volatile evaporation compared to the intense boiling during the wort boiling (Narziss and Back, 2009).

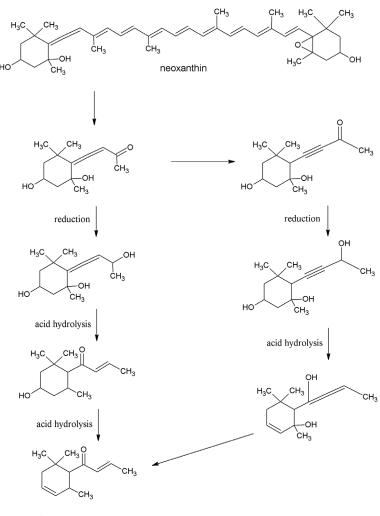
The reducing ability of the yeast diminishes the aldehyde content to very low concentrations during the main and secondary fermentation (Peppard and Halsey, 1981). The adduct formation is also considered as an important cause of aldehyde content reduction during fermentation. Formation of the most important adducts are depicted in Figure 7 (Baert et al., 2015).

3.3 Options of influencing the sensory stability of beer within the production process

The identification of factors that may influence the sensory stability of beer should start already during the malt production. Most attention has been paid to lipoxygenases. So that their activity is supressed, it is important to select varieties with low levels of lipoxygenases (Drost et al., 1990; Yu et al., 2014), to avoid unnecessary aeration during steeping (Baxter, 1982) and to conduct germination at lower temperatures (Yang and Schwarz, 1995). Although limited oxygen access during germination also reduces the activity of lipoxygenases, it negatively affects the malting process (Yang and Schwarz, 1995).

Even the selection of varieties with lower Kolbach index and total soluble nitrogen can affect beer stability as a correlation of these parameters with the amount of Strecker aldehydes formed during beer ageing has been observed (Stephan et al., 2007; Filipowska et al., 2021).

Great attention should also be paid to the way malt is stored. Storage without access of moisture reduces the activity of lipoxygenases (Kaukovirta-Norja et al., 1998). The



β-damascenone

Figure 4 Mechanism of β -damascenone formation (Chevance et al., 2002)

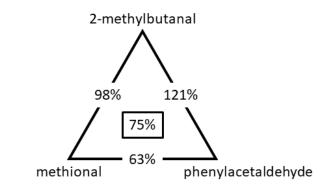


Figure 5 Sensory threshold values of mixtures of selected Strecker aldehydes (Saison et al., 2009)

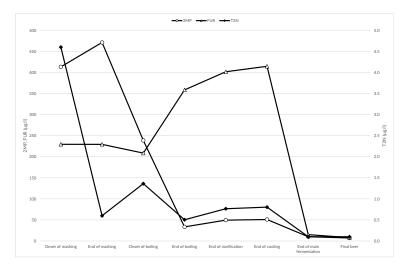
amount of Strecker aldehydes in malt is influenced by the rate of their formation and evaporation. However, it is supposed that storage at a higher temperature and humidity results in the largest changes in their content and therefore a significant negative effect on beer quality (Hoff et al., 2014). It is recommended to use as fresh malt as possible for beer brewing, since, among others, fatty acids are oxidized during storage (Wackerbauer et al., 2003; Baert et al., 2012).

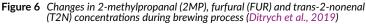
It is necessary to avoid over-aeration of the sweet wort and wort, which would lead to an increase in aldehyde formation. This can be achieved, for example, by a protective atmosphere of nitrogen or carbon dioxide, by filling vessels from the bottom or by using water with a minimum of dissolved oxygen (Drost et al., 1990; Takashio and Shinotsuka, 1998; Bamforth, 1999; Baert et al., 2012). Reduction of heat load is equally relevant. This reduction can be reached by the following setting:

- shortening the heating time and lowering its intensity;
- using the shortest possible transport paths for hot intermediates;
- minimizing the temperature gradient between the surface of the cooking vessel and the liquid (Narziss, 1986; Baert et al., 2012).

It is equally relevant to ensure sufficient evaporation with condensate trapping. The return of condensate would increase the aldehyde concentration since many undesirable compounds, including aldehydes, are removed with the vapor (Baert et al., 2012).

