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BEER AGING PROCESS®

Proces starzenia piwa®

Key words: beer, shelf life beer, sensory properties, volatile components, technological condition.

Currently, the main quality problem of beer is the change in its chemical composition during storage, which influences the sensory change of the drink. Unlike some wines, brewing is usually considered negative for the quality of the taste.
Properly carried out technological activities, from the selection of raw materials to the bottling, can significantly improve the flavor durability of the beer.
The aging process of the beer as expressed by the evaluation of the flavor stability of the beer is described by various analytical parameters as well as by sensory evaluation of beer. The analytical assessment usually relates to different tracer substances or to the capture of substances accelerating or inhibiting the oxidation process. However, the proper analysis to determine the flavor durability is the sensorics, which is the final sensory evaluation of the beer should always be carried out.

Słowa kluczowe: piwo, trwałość piwa, cechy sensoryczne, komponenty lotne, warunki technologiczne.

Obecnie głównym problemem jakościowym piwa jest zmiana jego składu chemicznego podczas przechowywania, co wpływa na zmianę sensoryczną napoju. W przeciwieństwie do niektórych win, starzenie piwa jest zwykle uważane za negatywne dla jakości smaku.
Odpowiednio przeprowadzone czynności technologiczne, począwszy od wyboru surowców aż po rozlew mogą w wyraźny sposób poprawić trwałość smakową piwa.
Proces starzenia piwa wyrażony oceną stabilności smakowej piwa jest opisany przy użyciu różnorodnych parametrów analitycznych jak również za pomocą oceny sensorycznej piwa. Ocena analityczna odnosi się zazwyczaj do różnych substancji wskaźnikowych lub wychwycenia substancji przyspieszających bądź hamujących proces utleniania. Właściwą analizą do określenia trwałości smakowej jest ostatecznie sensoryka, stąd też należy zawsze dodatkowo przeprowadzać ocenę degustacyjną piwa.

INTRODUCTION

As for other food products, also for beer, several quality aspects may be subject to changes during storage. Shelf-life of beer is mostly determined by its colloidal, microbiological, foam, colour and flavour stabilities. The appearance of hazes and the growth of beer spoilage micro-organisms is considered as the main troublecausing phenomena [7, 8].

Beer flavour is the result of a complex interaction between hundreds of chemical compounds and even more taste and olfactory receptors. Such compounds that impart taste can be sensed directly on the tongue, while aroma will refer to any volatised compounds that can be perceived either through the nose or retro-nasally through the back of the mouth [4].

With the increasing export of beer, due to market globalisation, shelf-life problems may become extremely important issues for all breweries. Beer aging is a very complex phenomenon and action. This overview on the chemistry of beer aging intends to illustrate the complexity of the aging reactions [8].

Several quality aspects of beer are subject to change during storage. Alteration of the flavor profile in particular is of great concern to brewers since flavor is considered as the main quality parameter. Moreover, a commercial beer should be consistent and satisfy the expectations of the consumer at all times [5].

At present, there is more to aged flavour than meets the eye. It is obvious that the fresh flavour profile is disturbed by the appearance of various aged flavours and, on the other hand, an increase or decrease of many compounds is observed during ageing. However, it remains difficult to explain observed sensory changes based on analytically determined chemical compounds [4].

Flavour deterioration is the result of both formation and degradation reactions. Formation of molecules, at concentrations above their respective flavour threshold leads, to new noticeable effects, while degradation of molecules to concentrations below the flavour threshold may cause loss of initial fresh beer flavours. Furthermore, interactions between different aroma volatiles may enhance or suppress the flavour impact of the molecules [8].

Oxidation processes, due to oxygen uptake during beer production, are considered to be a major cause of stale flavour development in beer. It is often reported that absorption of oxygen in the mash, during filtration, during boiling, in wort and beer, leads to oxidation, which can damage the flavour.

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The general belief is that wort aeration has a negative impact on wort quality, which results in more rapid beer staling, though literature describing aeration related wort oxidation processes is very scarce [3].

