Relevance of Oxygen for the Formation of Strecker Aldehydes During Beer Production and Storage

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Introduction & Beer Staling Mechanism

The stale character of beer is a quality issue for many producers and distributors. It is caused by certain carbonyl compounds emerging during storage and, once they exceed their flavor thresholds, producing distinct off-flavors. Despite decades of research, flavor instability is still a major problem for many breweries and pathways are still not clear.

A potential role of free radicals in beer staling was initially investigated by Bamforth and Parsons, and their harmful role in beer was further verified by others.

Free Radical Formation:
1. Activation of molecular oxygen
2. Formation of Reactive Oxygen Species (ROS)
3. Hydroxyl (·OH) and hydroxynitryl (·ESOH) formation in the so-called Fenton reaction; transition metals ions such as iron and copper act as catalysts
4. In beer, potential ‘reclaiming’ of metal ions by reducing substances

While oxygen exposure and oxidative conditions were reported to promote beer staling, the reasons for these findings remain speculative.

Aim of the Study:
To resolve the objective to deploy and further elucidate beer staling and off-flavor development, different factors which potentially affect beer staling were tested in model solutions and in finished beer. Particularly, it was to be tested if ROS are involved in the formation of Strecker aldehydes during beer storage and work production.

Research Justification & Approach

Initial Situation/Research Justification:

- Oxidative deterioration reactions during storage yielding off-flavors are far from being understood.
- Particularly Strecker aldehydes respond to oxygen exposure.
- No reasonable explanation in brewing-related literature.

Hypothesis:

- Reaction Oxygen Species (ROS) such as the hydroxyl radical and the hydroxynitryl radical are involved in the formation of Strecker aldehydes during beer production and storage.

1st step: Trials in buffered model systems at beer-like conditions

- Oxidative degradation of amino acids by Fenton-type reactions
- Effects of oxygen exposure during lab-scale work production

2nd step: Elucidating relevance during beer production/storage

- Beer storage trials using Response Surface Methodology (RSM)
- Labeling experiments to test de novo formation of aldehydes during beer storage

Analytical methods

Staining of aldehyde concentrations in beers and wines were measured using solvent-assisted flavor evaporation (SAFE-GLC) using selected ion monitoring (SIM) mode. Diethyl ether was used to extract beers. Pentanal was used as internal standard (IS).

Hydroxyl radical (·OH) and hydroxynitryl radical (·ESOH) levels were measured using a Bruker® Biotop X-band electron spin resonance spectrometer with a c6-gly-pro-1-oxide-N-tart.dioxyline (PDNO) serving as a spin trap.

Iron concentration in beer was quantified using an ICP-MS Inductively coupled plasma emission spectrometry (ICP-OES) system fitted with a C18 B6 detector and argon as the carrier gas. Extract (2:2:3, color (2:12), pH (2:13), free amino nitrogen (2:6:4:1.1), total polyphenols (2:8.6:1), and bitter units (2:7.1) in beers and wines were analyzed according to MEBAK.

Total purquashed oxygen in beers was measured according to MEBAK (2:28.1:1.2) using a DIGOX 6.1 apparatus (Dr. Thiedig, Berlin, Germany).

Response Surface Methodology (RSM)

High-order knowledge; low error:
- Evaluation of every variable’s effect on the response.
- It is possible to observe the interaction effect of the independent parameters on the response.
- Regression function used for complete design space allows calculation/prediction of variables.

Proposed for RSM analysis:
1. Determination of the fitted model parameters and their levels
2. Selection of the experimental design and prediction and verification of the model equation
3. Use of backward elimination to identify important variables and delete insignificant factors from the model
4. Examine the fitted model plot, interaction plots, and ANOVA statistics (%F, adjusted %F, lack-of-fit test, etc.).
5. Obtain the response surface plot and contour plot of the response as a function of the independent parameters.

Results: Beer Storage Trials Using RSM

Response surface methodology (RSM) and a central composite rotatable (CCRD) design was used to assess the relevance of different factors and potential involvement of ROS in the formation of Strecker aldehydes during beer storage. A commercially available filtered lager-type beer (11.5 °P 4.3 % v/v alcohol, pH 4.11, 32 litters; 46 µl/mg) available in 355 ml bottles served as the base beer for all trials. Labelling experiments with Fe(NO)3 were used to investigate the oxygen-dependent de novo formation of Strecker aldehydes during storage.

Results: Impact of Oxygen During Mashing on Aldehyde Formation

The influence of oxygen during mashing and mash separation was investigated by producing beers from 100 % Pilsner malt either under nitrogen atmosphere or under air atmosphere in a glove box.

- Strecker aldehydes are significantly lowered when oxygen is omitted during mashing.
- All other parameters are unaffected.

Potential involvement of amino acid oxidation during work production!

Conclusions and Outcomes of this Study

The beer staling mechanism was expanded by a lack of known pathway involving hydroxyl and hydroxynitryl radical attack on amino acids thereby forming the corresponding Strecker aldehydes. This study therefore helps to further clarify food staling mechanisms, particularly, as related to the oxidative degradation of amino acids and consequent formation of Strecker aldehydes during wort production and beer storage.

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