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Usability and Technological Opportunities for a Higher Isomerization Rate of α -Acids – A Review

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Response to Reviewers:	<p>Dear Reviewer,</p> <p>thank you very much for your very valuable comments on our literature review. We have incorporated your comments. Since this is a review and not a recommendation, we do not want to make any recommendations for Craft Brewers in particular. With the review, we would like to focus exclusively on hop isomerization/applications in the brewhouse. The systems and possibilities are compared and the readers can draw the most useful conclusions. Therefore, we have to leave out some aspects in order not to extend the scope too far. We included dynamic low-pressure boiling in the review and were very happy for your advice.</p> <p>Thank you very much!</p> <p>The authors</p>

Usability and Technological Opportunities for a Higher Isomerization Rate of α -Acids – A Review

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16 Declaration

17 The attend review “Usability and Technological Opportunities for a Higher Isomerization Rate of α -
18 Acids – A Review “ has not been previously published elsewhere in any language and is currently not
19 under consideration by any other publication.

20

Abstract

Hops are an essential raw material for beer production in the brewery. The hop constituents give the beer its bitter taste, additional aroma and can make it more stable. As hops are a cost-intensive ingredient, the bitter substance yield plays a major role for breweries. Various approaches are available to increase hop utilization in brewhouses. They range from pre-isomerized hop products or catalysts, which are only utilized outside the German Beer Purity Law, to different procedures, as well as novel brewhouse and dosing equipments. Examples include changes in the mashing process, pre-isomerization systems or fractional wort boiling.

Key words

hops, isomerization rate, hop utilization, iso- α -acids, brewhouse

Introduction

Hops (*Humulus lupulus* L.) with its constituents are an essential raw material for conventional beer production and for the manufacture of beers with additional organoleptic, functional or bacteriostatic properties [1–3]. The female hop plant is predominant [4, 5]. Over 100,000 mt of hops are produced worldwide, mostly for beer production [6]. In addition to its tannins from the leaves, hops also provide the essential oils for aroma and the bitter substances typical for beer from the lupulin glands [5, 7]. The main contributor to beer bitterness is the isomerized form of α -acids (humulones, cohumulones and adhumulones), the iso- α -acids (iso-humulones, iso-cohumulones and iso-adhumulones) [8–10]. In addition, the bitterness is also enhanced by other hop constituents: oxidized α -acids (humulinones), oxidized β -acids (hulupones) and hop polyphenols [11]. Further, α -acids, β -acids (lupulones) and their transformed products have a bacteriostatic and foam-stabilizing effect in beer [12–16]. The foam stabilizing effect is stronger with reduced iso- α -acids such as tetra-iso- α -acids and hexa-iso- α -acids [17]. This review focuses on the hop bitter substances and their isomerization reaction during wort production and how this can be influenced in the brewhouse with different procedures or applications. Up to the present state of knowledge, no review has been found which deals with the practical application opportunities in breweries. However, it is of great importance for the beer production and cost avoidance.

Fundamentals

The hop α -acids isomerization is a thermally driven chemical conversion of α -acids into iso- α -acids [4, 7]. The rearrangement within the molecule takes place via an acyloin ring contraction [18, 19], Figure 1. According to Aitken [20], the reaction is reversible. The isomerization depends on the temperature and must be above 80 °C [21]. De Keukeleire and Verzele [22] discovered in 1970 that the chiral α -acid is present in the absolute R configuration. Two epimers are formed during isomerization reaction: cis- and trans-iso- α -acids. In the boiled wort, six iso- α -acids are existent in total: iso-humulones, iso-cohumulones and iso-adhumulones with their respective cis and trans arrangement [23–25]. The ratio, in which the trans/cis isomers (T/C ratio) are formed, depends on the wort matrix. According to Verzele and De Keukeleire [26], at pH 5.5 and 7.0, 32% trans-iso- α -acids and 68% cis-iso- α -acids resulted. At higher pH values of 9.30 and 11.05, proportionally more cis-isohumulones were formed. Liu et al. [27] revealed that higher pH values (4.66 to 5.86) favor the formation of trans-iso- α -acids. Jaskula et al. [28] observed no significant difference at higher pH values (4.8 to 7.0) on the T/C ratio, despite faster α -acids conversion due to better solubility.