CHANGES (CHEMICAL AND PHYSICOCHEMICAL) IN BEER DURING STORAGE

Information on beer staling reveals only few reports dealing with the actual sensory changes during beer storage. Figure 1 is a description of the sensory changes during beer storage and is by no means applicable to every beer. A constant decrease in bitterness is observed during aging. In contrast to an initial acceleration of sweet aroma development, the formation of caramel, burntsugar and toffee-like aromas (also called leathery) coincides with the sweet taste increase [2, 8].

The intensity of the ribes flavour decreases. Cardboard flavour develops after the ribes aroma. In turn, cardboard flavour constantly increases to reach a maximum, followed by a decrease. Furthermore, a very rapid formation of what is described as ribes flavour is observed. The term ribes refers to the characteristic odour of blackcurrant leaves (Ribes nigrum). Besides these general findings, other reported changes in flavour are harsh after-bitter and astringent notes in taste and wine- and whiskey-like notes in strongly aged beer [8].

From the start of research on staling compounds, carbonyls attracted most attention. Such compounds were known to cause flavour changes in food products such as milk, butter, vegetables and oils. Remarkable increase in the level of volatile carbonyls in beer during storage, is parallel with the development of stale flavours. Acetaldehyde was one of the first compounds for which a concentration increase was observed in aged beer. First described (E)-2-nonenal as a molecule, which on addition to beer, induces a cardboard flavour similar to such flavour in aged beer. Further, the identification, in heated acidified beer, of (E)-2-nonenal, as the molecule responsible for cardboard flavour, was considered a breakthrough in beer flavour [8].

In turn, volatile esters introduce fruity flavour notes and are considered highly positive flavour attributes of fresk beer. Isoamyl acetate, produced by yeast, e.g., gives a banana-like flavour. However, during storage, the concentration of this ester can decrease to levels below its threshold level which results in a diminished fruity flavour of beer. In contrast, certain volatile esters like etyl lactate, ethyl phenylacetate, ethyl formate, ethyl furoate and ethyl cinnamate are synthesized during beer aging. The formation of ethyl 3-methyl-butyrate and 2-methylbutyrate to the development of winy flavours. Lactones or cyclic esters, such as c-hexalactone and c-nonalactone (peach, fruity) tend to increase in concentration and the latter molecule is considered important for the flavour of aged beer [8].

Other components, like non-volatile compounds in beer can be important for taste and mouthfeel. Changes in concentration may therefore induce important sensory alterations. Iso-α-acids, the main bitterness substances in beer, are particularly sensitive to degradation during storage which results in a decrease in sensory bitterness. The iso-a-acids comprise six major components: the trans and cis-isomers of isocohumulone, isohumulone and isoadhumulone. The trans-isomers are much more sensitive to degradation than the cis-isomers. The concentration ratio trans/cis isomer was proposed as a good marker for the flavour deterioration of beer. Apart from iso-a-acids, polyphenols are some of the more readily oxidized beer constituents There are only few reports on beer storage-related changes in amino acids. In general, a slight decrease is observed of some individual amino-acids and glutamine has been proposed as a staling marker [8].

