

Aging characteristics of different beer types

Bart Vanderhaegen^{*}, Filip Delvaux, Luk Daenen, Hubert Verachtert, Freddy R. Delvaux

Centre for Malting and Brewing Science, Katholieke Universiteit Leuven, Kasteelpark Arenberg 22, B-3001 Heverlee, Belgium

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Abstract

Eight commercial beers (3 lager beers, 2 dark ales and 3 high-alcoholic ales) were aged for one year under normal storage conditions, and the changes with time of flavour profile and the concentration of 15 volatile compounds were monitored. The compounds were chosen as markers to evaluate the importance of different reactions in the aging process of each beer type. The development of typical aging flavours during beer storage could be linked to the Maillard reaction, the formation of linear aldehydes, ester formation, ester degradation, acetal formation, etherification and the degradation of hop bitter compounds. A difference in the nature of aging flavours between lager and specialty beers was found and seemed to be mainly the result of an increased Maillard reaction in specialty beers. Based on the results, some practical strategies are proposed to improve the flavour stability, depending on the beer type.

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1. Introduction

The flavour of bottled beer changes with time of storage. Beer aging is considered to be a major quality problem since the aging flavours are mostly experienced as unpleasant. Furthermore, the type of flavour evolution during storage is uncontrollable, making it difficult for brewers to assure a constant product quality or to meet some consumers' expectations regarding flavour (Stephenson & Bamforth, 2002). Therefore, much research on beer has been devoted to the chemistry of the aging phenomenon (Bamforth, 1999; Hashimoto & Kuroiwa, 1975; Kaneda, Kobayashi, Takashio, Tamaki, & Shinotsuka, 1999). Most of these studies are focussed on lager beers, since they represent the largest part of the beer market. Consequently, the aging processes in specialty beers are less understood and methods to improve their flavour stability are scarce.

In the past, specialty beers were produced by small breweries and restricted to local markets. However, due

to market globalization, production volumes and export of the specialty beers are rapidly increasing. This has resulted in longer transportation times and variable storage conditions, which demand more attention to the production of beers with improved flavour stability. A first step in optimizing the brewing process, with respect to flavour stability, consists in characterizing the sensory and chemical aging properties of beer. Due to differences in production processes, it can be expected that the aging characteristics differ between beer types.

A comparison of the flavour stability of different beers is usually based on the determination of one of the following parameters: the endogenous reducing power, measured by one of the many procedures available (Araki et al., 1999; Chapon, Louis, & Chapon, 1981; Kaneda, Kobayashi, Furusho, Sahara, & Koshino, 1995), the concentration change during storage of a particular beer constituent, such as trans-2-nonenal (Larsen, Aastrup, Nielsen, & Lillelund, 2001), furfural (Brenner & Khan, 1976), 5-hydroxymethylfurfural (Shimizu et al., 2001), ethyl pyruvate (Shimizu, Nara, & Takashio, 2005), or storage-induced sensory changes (Mikyska, Hrabak, Haskova, & Srogl, 2002). However, each of the first methods evaluates only the

^{*} Corresponding author. Tel.: +32 16321948; fax: +32 16321576.

E-mail address: bart.vanderhaegen@biw.kuleuven.be (B. Vanderhaegen).

resistance of beer to just one type of staling process and gives only a partial insight into the total chemical changes causing the perceived stale flavour. On the other hand, sensory tests give an overall view of flavour stability, but generally little information about specific chemical reactions involved.

In this study, we analyzed the aging characteristics of eight different beers by determination of both the sensory profile and the evolution of chemical staling markers, during a storage period of one year at 20 °C. A correlation is sought and discussed between beer properties and the aging behaviour.

2. Materials and methods

2.1. Chemicals

The following substances, with corresponding purities were supplied by Sigma Aldrich Chemie GmbH (Munich, Germany): ethyl acetate (99.9%), *iso*-amyl acetate (99.7%), ethyl hexanoate (99+%), ethyl lactate (98%), ethyl 3-methylbutyrate (99.7%), ethyl 2-methylbutyrate (99%), acetaldehyde (99.5%), *n*-hexanal (98%), 3-methylbutanal (98%), diacetyl (99.5%), 4-methylpentan-2-one (99%) and 2-furfural (99%). 2-Furfuryl ethyl ether, with a purity of 95%, was purchased from Narchem Corporation (Chicago, IL, USA).

2.2. Beer aging conditions

Eight fresh commercial beers, obtained from different Belgian breweries, were used to examine the effect of natural aging. All beers were bottled with total oxygen levels below 0.2 mg/l. Beers were stored for one year at 20 °C in the dark.

2.3. Beer analysis

Beer colour was measured at 430 nm according to the method of Seaton and Cantrell (1993).

Bitterness of beer was measured according to Analytica EBC method 9.8 (European Brewery Convention, 1998).

2.4. Analysis of staling markers in beer

Prior to analysis, 200 µl of internal standard solution (250 mg/l of 2-heptanol) and 200 µl of a 10% antifoam solution (Sigma Aldrich Chemie GmbH, Munich, Germany) were added to 50 ml of degassed beer. Beer was degassed by Kieselguhr filtration. Five millilitres of beer were transferred by a Tekmar-Dohrman Aquatek 70 autosampler (Emerson, Mason, USA) into the Tekmar-Dohrman 3000 purge and trap concentrator (Emerson, Mason, USA) unit with a Vocab 3000 trap (Supelco, Bellefonte, PA, USA). The following conditions were used: helium was the carrier gas, 10 min purge at 140 °C, 8 min dry purge at 140 °C, 6 min desorption at 250 °C and 10 min bake at 260 °C.

