Technische Universität Berlin

Practical Aspects to Minimize the Risk of Oxidation and Haze Formation During Beer Production

Frank-Jürgen Methner | MBAA Brewing Summit 2014 | Chicago

Flavor and Haze Stability

Flavor and Haze Stability are important with respect to consumers‘ expectations and beer quality

Factors Influencing Flavor and Haze Stabiliy

- **Oxygen**
  - Brewhouse
  - Mashing-in
  - Brewing liquor
  - Pumping
  - Filtration
- **Metal ions (Fe, Cu)**
  - Raw materials
  - Water
  - Kieselguhr filtration
  - Sulfite content
  - Endogenous antioxidative potential
- **Heat intake**
- **Light (UV-light)**

Fenton- and Haber-Weiss Reaction System

Fenton-Reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (k_1 = 63\ M^{-1}sek^{-1})$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + O_2^{-\bullet} + 2\ H^+$$

Net:

$$2\ H_2O_2 \xrightarrow{Fe} OH^{\bullet} + OH^- + O_2^{-\bullet} + 2\ H^+$$

Haber-Weiss-Reaction:

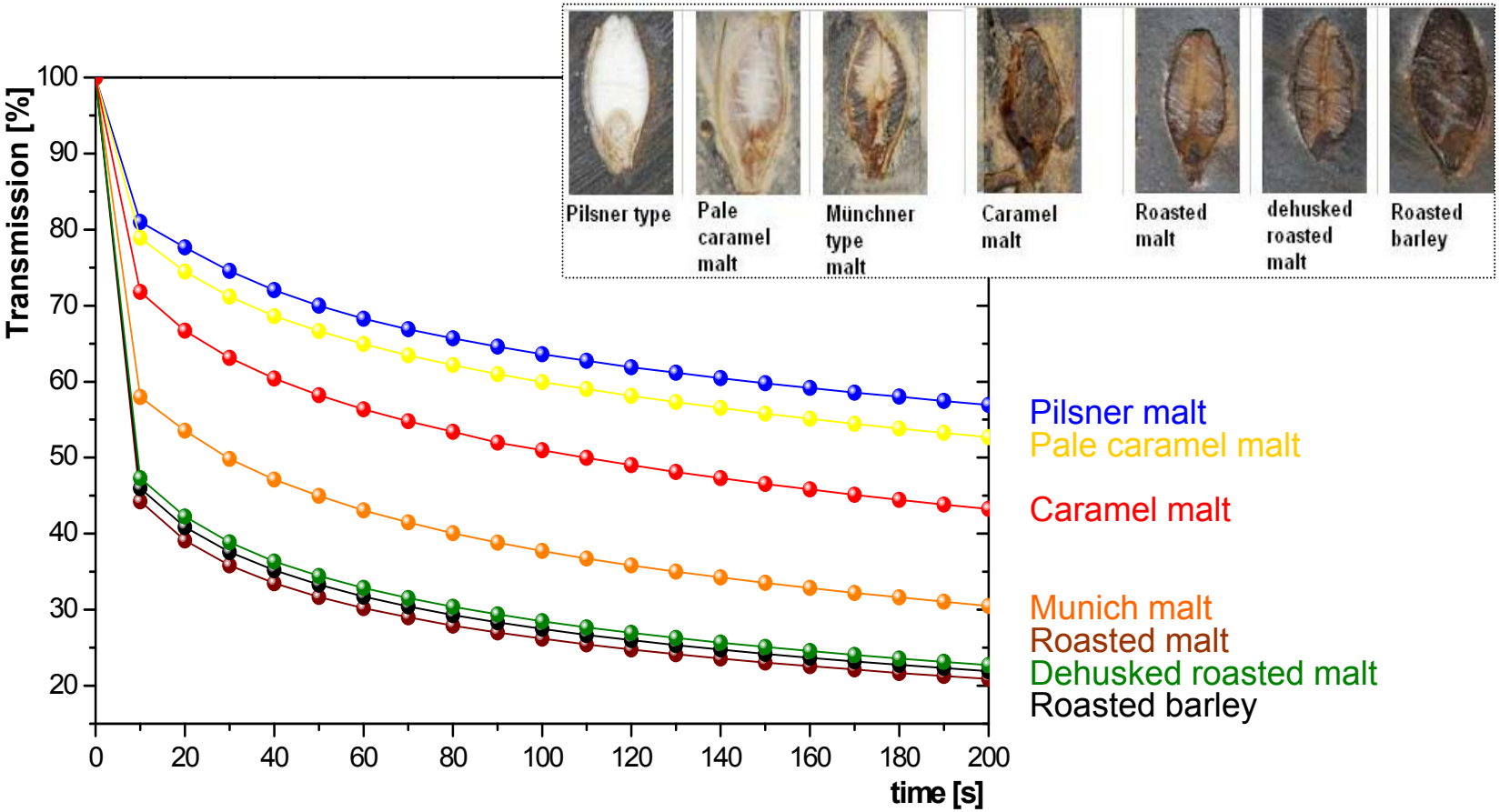
$$Cu^{2+} + O_2^{-\bullet} \longrightarrow Cu^+ + O_2$$

$$Cu^+ + H_2O_2 \longrightarrow Cu^{2+} + HO^{\bullet} + OH^-$$

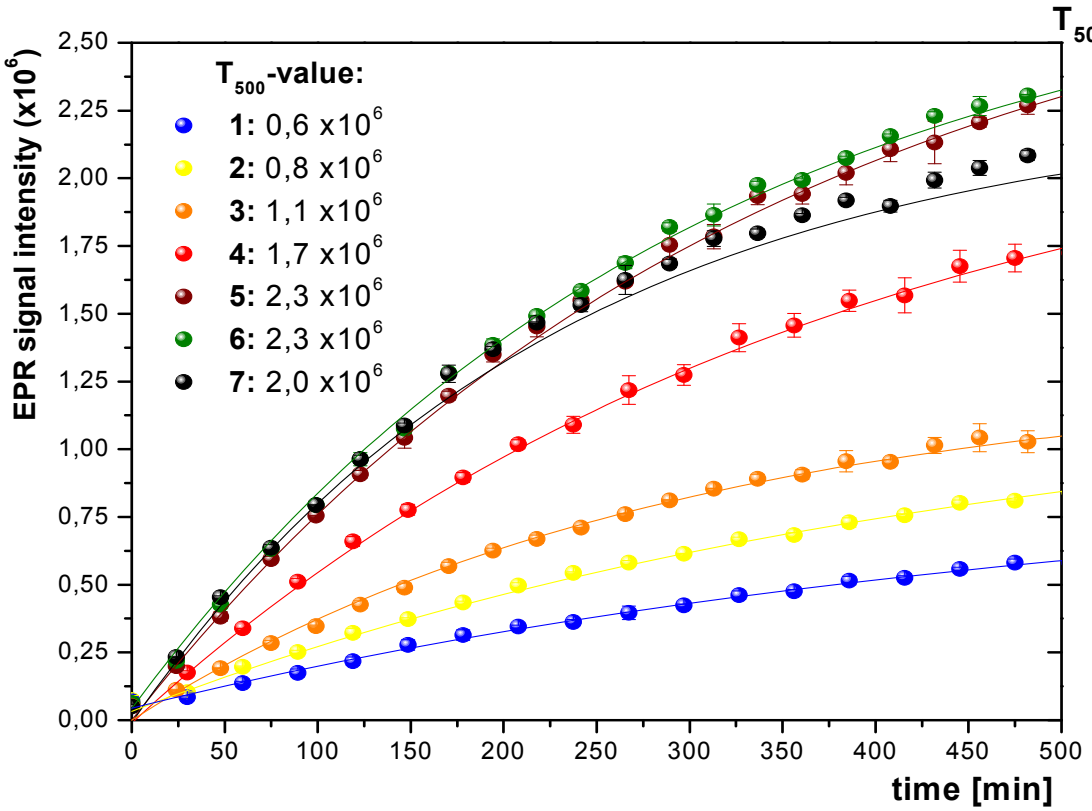
Net:

$$O_2^{-\bullet} + H_2O_2 \xrightarrow{Cu} O_2 + OH^{\bullet} + OH^-$$

Influence of Color Malt on the Reducing Potential



Influence of Colored Malt on the Oxidative Stability



Dehusked roasted malt
Roasted malt
Roasted barley

Caramel malt

Munich malt

Pale caramel malt

Pilsner malt

Acceleration of Fenton-Haber-Weiss Reaction by Reductones / Specific Sugars

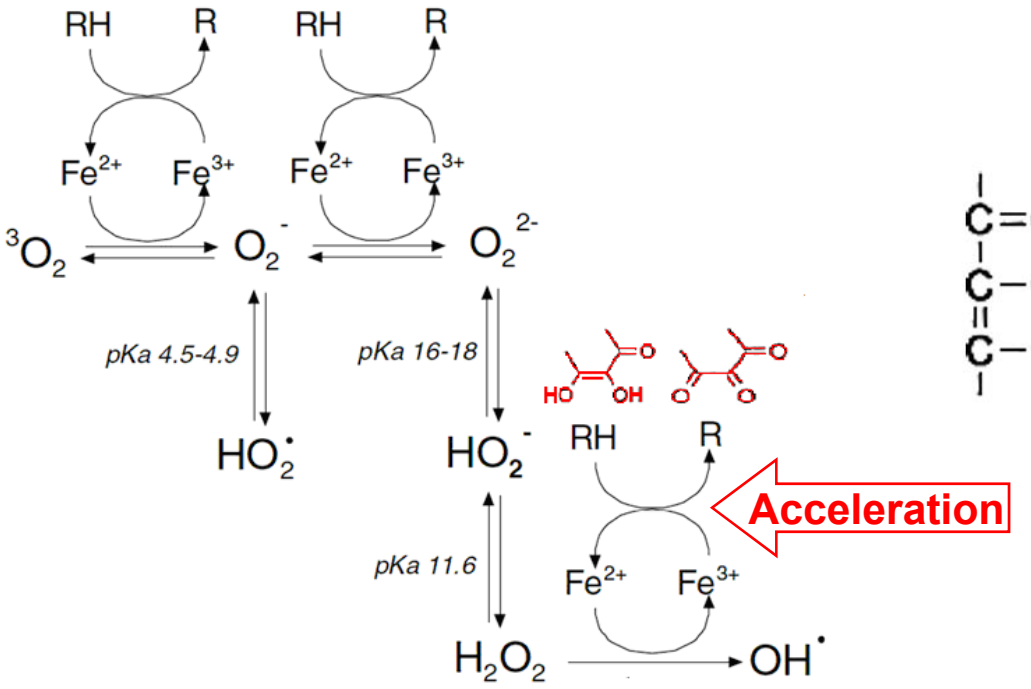
Fenton-Reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (k_1 = 63\ M^{-1}sec^{-1})$$

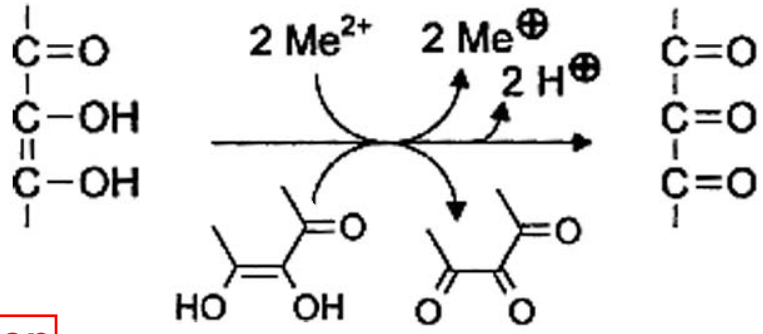
$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + O_2^{-\bullet} + 2\ H^+ \quad (k_2 = 0.01\ M^{-1}sec^{-1})$$

Net:

$$2\ H_2O_2 \xrightarrow{Fe} OH^{\bullet} + OH^- + O_2^{-\bullet} + 2\ H^+$$

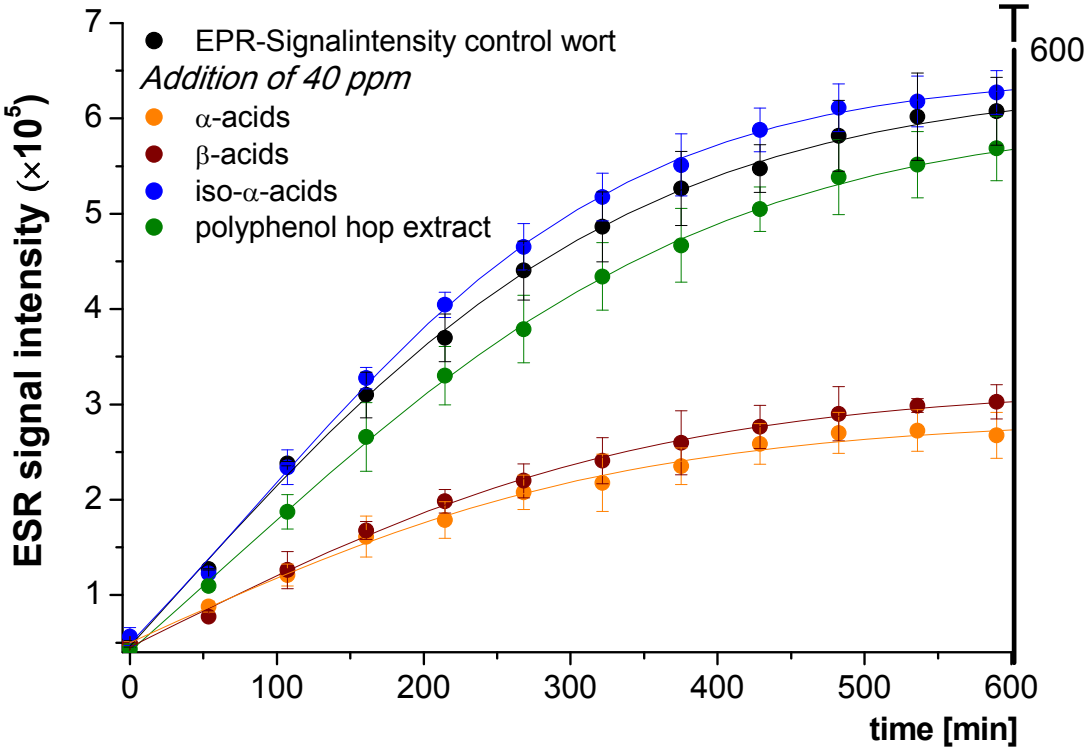


Fast reduction of metal ions (Me) by reductones & specific sugars



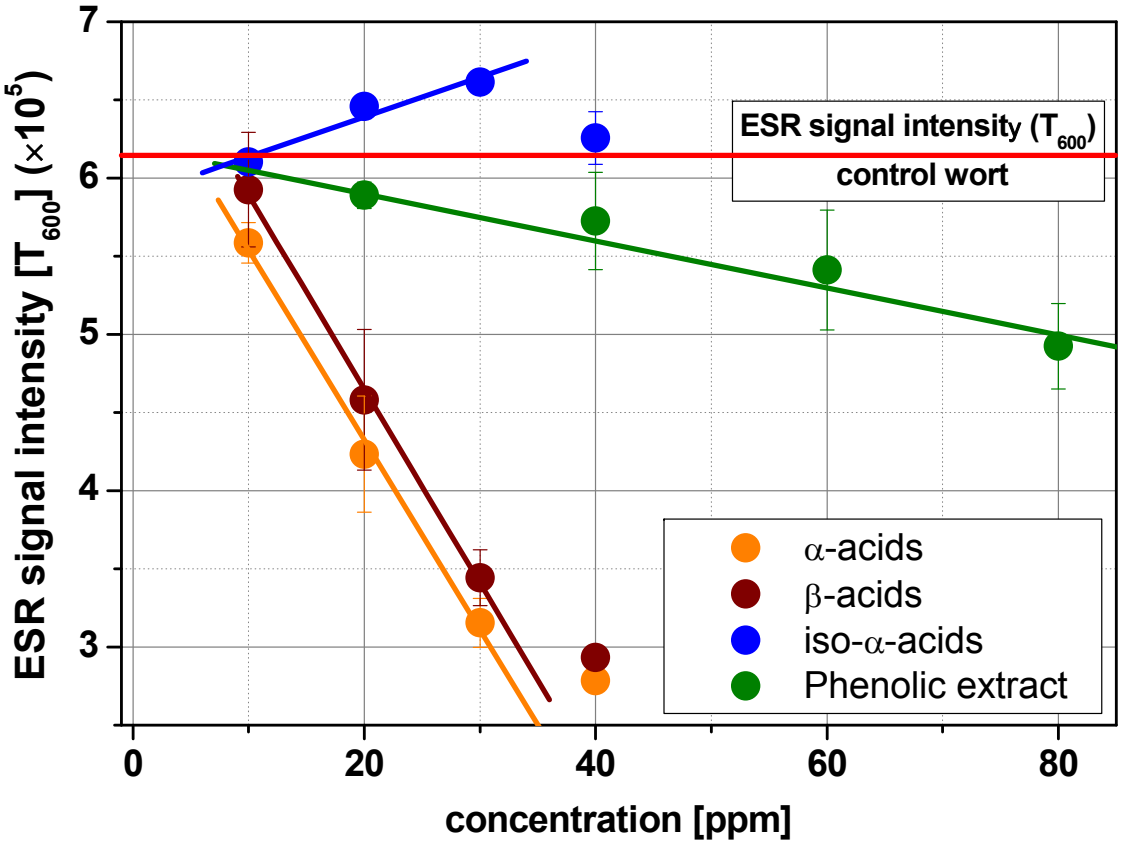
e.g. $2\ Fe^{3+} \rightarrow 2\ Fe^{2+}$
$2\ Cu^{2+} \rightarrow 2\ Cu^{+}$