Lipoxygenases that are present in malt can be quickly denatured during mashing-in at higher temperature and lower pH (Drost et al., 1990; Vanderhaegen et al., 2006; Takashio and Shinotsuka, 1998; Baert et al., 2012). Furthermore, attention should be paid to the lautering, as imperfect separation of the spent grain and wort is responsible for higher levels of aldehydes and their precursors in the wort (Drost et al., 1990; Baert et al., 2012). Wort boiling,





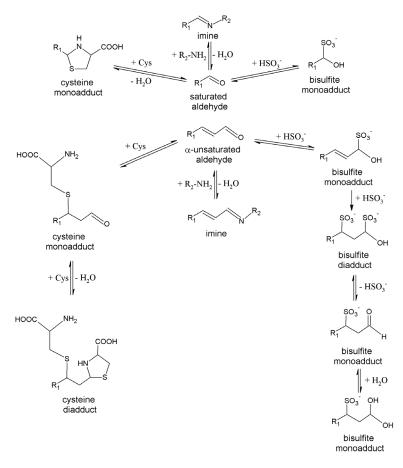


Figure 7 Adduct formation of saturated and unsaturated aldehydes with cysteine, amine and bisulfite, repectively (Baert et al., 2015)

which is performed at a lower pH leads to the increase in aldehyde formation. On the contrary, this process is desirable mainly in conjunction with intense evaporation, because the amount of aldehyde precursors is considerably decreased in the wort (Baert et al., 2012). Once wort boiling is finished,

the clarification of the wort in the whirlpool should be as fast as possible to avoid the formation of new aldehydes (see Figure 6). At the same time, the best possible separation of the solids is needed as aldehydes are bound to them and could be released into the solution again (Narziss, 1986). The pitching of the wort is the only time during the beer brewing process when the presence of oxygen is desired. The yeasts need the dissolved oxygen for their growth and are able to consume it efficiently. However, excessive aeration of the wort before fermentation limits the production of sulphur dioxide as an antioxidant agent and, in addition, may promote the formation of oxidized compounds (Takashio and Shinotsuka, 1998; Bamforth, 1999, Baert et al., 2012). The use of yeast strains with increased sulphur dioxide production is recommended to improve the sensory stability of beer (Baert et al., 2012). On the other hand, Perpète and Collin (1999) reported that the effect of different strains of yeasts on aldehyde reduction has not been proven.

The presence of copper and iron ions, as efficient catalysators, accelerates the progress of oxidation reactions and thus the deterioration of beer quality during storage (Vanderhaegen et al., 2006). Their presence in the brewing process can be controlled, for example, by the selection of suitable raw materials. But due to the decontaminating nature of the whole production, the main effect on metal concentration in the finished beer lies in the final operations, such as filtration (Čejka et al., 2009). For this reason, it is necessary to choose secure filtration material from which only a minimum of

metal ions are released during filtration. During the filling process, air access should be kept to a minimum in order to slow down the ageing process in the bottled beer as much as possible (Baert et al., 2012). If thermal pasteurization is used, the heat load should be limited to minimize sensory damage to the beer; an alternative is to use membrane filtration (Briggs et al., 2004).

The addition of antioxidants, e.g. ascorbic acid, to beer during bottling has been proposed to prolong sensory stability, but the positive effect of this approach has not been confirmed (Baert et al., 2012).

4 Effect of transport and storage conditions on beer aging

The rate and the way of beer aging are affected by numerous conditions that occur during transport and storage. The effect of oxygen has been mentioned many times above. The oxygen molecule itself is not very reactive. However, oxygen and iron ions form reactive oxygen species that react more readily with organic compounds (Vanderhaegen et al., 2006). The addition of oxygen to beer resulted in a higher sensory intensity of currant, Maillard reaction products and the perception of Madeira wine (Saison et al., 2010a). Moreover, the addition of Fenton's reagent (a mixture of hydrogen peroxide and ferrous sulfate) to beer resulted in an increase of cardboard flavour intensity (Saison et al., 2010a). However, other factors besides the presence of oxygen also contribute to beer aging. This fact is supported by a study (Furusho et al., 1999), in which the addition of a small amount of oxygen to beer had only a slight effect on the intensity of the old flavour (see Table 6).