The temperatures are those of the adsorbing trap while the beer sample temperature was kept at 20 °C during purging. Before entering the GC, volatiles were concentrated using a cold trap with a MFA 815 control unit (Thermo-Finnigan, San Jose, CA, USA) under the following conditions: initial temperature, –70 °C, final temperature; 200 °C. GC was performed using a Fisons GC 8000 gas chromatograph equipped with a Chrompack CP-WAX-52-CB column (length 50 m, internal diameter 0.32 mm, film thickness 1.2 µm; Varian, Palo Alto, CA, USA). The temperature programme was: 3 min at 50 °C / 4 °C min⁻¹ and 3 min at 240 °C. Total ion mass chromatograms were obtained in the Fisons MD 800 quadrupole mass spectrometer (ionization energy: 70 eV; source temperature: 250 °C) and analyzed using the Masslab software programme for identification and quantification of volatiles.

2.5. Quantification of volatile compounds

Quantification was performed for compounds of which a standard reference compound was commercially available. Peak areas were normalized using 2-heptanol as an internal standard. Calibration factors were determined using the standard addition method and creating linear regression models. Target ions were used in the identification and quantification of each component. For each compound, a coefficient of variance (CV) was calculated from the areas obtained from 8 consecutive injections of the same beer sample.

2.6. Sensory analysis

Sensory tests on aged beers were carried out with a trained panel of 10 members. Four beers were randomly presented in one session to the panellists. Besides an evaluation of the general aging character, the stale flavour was also evaluated for six aspects by giving a score from 0 to 8. Typical aged beer flavours (Sherry / Madeira, cardboard, solvent, old hops, red fruit and caramel), characterised in a previous study (Vanderhaegen et al., 2003), were used for the evaluation. A score of 0 meant the particular flavour aspect was not present, a score of 8 meant that the particular flavour aspect was extremely strong.

3. Results and discussion

3.1. General

The aging characteristics of 8 commercial Belgian beers; 3 pilsner beers (L-A, L-B and L-C) and 5 specialty beers (S-A, S-B, S-C, S-D and S-E) were compared. These beers differed by their alcohol percentage, pH, colour and bitterness (see Table 1). From the colour values, it is clear that S-A and S-C are dark beers. On the other hand, S-B, S-C, S-D and S-E are high alcoholic beers. Furthermore, S-D is characterized by a high bitterness and L-B by a relatively high pH.

Table 1
Alcohol percentage, colour, pH and bitterness of 8 commercial beers: 3 lager beers, L-A, L-B, L-C and 5 specialty beers, S-A, S-B, S-C, S-D, S-E

	Alcohol (% v/v)	Colour (EBC)	pH	Bitterness (EBU)
L-A	5.34	10.3	4.37	25.0
L-B	5.09	9.2	4.61	23.2
L-C	5.24	10.9	4.56	20.0
S-A	5.44	30.5	4.29	20.2
S-B	7.82	18.3	4.39	16.4
S-C	8.84	47.4	4.44	18.6
S-D	9.77	16.7	4.44	32.4
S-E	10.6	16.4	4.30	20.6

Table 2 shows the 15 volatile compounds monitored in each beer during a storage period of one year at 20 °C. Their presence is the result of aging reactions. Table 2 indicates the relationship between the presence of specific volatiles and the type of involved aging reaction. The different types of aging markers were selected to represent, as much as possible, the main staling reactions (Vanderhaegen, Neven, Verachtert, & Derdelinckx, 2006). Quantification of the volatile compound contents allows evaluation of the extent of a particular aging reaction which occurs in a particular beer. The coefficients of variance in Table 2 give an indication of the reproducibility of concentration measurements. Based on the selected aging markers, the particular aging characteristics of the 8 beers were compared.

3.2. Maillard reaction and Strecker degradation

Strecker degradation of leucine may form 3-methylbutanal during beer storage (Blockmans, Devreux, & Maschelein, 1975). In the eight analyzed beers, its concentration remained either constant or increased (Fig. 1A). The largest increases in 3-methylbutanal occurred in beers with a high alcohol content (S-E, S-D, S-B and S-C). In lager beers, concentrations remained rather constant.

As a result of a condensation reaction between 3-methylbutanal and 2,3-butanediol (Peppard & Halsey, 1982), 2-isobutyl-4,5-dimethyl-1,3-dioxolane can appear. This was found during storage of the eight beers (Fig. 1B). The highest concentration increase was measured for S-C, which is most likely related to its high 3-methylbutanal content.

The formation of the Maillard intermediate, furfural (Fig. 1C), is clearly correlated with the alcohol content and colour. The lowest concentrations were present in the lagers and the highest in high alcoholic and dark beers.. The same holds for 2-furfuryl ethyl ether (Fig. 1D), which is a condensation reaction product of furfuryl alcohol and ethanol (Vanderhaegen et al., 2004a). These results clearly support our previous study (Vanderhaegen et al., 2004b), indicating that levels of the Maillard intermediate, furfuryl alcohol, are higher in beers with an elevated alcohol content and darker colour. The combined effect of a high ethanol and furfuryl alcohol content makes beer S-E very sensitive to 2-furfuryl ethyl ether formation during aging. In the specialty beers, the furfuryl ethyl ether levels largely exceed the flavour threshold of 6 µg/l (Vanderhaegen et al., 2003), creating a typical stale flavour (solvent-like aroma, harsh taste). As the concentration increases in the eight beers were rather linear with storage time, 2-furfuryl ethyl ether concentration is a very interesting indicator for the storage conditions of various beer types.

Under the given storage conditions, the Maillard reaction is probably responsible for the gradual diacetyl increase (Fig. 1E) in the eight beers. Formation of this compound is again greater in beers with a dark colour or high alcohol content.