Favorable for the final product is the cis-isomer, because it is the most thermodynamically stable, since both vicinal side chains are in trans configuration [26, 29]. The trans-iso- α -acids are more susceptible to radical autoxidation due to their arrangement of the side chains [30]. De Clippeleer et al. [31] determined, that a beer bittered with cis-iso- α -acids does not necessarily result in an improved flavor stability in addition to the better stability against degradation, compared to the trans-iso- α -acids. They further concluded that the specific degradation of trans-iso- α -acids cannot be linked to the formation of aldehydes attributed to hop bitter acids, such as 2-methylpropanal, 2-methylbutanal and 3-methylbutanal. By contrast, the cause of aldehyde formation during beer aging depends on the malt utilized for brewing, irrespective of the type of bittering.

Hop bitter substance utilization

The utilization for the conversion of α -acids to iso- α -acids during wort boiling is only between 40-65% [26, 32, 33]. Since there is a large number of influencing factors, it is difficult to give an exact estimation. Isomerization in the brewhouse is prevented or blocked by impediments in extracting the α -acids from the hops, the limited solubility of α -acids in wort in combination with the pH value, incomplete isomerization during wort boiling as well as adsorption of α -acids and iso- α -acids on the hot trub. It should be mentioned that, in addition, an oxidative and non-oxidative breakdown of iso- α -acids during wort boiling and in beer takes place, which affects the quality and intensity of bitterness [34, 35]. Reactive oxygen species from lightphotons can be responsible [34, 36, 37]. To prevent degradation of iso- α -acids by UV light in beer, breweries can dose reduced iso- α -acids such as rho-iso- α -acids, hexahydro-iso- α -acids or tetrahydro-iso- α -acids in the cold end [7, 38, 39]. However, different qualities of bitterness must be taken into account [38]. While tetrahydro- and hexahydro-iso- α -acids in lager beer have a similar bitterness to iso- α -acids, rho-iso- α -acids show a significantly lower degree of bitterness [40]. In water solution, rho-iso- α -acids also present a lower bitterness of 67%, hexahydro-iso- α -acids exhibit a slightly increased bitterness of 115% and tetrahydro-iso- α -acids have a doubling with 203% compared to iso- α -acids [41].

The solubility of α -acids has been frequently investigated in the literature [42, 43]. For wort, a compromise has to be determined between a suitable pH value for the solubility of the α -acids and the isoelectric point for proteins, pH 5.2 [44, 45]. Narziss and Back [46] cited from Wöllmer [47], that the α -acids have a solubility limit of 84 mg/L at boiling temperature and a pH value of 5.2. Iso- α -acids show, according to Hertel and Dillenburger [48], a more than 28-fold increase in solubility with over 2400 mg/L. However, the solubility is strongly pH dependent, the higher the alkalization the higher the solubility of the α -acids and the higher the isomerization rate, since a larger amount of α -acids is dissolved. Above a pH value of 12.0 the degradation of iso- α -acids predominates, therefore strong bases should be excluded as isomerization medium [26]. This pH value is not the norm in breweries; hence, this finding is rather decisive for pre-somerization outside the brewery. Nevertheless, it should be noted that mash or wort acidification, and thus a lower pH value for isomerization reaction, results in a pleasant bitterness in beer [49].