Temperature and storage time have a major influence on the rate of beer aging. A study of the ageing of Czech lager at temperatures around 0 °C, 20 °C and 30 °C can be given as an example (Olšovská et al., 2016). The concentration of furfural as one of the most important indicators of beer aging (see Table 3) was 5 μ g/l in fresh beer. At a temperature of 30 °C, the furfural concentration exceeded three times the original value, i.e. 15 μ g/l, after only one week. This value was exceeded after one month of storage at 20 °C, and at temperatures around 0 °C. The highest measured concentration was 12 μ g/l until after

Table 6 Effect of oxygen addition on the development of old flavour (Furusho et al., 1999)

| Oxygen amount in beer (mg/l) | Old flavour intensity ^a (1 month, 20 °C) | Old flavour intensity ^a (3 months, 20 °C) |
|---------------------------------|--------------------------------------------------------|---------------------------------------------------------|
| 0.16 | 2.7 | 2.6 |
| 0.42 | 2.8 | 2.7 |
| 0.69 | 3.2 | 2.8 |

^aThe samples were evaluated on the scale 0 (not present) – 5 (very strong) by sensory panel consisting of 9 extensively trained members. However, uncertainty has not been stated in the study.

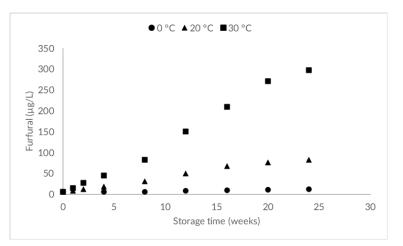


Figure 8 Effect of beer storage temperature on furfural formation (Olšovská et al., 2016)

half a year of storage (see Figure 8). In general, temperatures below 10 °C are recommended for beer storage (\check{C} ejka et al., 2013).

The stability of the finished beer is increased by the content of substances with antioxidant properties. In the first place, sulphur dioxide should be mentioned as a by-product of fermentation. Its addition to old beer has been shown to reduce the intensity of the old taste (Dvořák et al., 2008). Similarly, the addition of yeast to filtered beer improves its sensory stability. Also in this case, a reduction of old flavour intensity after yeast addition has been described (Saison et al., 2010b; Saison et al., 2011).

Other antioxidants in beer include polyphenols, however their effect on sensory stability is not clear. Some of them (e.g. catechin) are antioxidant, others (e.g. delphinidin) are pro-oxidant due to their ability to transfer electrons to metal ions (De Schutter et al., 2009; Wietstock, 2017).

The aging of beer can also be accelerated by careless handling during transport. It has been proven that vibration during storage or transport of beer, especially in combination with higher storage temperatures, can negatively affect the sensory profile of beer and accelerate the formation of old flavour components, probably due to increased oxygen consumption from the headspace for intense aging reactions (Jaskula-Goiris et al., 2019).

The quality of stored beer is also negatively affected by light. In the presence of light fatty acids are oxidized to aldehydes (see Figure 2c) (Baert et al., 2012). Moreover, visible and UV light decompose iso- α -acids to form 3-methylbut-2-en-1-thiol with a characteristic undesirable skunk-like aroma, which is known as lightstruck. To minimize the effect of light, beer is most often bottled in brown or green bottles, whereas brown bottles provide better protection against this damage (Bamforth, 2011). As an alternative method of protection, removal of riboflavin has been suggested since it acts as an initiator of the above-mentioned degradation (Borrelli et al., 2011).

5 Conclusion

Due to the long transport of beer to the customer and the requirements for the longest possible shelf life, it is necessary to achieve the best possible stability of the beer. The correct method of storage, i.e. in a cool and dark place, without access to oxygen and with minimum mechanical shock, is essential for sensory stability. There are several ways how the beer aging in production process can be influenced. Particularly we should stress a selection of raw material and a reduced presence of oxygen at all stages of the brewing process except fermentation. It is also highly recommended to avoid excessive heat load, e.g. during pasteurisation.

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