Increases in colour are shown for the eight beers in Fig. 1F. Colour increases during storage are due to coloured molecules derived mainly from the Maillard reaction and the oxidation of polyphenols. A somewhat higher increase in colour was observed in samples with a darker colour or higher alcohol content.

The results indicate that Maillard reactions are more prominent during aging of dark and high alcoholic beers.

Table 2
Coefficient of variance (CV) of aging markers in beer and the type of aging reaction involved in their formation or degradation during storage

Aging marker	CV (%)	Aging reaction
3-Methylbutanal	2.67	Strecker degradation, oxidation of alcohol
2-Isobutyl-4,5-dimethyl-1,3-dioxolane	7.19	Cyclic acetal formation of aldehyde with 2,3-butanediol
Furfural	7.01	Maillard reaction
Furfuryl ethyl ether	5.35	Etherification of ethanol and Maillard compounds
Diacetyl	4.97	Maillard reaction
Acetaldehyde	2.16	Oxidation of ethanol
<i>n</i> -Hexanal	6.22	Release of lipid oxidation products in beer
<i>Iso</i> -amyl acetate	5.11	Hydrolysis of esters produced by yeast
Ethyl acetate	5.24	Hydrolysis of esters produced by yeast
Ethyl caproate	1.96	Hydrolysis of esters produced by yeast
Ethyl lactate	5.94	Esterification of ethanol and organic acid
4-Methylpentan-2-one	7.00	Degradation of hop bitter compounds
3-Penten-2-one	7.04	Degradation of hop bitter compounds
Ethyl 2-methylbutyrate	6.01	Esterification of ethanol and organic acid
Ethyl 3-methylbutyrate	7.57	Esterification of ethanol and organic acid

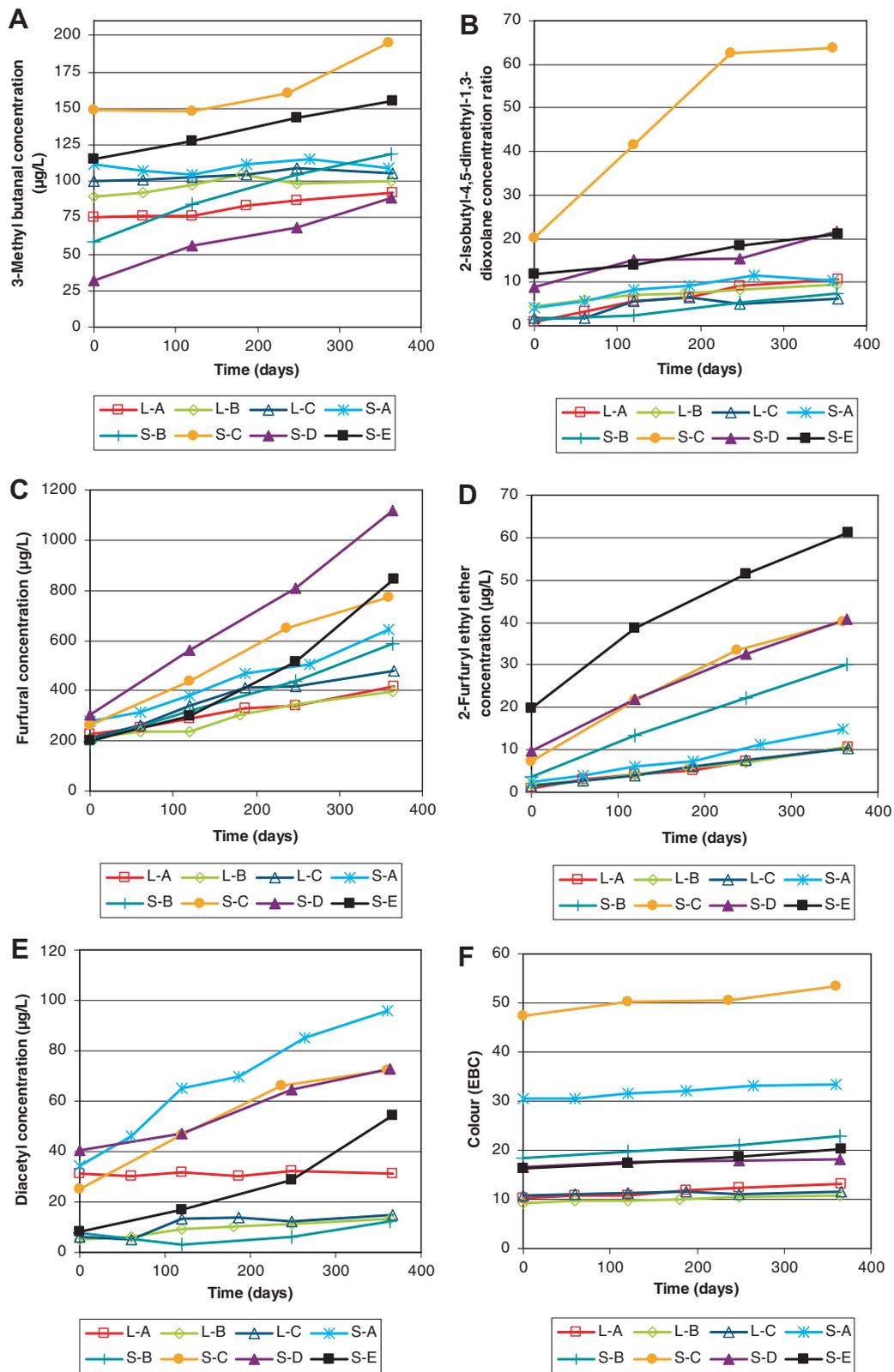


Fig. 1. Concentrations of 3-methylbutanal (A), 2-isobutyl-4,5-dimethyl-1,3-dioxolane (B), furfural (C), furfuryl ethyl ether (D) and diacetyl (E) and the evolution of beer colour (F) during storage of eight beers for one year at 20 °C.