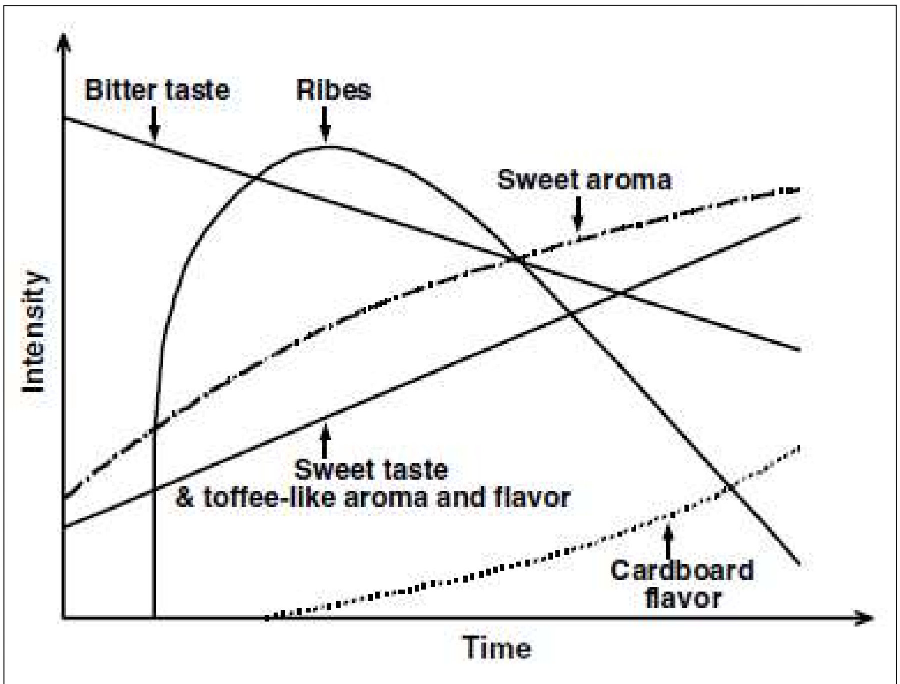

Fig. 1. Sensory changes during beer aging.
Rys. 1. Zmiany sensoryczne piwa podczas jego starzenia.
Source: Dalglish 1977 [2]
Źródło: Dalglish 1977 [2]

MECHANISMS OF AGING OF BEER

Chemically, beer can be considered as a water-ethanol solution with a pH of around 4.2 in which hundreds of different molecules are dissolved. These originate from the raw materials (water, malt, hops, adjuncts) and the wort production, fermentation and maturation processes. However, the constituents of freshly bottled beer are not in chemical equilibrium. Thermodynamically, a bottle of beer is a closed system and will thus strive to reach a status of minimal energy and maximal entropy. Consequently, molecules are subjected to many reactions during storage, which eventually determine the type of the aging characteristics of beer. Although many conversions are thermodynamically possible, their relevance to beer aging is mainly determined by the reaction rates under practical storage conditions. The reaction rate is a function of substrate concentrations and rate constants, which differ between reaction types and which are temperature-dependent. In practice, reaction rates increase with higher substrate concentrations and storage temperatures [4].

Soon after the importance of carbonyl compounds for beer staling was revealed, pathways for their formation were suggested. From the beginning, reaction mechanisms leading to (E)-2-nonenal have been the focus of this research. Many routes have been studied in beer model systems and it therefore remains difficult to tell to what extent a particular reaction mechanism is relevant under normal storage conditions.

The most important alcohols in beer are ethanol, 2-methyl-propanol, 2-methyl-butanol, 3-methyl-butanol and 2-phenyl-ethanol. Various researchers have reported that the concentrations of the corresponding aldehydes increase during beer aging, in particular when oxygen was present. High temperatures, low pH and the supplementation of additional higher alcohols to beer led to higher concentrations of aldehydes. Moreover, direct oxidation of alcohols by molecular oxygen was not possible in beer model systems, unless melanoidins were present. A reaction mechanism was proposed in which alcohols transfer electrons to reactive carbonyl groups of melanoidins. Molecular oxygen accelerates the oxidation of the alcohols, probably because the melanoidins are transformer in such a way that the reactive carbonyl groups are involved in the electron-transfer system [4].

Amino acids in stored beer can be a source of aldehydes. observed an increased formation of 2-methyl-propanal and 3-methyl-butanal when either valine or leucine were added to beer and oxygen was present. The reaction was catalysed by Fe and Cu ions. This was explained by a Strecker reaction between amino acids and α-dicarbonyl compounds. The reaction involves transamination, followed by decarboxylation of the subsequent a ketoacid, resulting in an aldehyde with one carbon atom less than the amino acid. Additional α-dicarbonyl compounds in beer are possibly formed by the Maillard reaction, the oxidation of reductones or the oxidation of polyphenols. Strecker degradation is only important at strongly increased amino acids contents, but not at the amino acid concentrations normally present in beer (±1 g/l) [4, 8].