Influence of Hop Acids on Radical Generation (T_{600}) in Wort

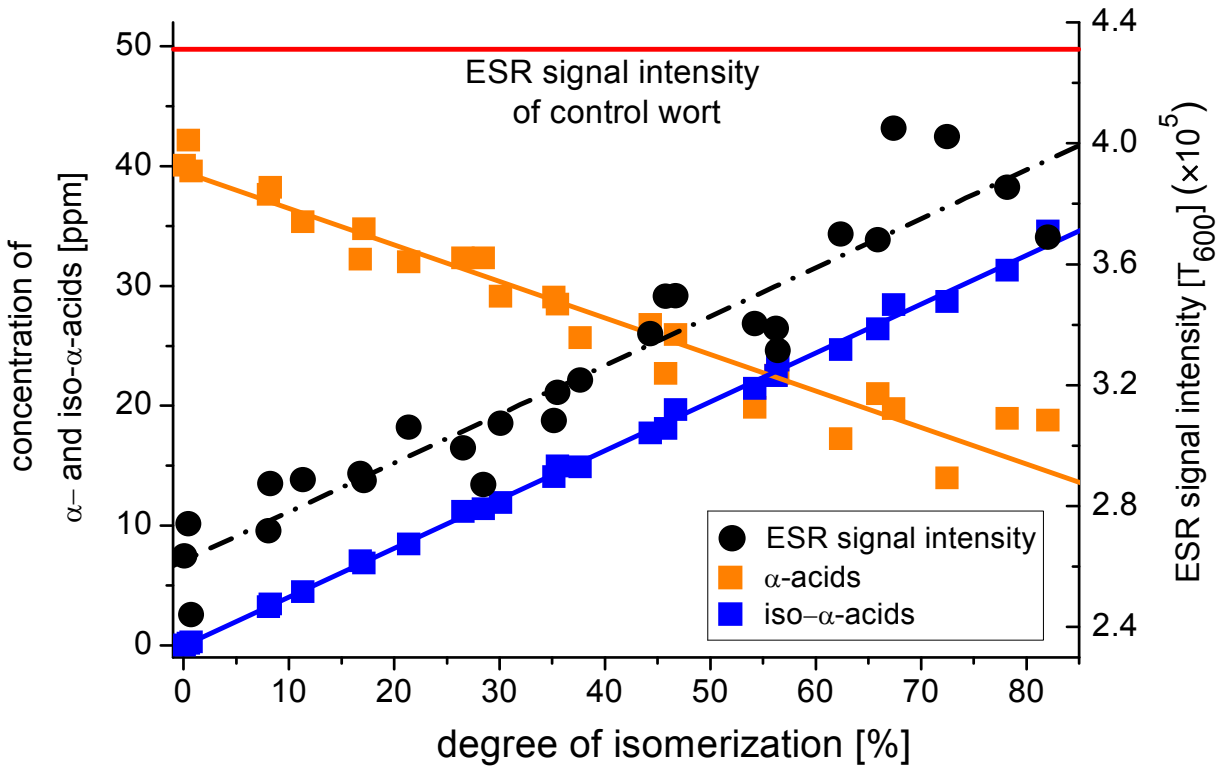


α-acids > β-acids > phenolic extract > iso-α-acids

Influence of Hop Acids on Radical Generation (T_{600}) in Wort



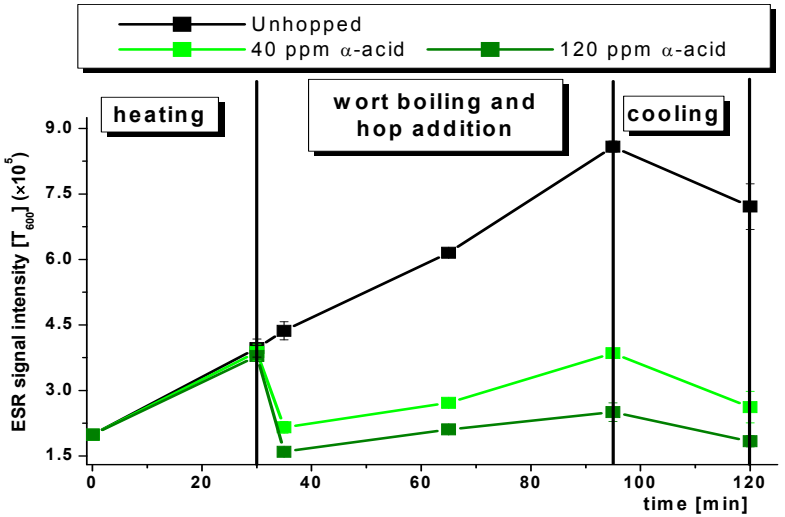
Influence of Hop Isomerization on the Oxidative Wort Stability

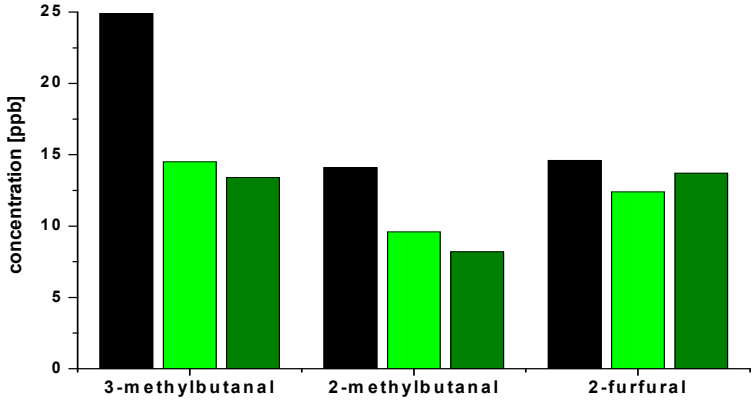


Brewing with 0, 40, 120 ppm Hop α-acids

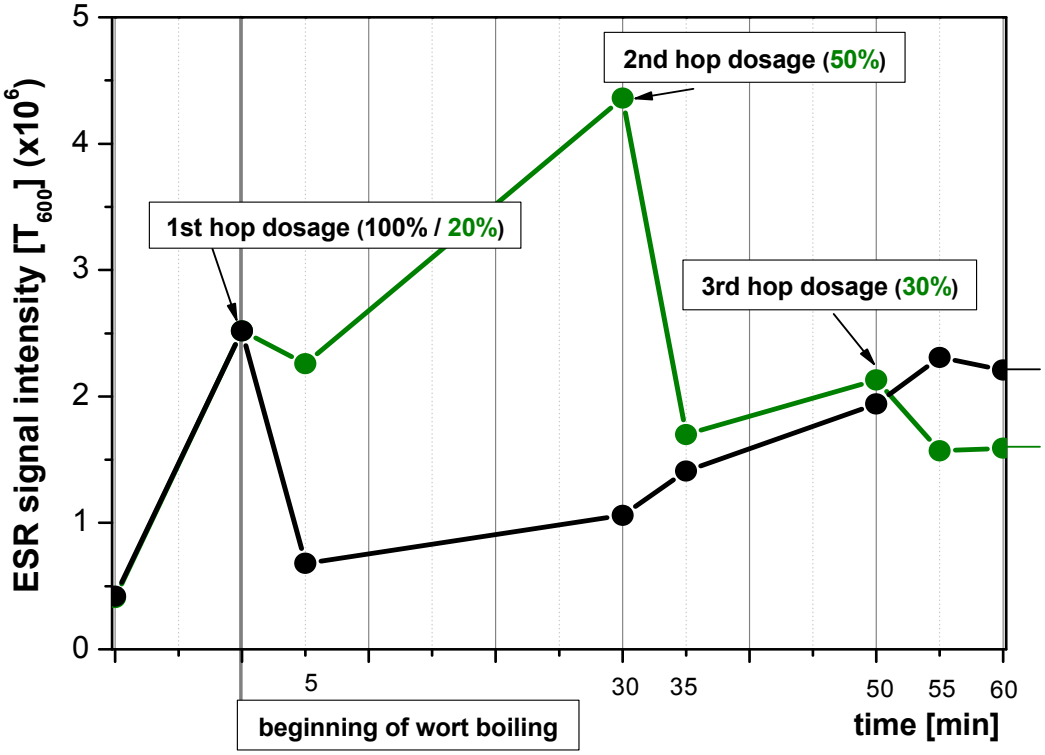
- 100 % Pilsner malt
- CO_2-extract (Hallertauer Perle)
- Hop dosage: 100 %
- at beginning of wort boiling
- Fermenation: 12°C, 6 days
- Forced aging: 30 °C, 4 days

Fermentation, Packaging, forced aging





Standard Hop Dosage vs. Incremental Hop Dosage (100 %)