High alcoholic beers are produced from high density worts. Previously, it was shown (Vanderhaegen et al., 2004b) that, during the wort boiling process, the forma-

tion rate of certain Maillard intermediates (e.g., furfuryl alcohol) increases quadratically with the wort density. Furthermore, the malts used for dark beers are produced

by heating germinated barley to higher temperatures than pilsner malts, which results in the formation of more Maillard intermediates (Coghe, Martens, D'Hollander,

Dirinck, & Delvaux, 2004). Consequently, dark beers and high alcoholic beers must contain many Maillard intermediates (e.g., furfuryl alcohol, α -dicarbonyl com-

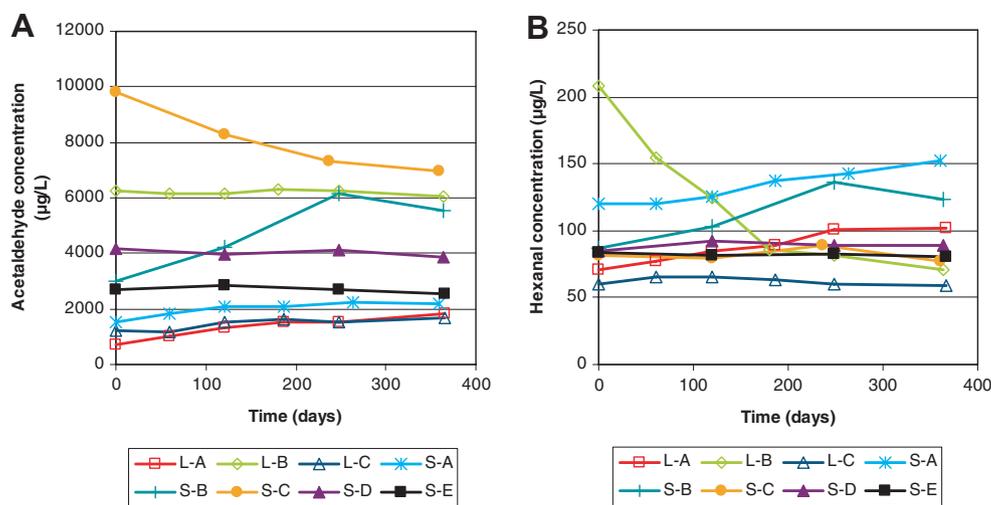


Fig. 2. Concentrations of acetaldehyde (A) and *n*-hexanal (B) in eight beers during storage for one year at 20 °C.

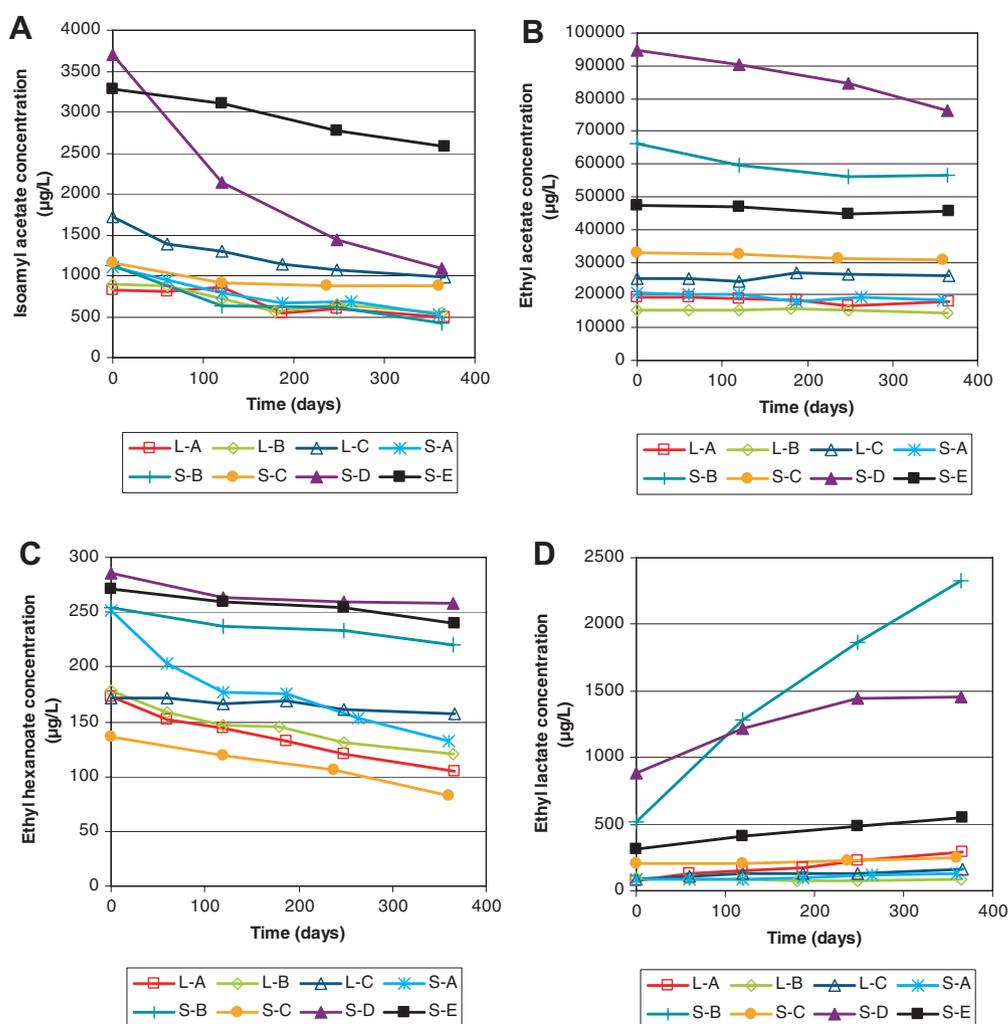


Fig. 3. Iso-amyl acetate (A), ethyl acetate (B), ethyl hexanoate (C) and ethyl lactate (D) concentrations in eight beers during storage for one year at 20 °C.

pounds), which are reactive substrates for aging reactions and many different (off)flavours.

