Improved bitter substance yield by
Recovery from hot break and yeast washing solution

Francisco Pereira, Thomas Kunz, Mario Marinoff and Frank-Jürgen Methner
Technische Universität Berlin, Institute of Food Technology and Food Chemistry, Brewing and Beverage Technology, Germany

INTRODUCTION
Bitter substance utilization of just 33% of the hop dosage during beer production is considerably low and a disadvantage for the brewing industry.

The aim of this study was to get a deeper insight in the losses of bitterness during different process steps and the investigation of specific influencing factors on the bitterness like pH-value and iron content. Therefore the losses of the bitter units and precipitation of hop bitter acids (α-/iso-α-acids) was monitored during brewing. Furthermore the influence of pH-value and iron content on the precipitation of hop acids was investigated in wort, with and without yeast addition. The scientific findings were applied to develop a new procedure to improve the bitter yield significantly during brewing.

TEST METHODS
Standard beer analyses according to MEBAK [1]:
- pH-value (2.17), Turbidity (2.14.2.1), apparent and real extract (2.13.2.3), Bitter units (2.22.1)
Hops α-/β-acid and iso-α-acid analyses via HPLC:
The hops were isolated and evaluated according to Donley [2] via SPE-HPLC using two different mobile phases (mobile Phase A: 100% methanol, mobile phase B: 55% methanol, 44% water and 1% phosphoric acid). The absorbance was measured at 270 nm and 314 nm, respectively. EBC International Calibration Extracts ICE-12 (iso-α-acids) and a standardized hop extract (α-/β-acids) were used as standards for all HPLC measurements.

Iron concentrations:
Iron concentrations were determined via GF-AAS (graphite furnace atomic absorption spectrometry). After diluting the samples with HNO₃ (10.14 N), the autosampler mixed 20µL of the sample with 20µL of a magnesium matrix modifier solution (0.015mg/5µL) and subsequently sprayed into the graphite-coated furnace.

RESULTS
The results in figure 1 & 2 give an overview of the bitter unit (BU) and Hop acids (α-/iso-α-acids) development in different stages during the brewing process. Beside the losses during wort boiling the major losses in BU occur within the first days of fermentation.

Recent studies have shown that the precipitation of α-acids, linked to iron/copper ions are mainly responsible for losses of bitter substances after hop dosage [3]. The pH-value has a decisive influence on the precipitation of hop acids by complex formation. Consequently acidifying the system leads to reduced BU and iron contents in the wort and beer matrix. The results in Fig. 3, 4 and 5 demonstrate that the pH depending complex formation between hop acids and iron ions are reversible. Regardless of initial pH, adjusting the system to more alkaline conditions leads to an increased yield in BU and higher iron contents in the wort matrix.

Without hop dosage the iron content in wort is unaffected by the pH adjustments (Fig. 4), because of the high affinity of iron ions to hop acids.

The HPLC analysis results in figure 5 demonstrate, that mainly α-acids are affected by the reversible chelate formation with metal ions. Iso-α-acids remain nearly unaffected in combination with α-/β-acids in wort.

Extended trials about the influence of the fermentation process, reveal that the bitter substances precipitate mainly at the beginning of the fermentation process due to the pH drop caused by yeast but the pH-depending precipitation in complexes is reversible. In consequence the absorption of BU by the yeast surface is just circumstantial during fermentation (Tab. 1).

CONCLUSION
Altogether, the results suggest that reversible, pH dependent hop acid complexes including iron ions are mainly responsible for the loss of BU. On this way the bitter substances precipitate with the wort hot break and during the first days of fermentation due to the pH drop caused by yeast. The achieved knowledge about the reversibility of the pH depending precipitations can be used to improve the bitter yield by recovering the hop acids from the hot break and yeast washing solution under specific alkaline conditions and high temperatures. Whereby mainly iso-α-acids with a lower chelate-complex forming potential are generated. After pH readjustment the generated iso-α-acids can be transferred to the brewing process (e.g. start of wort boiling) resulting in an over 100% increased bitter yield. The usually applied method of recirculating the hot break to the lautering process to increase the bitter yield should be reconsidered, since the new method supplementary separates the prooxidative acting iron ions, resulting in a better oxidative beer stability.

BIBLIOGRAPHY
1. MEBAK, Braustechische Analysemethoden. Würze, Bier, Biermischgetränke (s.1): Hamburger Braustechische Analysemethode, 2012