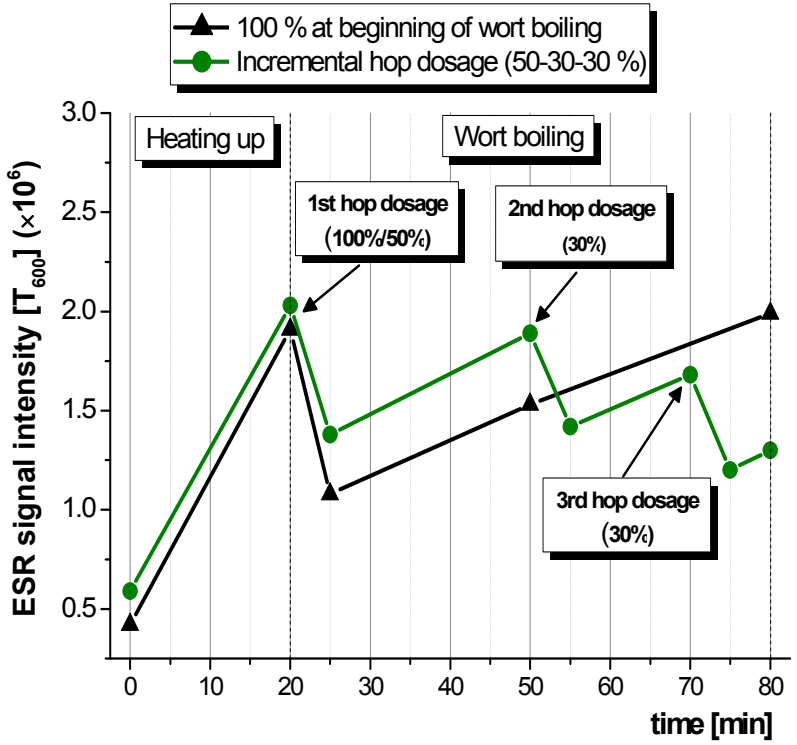


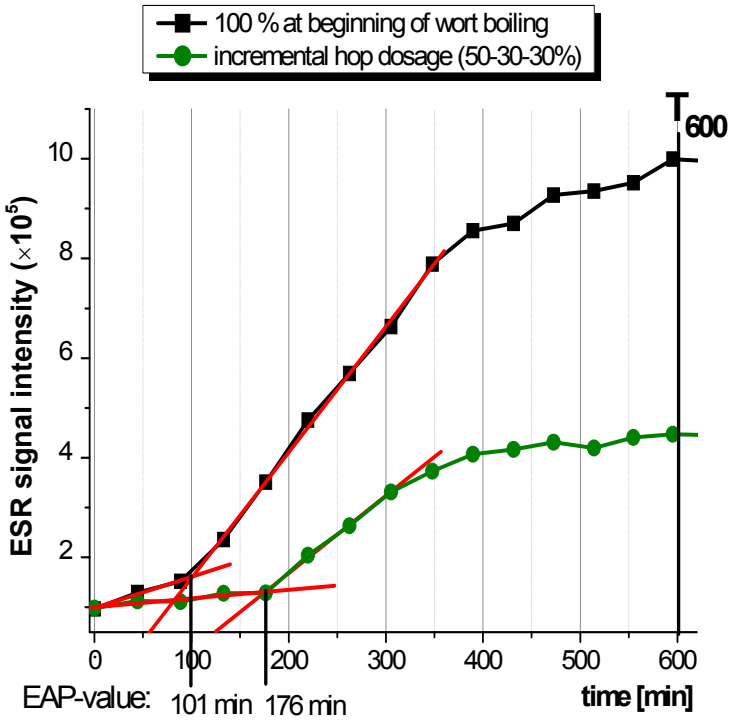
100% hop dosage at the beginning of boiling
incremental hop dosage (20% + 50% + 30% = 100 %)

Lower ESR signal intensity but also 10% lower BU's (BU: 43 / 39)

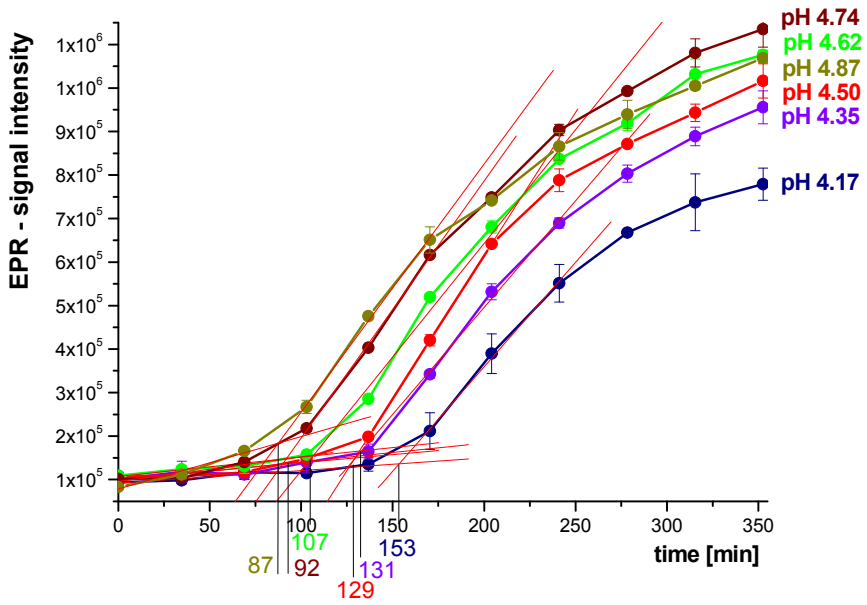
Standard Hop Dosage vs. Incremental Hop Dosage (110 %)

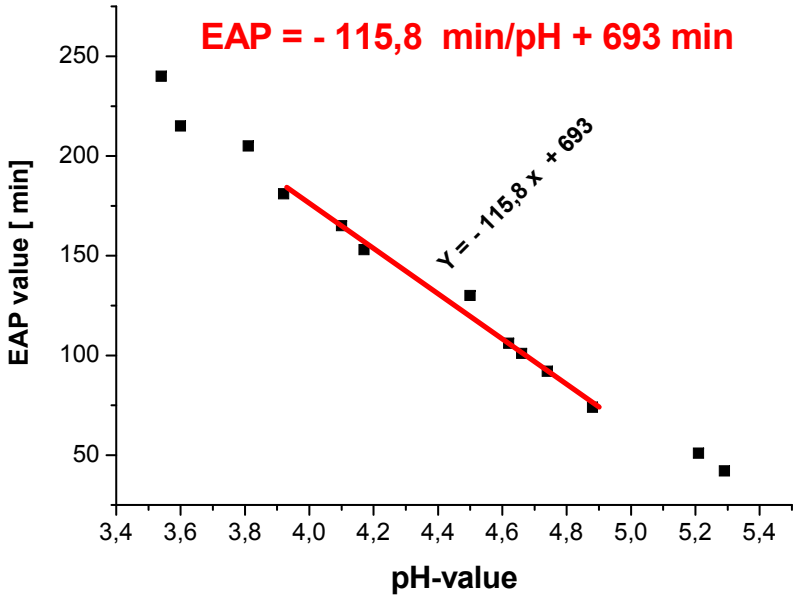
Wort boiling (110 % hops) → Fermentation → Packaging → Beer