Typical stale flavours originating from the Maillard reaction are burnt, caramel and Madeira-like flavours (Camara, Marques, Alves, & Ferreira, 2004). This corresponds well with the general sensory observation that these stale flavours are perceived as more dominant in specialty beers, in contrast to lager beers.

3.3. Formation of linear aldehydes

The profiles of the linear aldehydes, acetaldehyde and *n*-hexanal, were different among the eight beers. Acetaldehyde (Fig. 2A) slightly increased in L-A, L-C, and S-A, whereas it remained constant in S-E, S-D and L-B. A greater increase was found for S-B and a decrease for beer S-C which showed a high initial level. Acetaldehyde is easily formed from ethanol when oxygen is present. However, most commercial beers are now bottled with extremely low oxygen levels (<0.2 mg/l), resulting in few oxidative aging reactions during storage. *n*-Hexanal levels (Fig. 2B) increased in L-A, S-A and S-B, but remained constant in

L-C, S-C, S-D and S-E. In L-B, a high initial *n*-hexanal concentration rapidly decreased upon storage. *n*-Hexanal is a well-known product of lipid oxidation (Belitz & Grosch, 1999) and can be formed during beer production. Aldehydes originating from lipid degradation can be released during beer storage from adducts with amino acids or proteins (Noël & Collin, 1995). Consequently, differences in lipid oxidation during beer production and aldehyde release during storage, but also reactions of aldehydes with alcohols, water or sulfite, producing acetals, enols or sulfite adducts (Dufour, Leus, Baxter, & Hayman, 1999), may affect their concentration and explain the differences among the eight beers and also the decrease of acetaldehyde levels in S-C and of *n*-hexanal in L-B. Aldehydes generally create a paper- or cardboard-like stale flavour in beer (Meilgaard, 1975).

3.4. Ester hydrolysis and ester formation

Some specialty beers (S-D and S-E) are characterized by high levels of esters, such as *iso*-amyl acetate, ethyl acetate and ethyl hexanoate (Fig. 3A–C). Esters are produced by

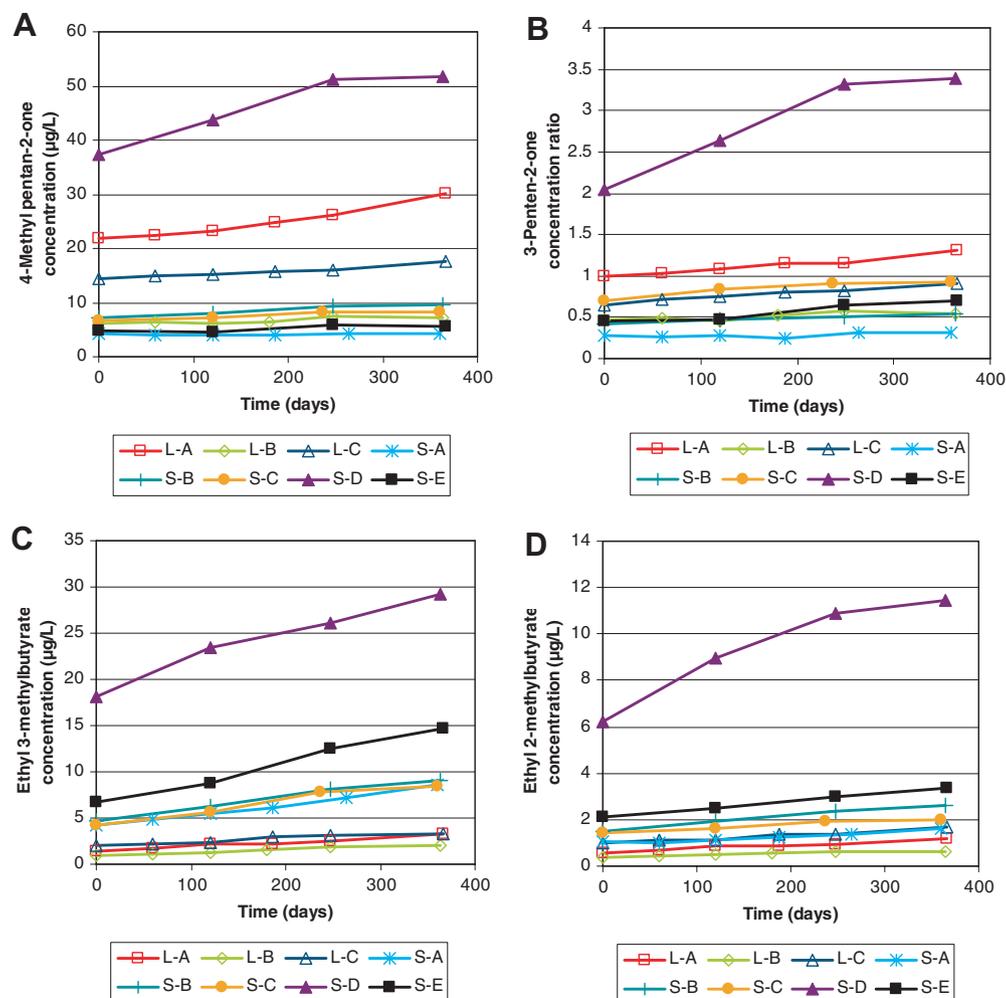


Fig. 4. Evolutions of 4-methylpentan-2-one (A), 3-penten-2-one (B), ethyl 3-methylbutyrate (C) and ethyl 2-methylbutyrate (D) concentrations in eight beers during storage for one year at 20 °C.