In turn aldol condensation of carbonyl compounds is possible under the mild conditions existing in beer during storage. For example, (E)-2-nonenal was formed by aldol condensation of acetaldehyde with heptanal in a model beer stored for 20 days at 50°C and containing 20 mmol/l of proline. In these reactions, the amino acids may be the basic catalysts through the formation of an imine intermediate. This pathway can produce carbonyl compounds with lower flavour thresholds from carbonyls present in beer which are less flavour active, and which can be formed by other pathways. Although the aldol condensation pathway seems plausible, it is not clear whether the amounts of reaction products are sufficiently high to reach threshold concentrations under normal beer storage conditions.

Formation of many distinct compounds during ageing, degradation of acetate esters can occur, resulting in a decrease of fresh flavour. Acetate esters determine the fresh flavour of beer greatly and might be able to mask the perception of other flavour compounds. Therefore, the appearance of aged flavour notes can be accelerated upon acetale ester degradation. Hence, the potential masking effect of IAA (Iso-Amyl Acetate) on 2-MB and methional was studied. This was performed by determining THs (thresholds) of aldehydes in beer with an extra added amount of IAA to the test, as well as the reference beer. Comparing the THs with those determined in beer without addition might give an idea of masking effects exerted by IAA.

Nevertheless, it can be concluded that the presence of higher IAA concentrations can affect the TH value considerably, indicating once again that the TH of a compound is highly dependent on the reference beer and that masking effects might play an important role in decelerating the appearance of aged flavours [1, 4].

From the point of view of improving beer flavor stability, wort aeration methods used in modern fermentation technology, such as high gravity brewing and large cylindroconical tank systems, were investigated in detail using a novel electron spin resonance method, which could determine the endogenous antioxidant activity (EA) value. The results showed that the optimization of wort aeration methods in the multifilling fermentation systems ("Drauflassen") was essential for controlling the EA value of the finished beer as well as fermentation performance. The key point in the optimization of wort aeration methods was to consider the yeast growth phase at the time of wort aeration and the quantitative ratio of additional aeration to the first aeration depending on the fermentation conditions. Based on the extensive series of studiem on improving the oxidative flavor stability of beer, the relationships between the EA value and sulfite level in beer are considered. A strategy for improving oxidative flavor stability of beer is also proposed [3, 6].

The ESR (Electron Spin Resonance) is one of the method can be successfully applied to analyze the effect of wort aeration methods on the oxidative flavor stability of beer when using multifilling methods. The results show that optimization of wort aeration methods and of other multifilling methods such as the filling time of additional wort, pitching procedures, the quantity of additional aeration, are very important in influencing fermentation performance and the EA value of finished beer. The key points in the optimization of wort aeration methods are the yeast-growth phase at the time of additional aeration and the quantitative ratio of additional aeration to the first aeration. Sulfite is one of the most important antioxidants to enhance the EA value of beer. However, it is also shown that the EA value of beer is determined not only by sulfite levels in beer, but also by the balance in levels of both prooxidants and antioxidants. These results show that the EA value is a useful tool to predict the flavor stability of beer, because the EA value is a total index that may reflect the balance of prooxidants and antioxidants in beer [6].

PODSUMOWANIE

Niniejszy przegląd podsumowuje aktualną wiedzę na temat procesów starzenia piwa przechowywanego w dłuszym okresie czasu. Materiał opisuje również mechanizmy reakcji, które odpowiadają za niniejsze procesy „aging beer". Ponadto omówiono związek między procesem produkcji a stabilnością smaku piwa. Opóźnienie procesu starzenia a jednocześnie wydłużenie świeżości piwa na półkach sklepowych jest jednym z najważniejszych działań podejmowanych przez producentów piwa. Browary przeprowadzają próby jakościowe z różnymi ustawieniami parametrów technologicznych w celu poprawy jakości piwa po dłuższym okresie czasu.

CONCLUSION

This overview summarizes the current knowledge about the aging processes of beer stored over a long period of time. The material also describes the reaction mechanisms that are responsible for this "beer staling" process. In addition, the relationship between the production process and the stability of the beer flavor was reported. Delaying the aging process and at the same time extending the freshness of beer on store shelves is one of the most important activities undertaken by beer producers. Breweries carry out quality tests with various settings of technological parameters in order to improve the quality of beer over a longer period of time.

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