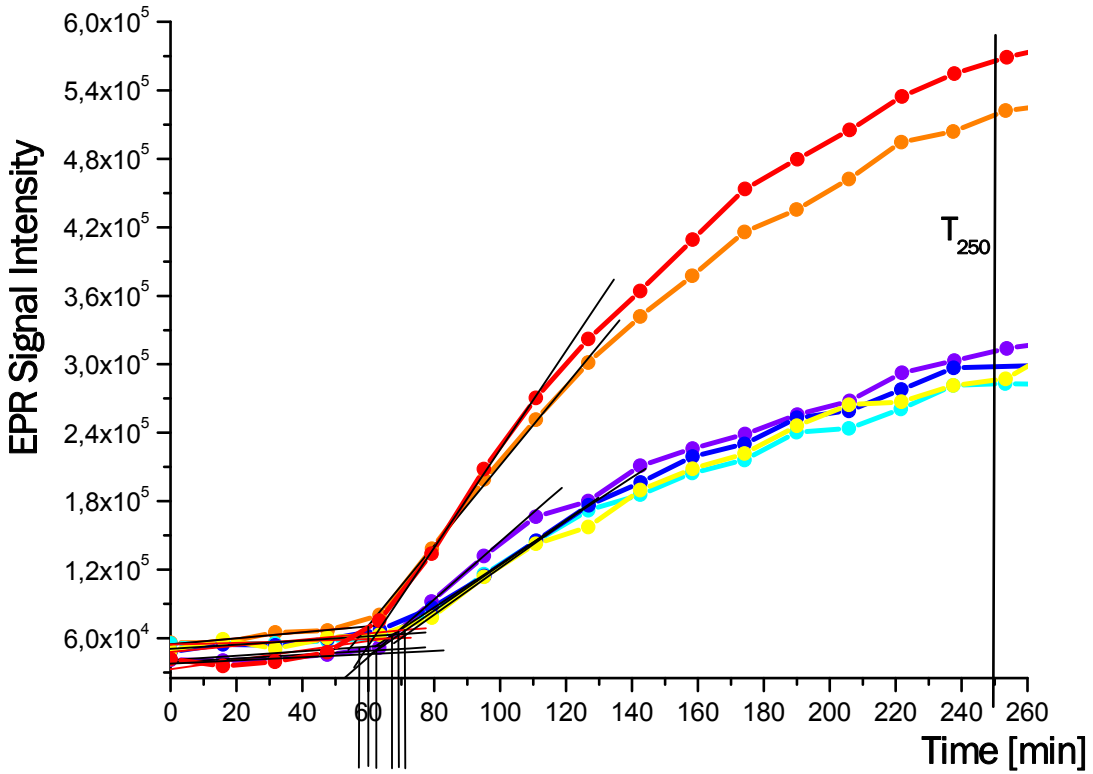


Dependence of the pH-Value on the Oxidative Stability



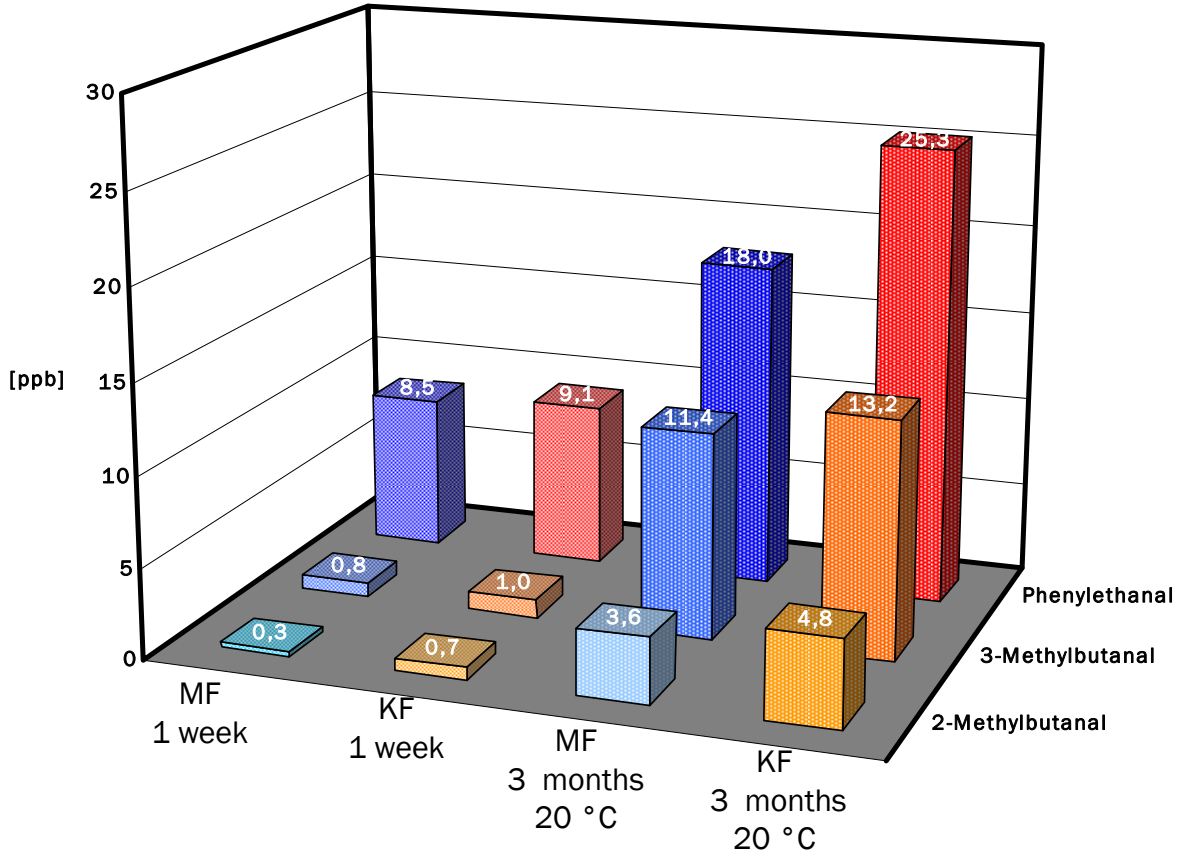


CMF and Kieselguhr Filtration of Beer

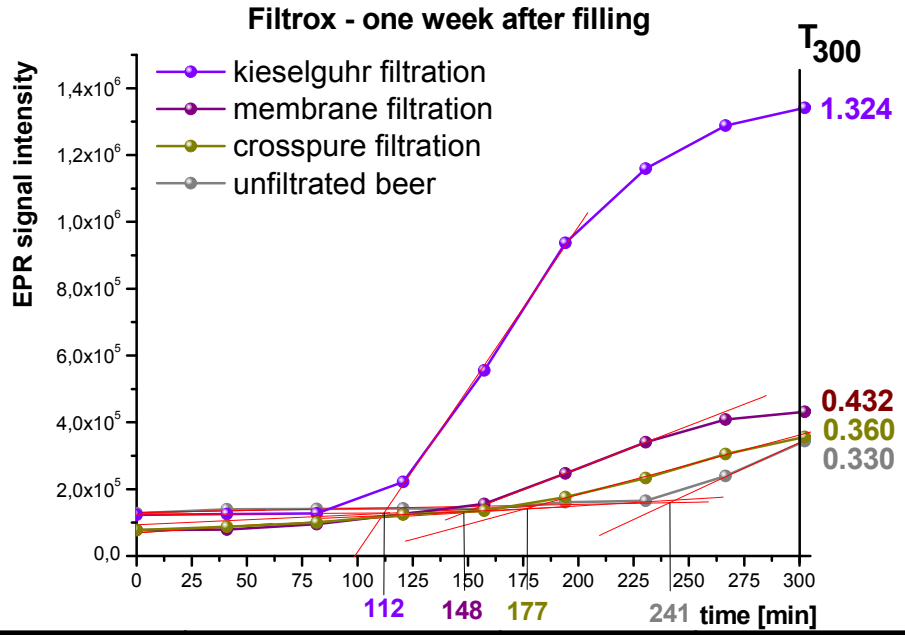


Fe^{2+} CCT: 0.02 mg/L; Fe^{2+} KF: 0.06 mg/L; Fe^{2+} CFF: 0.03 mg/L

Comparison of Strecker Aldehydes in Kieselguhr- and CF-Filtered Beer