yeast during fermentation and give pleasant fruity flavours to beer. However, in the eight stored beers, the ester concentrations decrease due to hydrolysis. *Iso*-amyl acetate (Fig. 3A) is present in comparable high concentrations in fresh S-D and S-E but, on storage, levels decrease much more rapidly in S-D. According to Neven, Delvaux, and Derdelinckx (1997), this can be related to the initial inactivation of esterases in beer S-E which, contrary to beer D, is pasteurized. The slower decrease in *iso*-amyl acetate in S-E is due to chemical hydrolysis. Due to ester hydrolysis, the concentrations of *iso*-amyl acetate in S-D and in L-C decrease from levels above threshold to below threshold (1400 µg/l). Such particular change to levels below threshold also occurs in beer S-A with ethyl hexanoate (210 µg/l). Consequently, fruity flavours, initially present in some beers, may disappear during aging, which decreases the intensity of the “background” flavour and increases the perception of eventual stale flavours.

In contrast to ester hydrolysis, an ester such as ethyl lactate (Fig. 3D) was formed in the eight beers. This results from an esterification reaction between ethanol and an organic acid (e.g., lactic acid). The reaction rate is determined by the concentrations of the precursors, the beer pH and the storage temperature. The highest reaction rates were recorded in high alcoholic beers (S-B, S-D and S-E).

However, the final concentrations remained relatively low, which is expected, as the concentrations of lactic acid are very low. In acidic beers, such as the Belgian gueuze beers, the concentration of lactic acid is high and ethyl lactate is present at significantly high levels (Spaepen, Vanoevelen, & Verachtert, 1978).

3.5. Degradation of hop compounds

Both 4-methylpentan-2-one (Fig. 4A) and 3-penten-2-one (Fig. 4B) are formed by degradation of *iso*- α -acids during beer aging (Hashimoto & Eshima, 1979) and this is faster at increased oxygen concentrations in the bottle (Kaneda, Kano, Osawa, Kawakishi, & Kamada, 1989). Huvaere et al. (2003) demonstrated that electron acceptors other than oxygen species can also be involved. This may occur in the eight beers, which have low oxygen levels. Particularly the beers with a high bitterness (S-D and L-A) are characterized by a relatively high initial concentrations and a large increase of 4-methylpentan-2-one and 3-penten-2-one. The initial concentration in fresh beers of both ketones are determined by oxidation of *iso*- α -acids during wort production.

The acids, 3-methylbutyric acid and 2-methylbutyric acid, can also result from the degradation of hop bitter

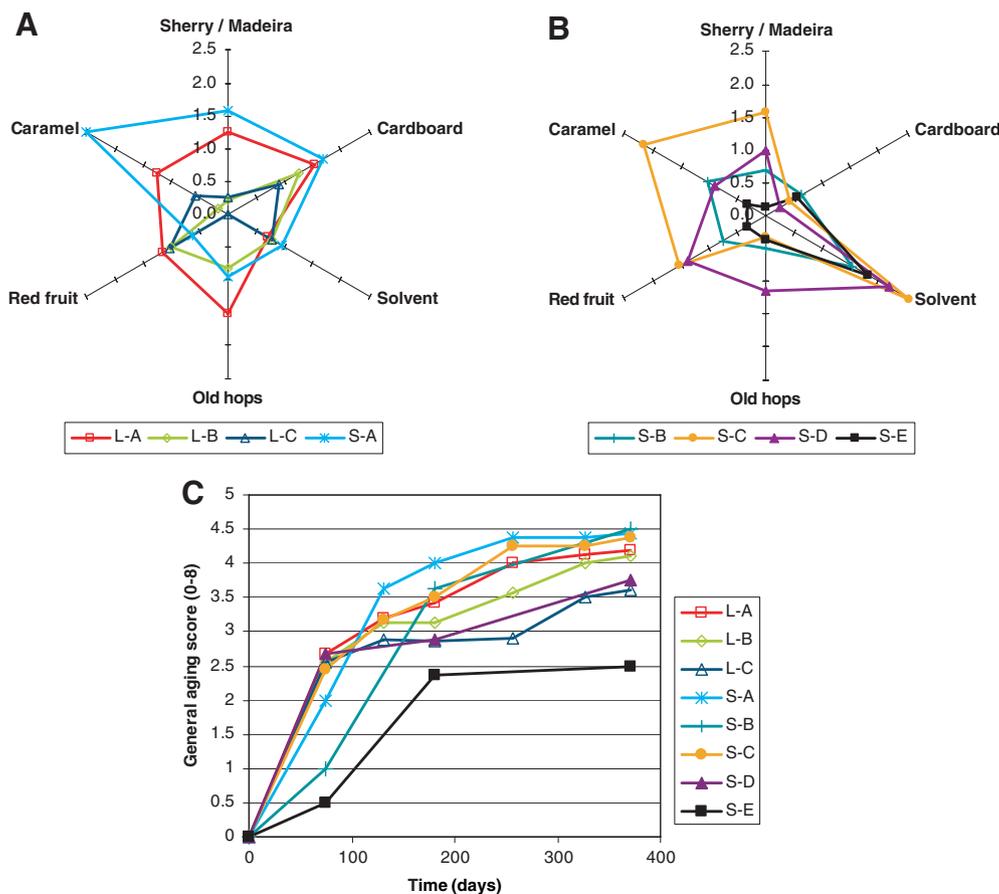


Fig. 5. Flavour profiles (A/ B) of beer samples stored for 180 days at 20 °C and evolutions of the general aging intensity of beer samples aged for one year at 20 °C (C).