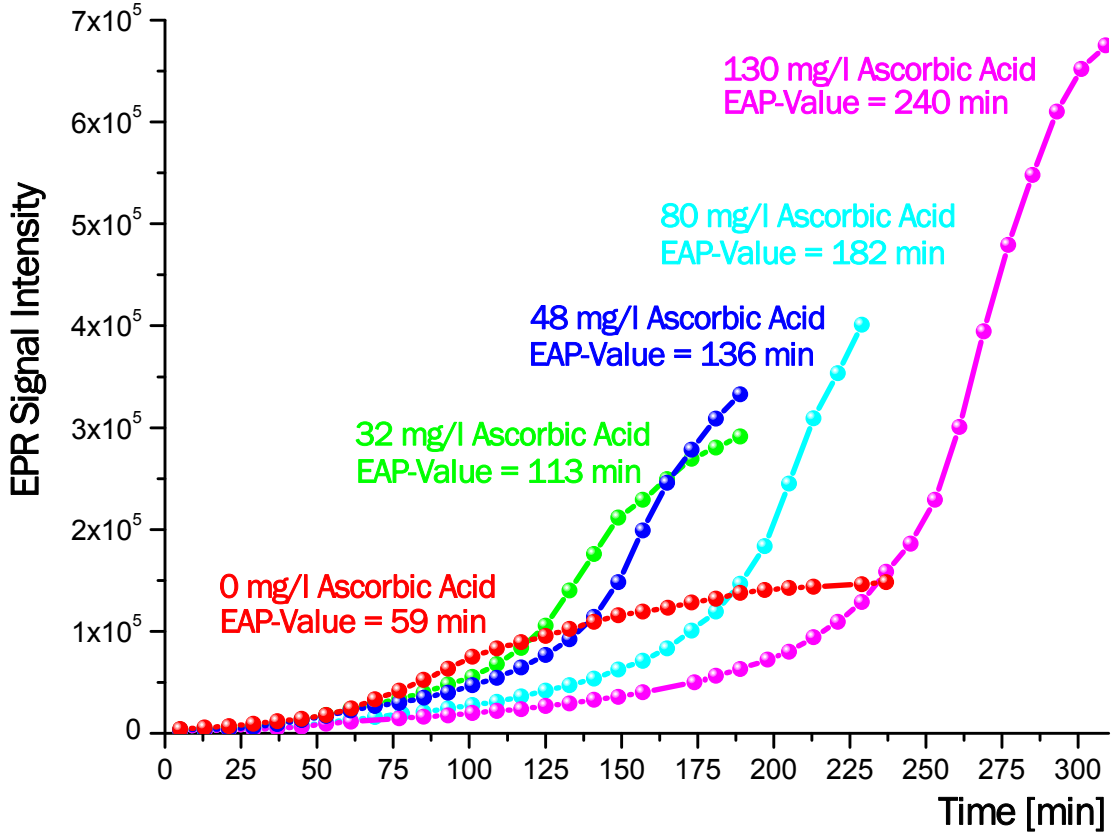


Influence of Filtration on Radical Generation and Iron Content

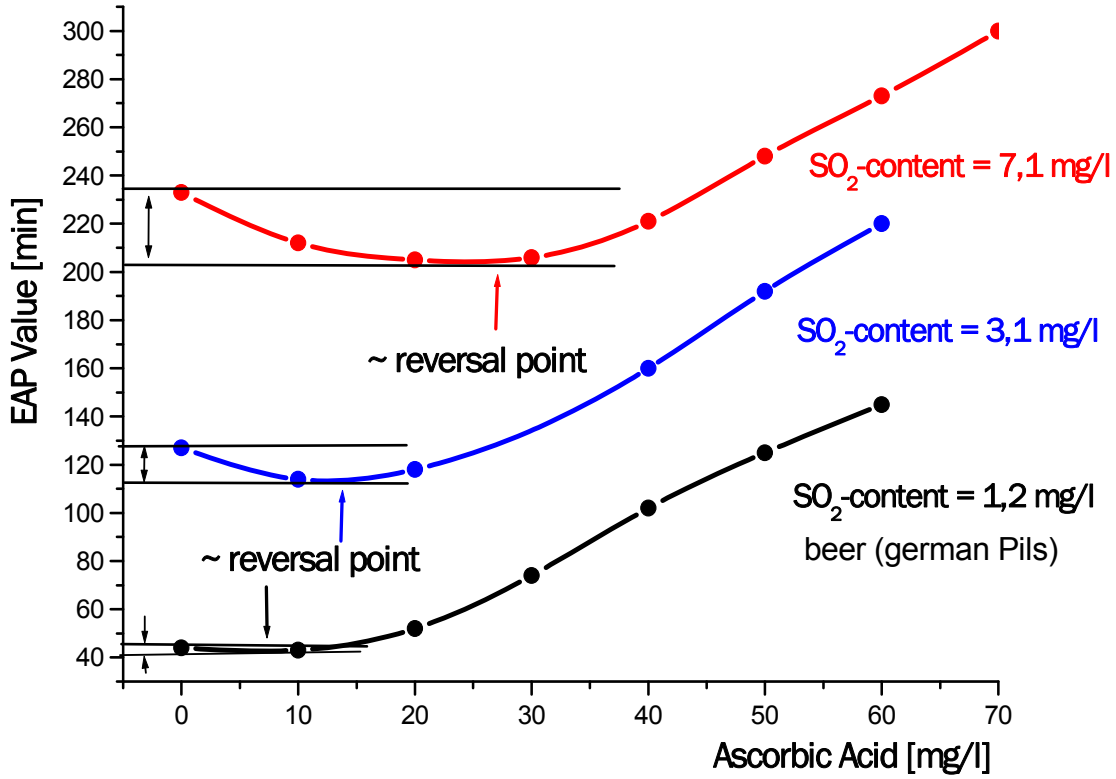


	unfiltered beer	Kieselguhr	Crosspure	Membrane
Fe [µg/L]	–	63	14	17
pH-Value	4.29	4.35	4.33	4.34
EAP-value [min]	241	112	177	148
T_{300}	1.32	0.33	0.36	0.43

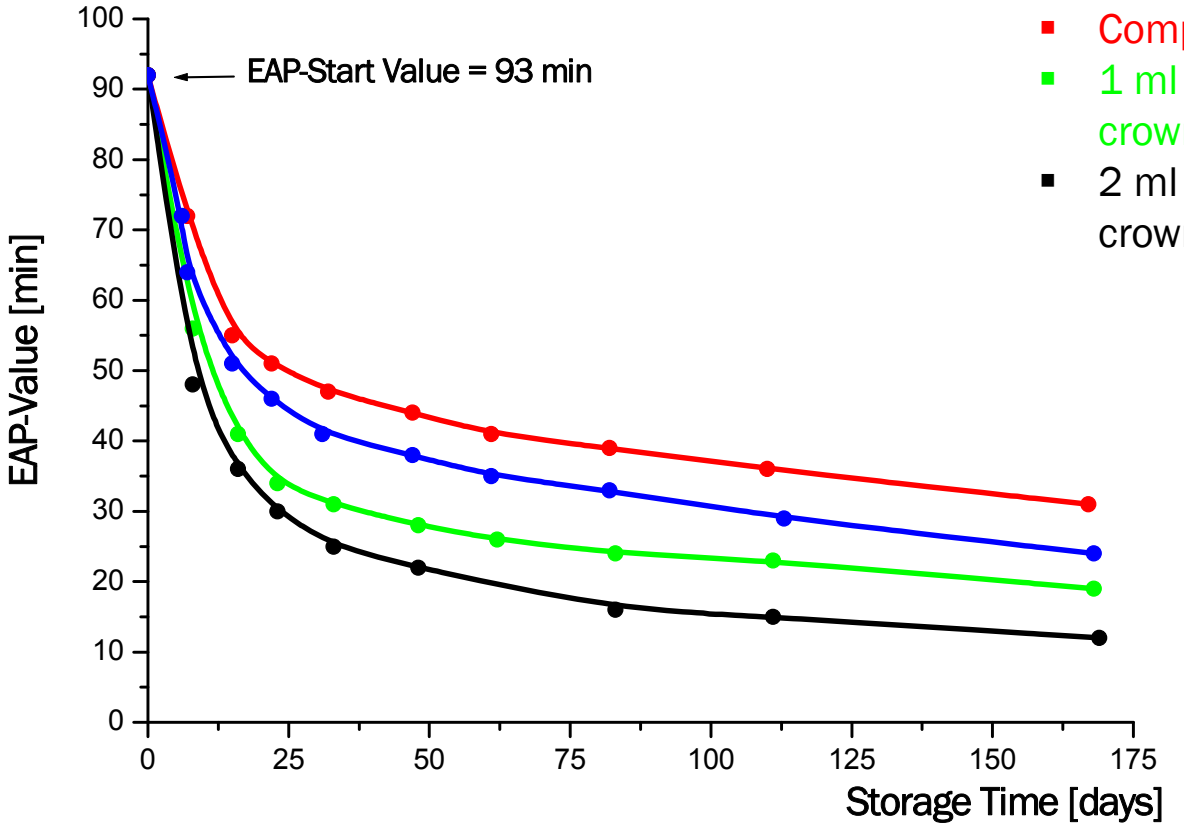
Effect of Ascorbic Acid in Beer as an Antioxidant



Ascorbic Acid in Combination with SO_2-Content

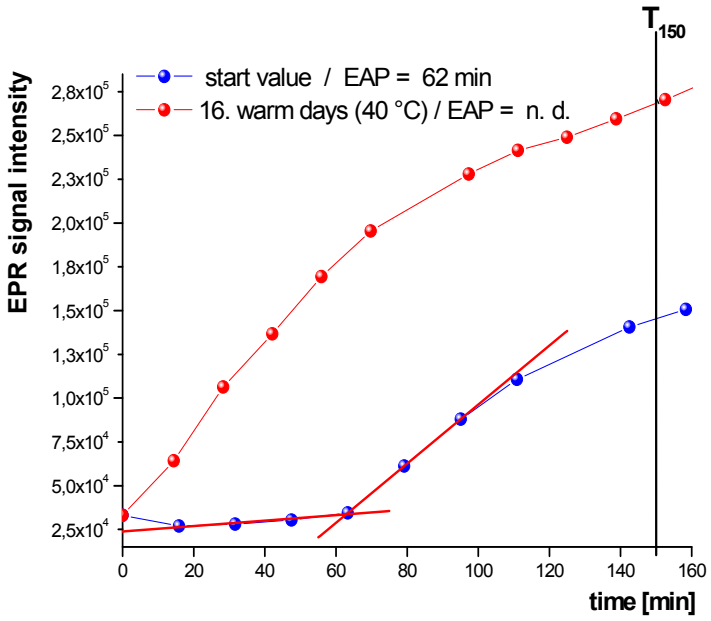


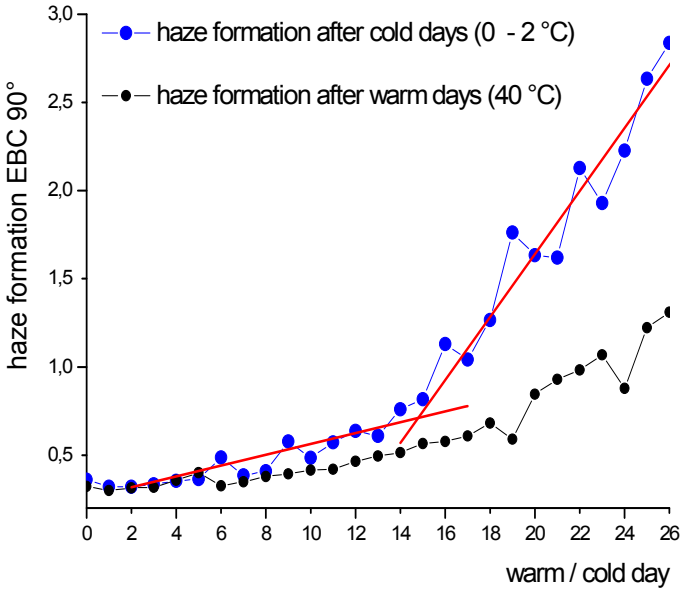
Influence of Crown Cork and Oxygen on the Endogenous Antioxidant Potential



- Standard crown cork
- Compound with O_2-Scavenger
- 1 ml air injection; Standard crown cork
- 2 ml air injection; Standard crown cork

EAP-Value and Haze Formation





- Haze measurements:
- chill haze at 0 ° C
- permanent haze at 20 ° C

- Storage conditions:
- - warm storage 24 h at 40 ° C
- - cold storage 24 h at 0 – 2 ° C

Conclusion

- The oxidative stability and haze stability are closely connected to each other
- Dark malt and dark malt extract lead to an increase of reducing substances, but by reducing Fe^{3+} new catalytic potential is available to accelerate oxidation
- An incremental hop dosage leads to a better flavor stability due to the complexing properties of alpha-acids from hops
- A decreasing pH-value has a positive influence on oxidative stability of beer, but with respect to haze stability it should be not lower than 4.2
- Membrane filtration and alternative filtration aids lead to an improved flavor stability compared to kieselguhr because of lower iron intake
- Ascorbic acid as an antioxidant should not be used in case of higher SO2 content since ascorbic acid has pro-oxidative properties when it is completely oxidized
- The haze formation in beer is increasing, when the EAP (Endogenous Antioxidative Potential) is completely used.

Acknowledgement

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- all other members of our team