compounds during aging. During beer storage, these acids react with ethanol to form ethyl 3-methylbutyrate and ethyl 2-methylbutyrate, which have thresholds of 18–20 µg/l and 7–20 µg/l, respectively (Williams & Wagner, 1978). In the eight beers, levels of these esters (Fig. 4C and D) showed an increase. The highest increase was found with beer S-D, which had the highest bitterness and a high ethanol content. In this beer, the threshold value for ethyl 3-methylbutyrate was exceeded after about 3 months of storage. The formation of ethyl 2-methylbutyrate and ethyl 3-methylbutyrate has been linked with the appearance of winy aging flavours in beer (Williams & Wagner, 1978).

3.6. Sensory results

The determination of the individual flavour characteristics of the 8 beers after storage for 180 days at 20 °C (see Fig. 5A/B) indicates that the dark beers, S-A and S-C, are characterized by intense caramel and Sherry/Madeira-like stale flavours. This must be related to Maillard reactions, which were found to occur more rapidly in these beers. Furthermore, a cardboard flavour was dominant in aged S-A and aged L-A. This can be related to linear aldehyde formation during storage. On the other hand, a solvent-like stale flavour clearly developed in S-C, S-D and S-E. These beers developed the highest concentrations of furfuryl ethyl ether, having such aging flavour. The beer samples S-D and L-A, with a high bitterness, developed a cheesy flavour, similar to the flavour of old hops. The largest levels of degradation products of hop bitter acids were also found in these beers.

When the evolutions of the general aging scores (see Fig. 5) are compared, it becomes clear that the dark beers S-A and S-C, showed the strongest tendency to age, while the beers S-E and S-D, with a high ethanol level, showed the least sensory aging. A high ethanol concentration may, however, cause sensory masking of the stale flavours.

4. Conclusion

In conclusion, the results make it possible to develop effective methods to improve the flavour stability of a beer, depending on the type. In dark and high alcoholic beers, Maillard reactions are the major staling processes and here procedures to reduce the reaction rate must be considered to improve the flavour stability. This can be done by reducing the thermal load on wort during the beer production process, leading to less reactive Maillard intermediates.

When the formation of linear aldehydes is the common staling cause, an attempt at further reduction of the enzymatic lipid oxidation, during mashing or lipid autoxidation during boiling, appears beneficial for the flavour stability of these beers.

Degradation products of hop bitter acids significantly accumulated in the strongly hopped beers during storage. Particularly for these beers, bittering with, e.g., reduced *iso-α*-acids, should improve flavour stability. Moreover,

as in high alcoholic beers, the hop degradation products may react with ethanol to form flavour-active esters, increasing the beer pH may reduce the esterification rate and the rate of various staling processes as well (Kaneda, Takashio, Tomaki, & Osawa, 1997; Lermusieau, Noel, Liegeois, & Collin, 1999; Gijs, Chevance, Jerkovic, & Collin, 2002). Top-fermenting beers often contain high levels of certain esters produced by yeast, which create pleasant fruitiness flavours. The hydrolysis of these esters can be avoided when a pasteurization of the fresh beer is included in the process.

References

- Araki, S., Kimura, T., Shimizu, C., Furusho, S., Takashio, M., & Shinotsuka, K. (1999). Estimation of antioxidative activity and its relationship to beer flavor stability. *Journal of the American Society of Brewing Chemists*, 57, 34–37.
- Bamforth, C. W. (1999). The science and understanding of the flavour stability of beer: a critical assessment. *Brauwelt International*, 98–110.
- Belitz, H. D., & Grosch, W. (1999). *Food chemistry*. Berlin: Springer Verlag.
- Blockmans, C., Devreux, A., Masschelein, C. A. (1975). Formation de composés carbonyles et alteration du goût de la bière. In: *Proceedings of the European Brewery Convention Congress*, 699–713.
- Brenner, M. W., & Khan, A. A. (1976). Furfural and beer color as indices of beer flavor deterioration. *Journal of the American Society of Brewing Chemists*, 34, 14–19.
- Camara, J. S., Marques, J. C., Alves, M. A., & Ferreira, A. C. S. (2004). 3-hydroxy-4,5-dimethyl-2(5H)-furanone levels in fortified Madeira wines: relationship to sugar content. *Journal of Agricultural and Food Chemistry*, 52, 6765–6769.
- Chapon, L., Louis, C., Chapon, S. (1981). Estimation of the reducing power of beer using an iron-dipyridyl complex. In: *Proceedings of the European Brewery Convention Congress*, 307–322.
- Coghe, S., Martens, E., D'Hollander, H., Dirinck, P. J., & Delvaux, F. R. (2004). Sensory and instrumental flavour analysis of wort brewed with dark specialty malts. *Journal of the Institute of Brewing*, 110, 94–103.
- Dufour, J. P., Leus, M., Baxter, A. J., & Hayman, A. R. (1999). Characterization of the reaction of bisulfite with unsaturated aldehydes in a beer model system using nuclear magnetic resonance spectroscopy. *Journal of the American Society of Brewing Chemists*, 57, 138–144.
- European Brewery Convention (1998). *Analytica EBC*. Nürnberg: Getränke-Fachverlag.
- Gijs, L., Chevance, F., Jerkovic, V., & Collin, S. (2002). How low pH can intensify beta-damascenone and dimethyl trisulfide production through beer aging. *Journal of Agricultural and Food Chemistry*, 50, 5612–5616.
- Hashimoto, N., & Eshima, T. (1979). Oxidative degradation of isohumulones in relation to flavour stability of beer. *Journal of the Institute of Brewing*, 85, 136–140.
- Hashimoto, N., & Kuroiwa, Y. (1975). Proposed pathways for the formation of volatile aldehydes during storage of bottled beer. *Proceedings of the American Society of Brewing Chemists*, 33, 104–111.
- Huvaere, K., Andersen, M. L., Olsen, K., Skibsted, L. H., Heyerick, A., & De Keukeleire, D. (2003). Radicaloid-type oxidative decomposition of beer bittering agents revealed. *Chemistry – A European Journal*, 9, 4693–4699.
- Kaneda, H., Kano, Y., Osawa, T., Kawakishi, S., & Kamada, K. (1989). The role of free radicals in beer oxidation. *Journal of the American Society of Brewing Chemists*, 47, 49–53.
- Kaneda, H., Kobayashi, M., Furusho, S., Sahara, H., & Koshino, S. (1995). Reducing activity and flavor stability. *MBAA Technical Quarterly*, 32, 90–94.

- Kaneda, H., Kobayashi, M., Takashio, M., Tamaki, T., & Shinotsuka, K. (1999). Beer staling mechanism. *MBAA Technical Quarterly*, 36, 41–47.
- Kaneda, H., Takashio, M., Tomaki, T., & Osawa, T. (1997). Influence of pH on flavour staling during beer storage. *Journal of the Institute of Brewing*, 103, 21–23.
- Larsen, O. V., Aastrup, S., Nielsen, H., Lillelund, A. C. (2001). Improvement of flavour stability by reduction of trans-2-nonenal – a case study. In: *Proceedings of the European Brewery Convention Congress*, 533–539.
- Lermusieau, G., Noel, S., Liegeois, C., & Collin, S. (1999). Nonoxidative mechanism for development of Trans-2-nonenal in beer. *Journal of the American Society of Brewing Chemists*, 57, 29–33.
- Meilgaard, M. C. (1975). Flavor chemistry of beer; Part II: flavour and threshold of 239 aroma volatiles. *MBAA Technical Quarterly*, 12, 151–168.
- Mikyska, A., Hrabak, M., Haskova, D., & Srogl, J. (2002). The role of malt and hop polyphenols in beer quality, flavour and haze stability. *Journal of the Institute of Brewing*, 108, 78–85.
- Neven, H., Delvaux, F., & Derdelinckx, G. (1997). Flavor evolution of top fermented beers. *MBAA Technical Quarterly*, 34, 115–118.
- Noël, S., & Collin, S. (1995). trans-2-nonenal degradation products during mashing. *Proceedings of the European Brewery Convention Congress*, 483–490.
- Peppard, T. L., & Halsey, S. A. (1982). The occurrence of 2 geometrical-isomers of 2,4,5-trimethyl-1,3-dioxolane in beer. *Journal of the Institute of Brewing*, 88, 309–312.
- Seaton, J. C., & Cantrell, I. C. (1993). The determination of beer color – collaborative trial. *Journal of the Institute of Brewing*, 99, 21–23.
- Shimizu, C., Nakamura, Y., Miyai, K., Araki, S., Takashio, M., & Shinotsuka, K. (2001). Factors affecting 5-hydroxymethyl furfural formation and stale flavor formation in beer. *Journal of the American Society of Brewing Chemists*, 59, 51–58.
- Shimizu, C., Nara, Y., & Takashio, M. (2005). Ethyl pyruvate – a new indicator of flavor stability of beer and its controlling factors. *Journal of the American Society of Brewing Chemists*, 63, 135–141.
- Spaepen, M., Vanoevelen, D., & Verachtert, H. (1978). Fatty-acids and esters produced during spontaneous fermentation of Lambic and Gueuze. *Journal of the Institute of Brewing*, 84, 278–282.
- Stephenson, W. H., & Bamforth, C. W. (2002). The impact of lightstruck and stale character in beers on their perceived quality: a consumer study. *Journal of the Institute of Brewing*, 108, 406–409.
- Vanderhaegen, B., Neven, H., Coghe, S., Verstrepen, K. J., Verachtert, H., & Derdelinckx, G. (2003). Evolution of chemical and sensory properties during aging of top-fermented beer. *Journal of Agricultural and Food Chemistry*, 51, 6782–6790.
- Vanderhaegen, B., Neven, H., Daenen, L., Verstrepen, K. J., Verachtert, H., & Derdelinckx, G. (2004a). Furfuryl ethyl ether: important aging flavor and a new marker for the storage conditions of beer. *Journal of Agricultural and Food Chemistry*, 52, 1661–1668.
- Vanderhaegen, B., Neven, H., Verachtert, H., & Derdelinckx, G. (2006). The chemistry of beer aging – a critical review. *Food Chemistry*, 95, 357–381.
- Vanderhaegen, B., Neven, H., Verstrepen, K. J., Delvaux, F. R., Verachtert, H., & Derdelinckx, G. (2004b). Influence of the brewing process on furfuryl ethyl ether formation during beer aging. *Journal of Agricultural and Food Chemistry*, 52, 6755–6764.
- Williams, R. S., & Wagner, H. P. (1978). The isolation and identification of new staling related compounds from beer. *Journal of the American Society of Brewing Chemists*, 36, 27–31.