In a series of experiments, Askew [50] determined the losses of α -acids and the increase of iso- α -acids in different solutions, at various pH values and temperatures. As a result, the loss of α -acids follows first order reaction. In addition, the experiments showed that this first-order kinetics is not valid back to zero time, if there are large losses in the first minutes after α -acid dosage. Malowicki and Shellhammer [51] confirmed the isomerization reaction to be a reaction first order, where reaction rate depends on the temperature. Additionally, the rate constants and the activation energies for the

isomerization reaction and for the degradation reaction of the iso- α -acids to non-determined substances were specified. Significant degradation reactions of iso- α -acids to humulinic acids, which have no sensory bitterness [52], and other substances [53] occur especially at extended boiling times, which exceeded two half-lives of the α -acids concentration [51]. In order to better assess the degradation of the iso- α -acids, Kappler et al. [54] conducted a series of experiments where pre-isomerized pure iso- α -acids were treated in a variety of liquid media. Degradation of iso- α -acids could be minimized by reducing the original gravity, temperature, water hardness and increasing the pH value. To apply these results in the brewery, e.g. in high-gravity brewing, separate boiling of the hops in the last runnings is suggested [54]. Huang et al. [53] investigated in 2013 the kinetics of iso- α -acids degradation as a function of time, temperature and pH by boiling experiments in an aqueous buffer model system. The results showed that an increase in the pH value of the liquid medium led to an increase in degradation. At the same time, the reaction energy is reduced by about 20 kJ/mol if the pH value is increased from 4.5 to 5.5 and from 5.5 to 6.5. However, with the increase in temperature, the influence of the pH value on the degradation of iso- α -acids decreased significantly.

Another decisive factor, which influences the hop bitter substance yield, is the original gravity. With increasing original gravity the losses of the bitter substance yield increase respectively [27, 55, 56]. Malowicki and Shellhammer [57] revealed in laboratory experiments with different sugar solutions (glucose and maltose each with 10 % w/w), pH values and calcium concentrations that both the different sugar concentrations and the calcium have no influence on the isomerization rate. In the actual wort matrix, trub formation still influences the isomerization reaction, which was not considered in this series of experiments. Jaskula et al. [28] confirmed with a buffer model system that the presence of glucose has no effect on the isomerization reaction at the concentrations used, 12 g glucose/100 g buffer solution and 16 g glucose/100 g buffer solution. In addition, it was found that hop polyphenols also do not have an effect on the conversion of the α -acids.

In the colloid chemical investigations of hop bitter acids, Lüers and Baumann [58] discovered that coagulated protein acts as a strong adsorbent for the bitter substances in hops. This finding was also described by Walker and Parker [59], losses of humulone are depending on the amount of coagulated and precipitated nitrogenous material present in the wort. By removing the coagulated and precipitated colloids before adding the humulone, the adsorption losses could be minimized [59, 60]. Furthermore, it is described that the hop bitter acids, especially iso-humulones, form ionic bonds to the ϵ -amino group of lysine in foaming proteins due to their higher concentration [61]. According to their experimental results, Howard and Slater [62] published an order of chemical reactivity of hop bitter acids for precipitation with proteins (highest first): adhumulone, humulone, cohumulone, iso-adhumulone, iso-humulone, iso-cohumulon. Thereby, the reaction behaviour of the acids is competitive rather than independent [62]. Askew [50] noted that in addition to proteins and tannins, other substances, such as proteoses and peptones, might be responsible for losses of α -acids. Further studies confirmed that cohumulone has the best utilization compared to n- or adhumulone [31–34]. This finding is independent of hop variety or brewhouse [32, 33]. Furthermore, there was no change in the ratio of iso-cohumulone to other iso- α -acids observed during fermentation and maturation [32]. Irwin [35] added, that the better utilization of cohumulone is due to enhanced losses of humulone and adhumulone while wort boiling and of the isomerized products (iso-humulone and iso-adhumulone) during fermentation. On the other hand, it is reported that the less polar iso- α -acids, isohumulones and isoadhumulones, react more strongly with yeast cells, which leads to an increase of isocohumulone in beer [63].

Hanke et al. [64] revealed that increased hot trub is produced with increasing boiling time, with addition of hops, especially during short boiling times, and with wort acidification (Figure 2, a). Acidifications with technical lactic acid (90%) to pH 4.8 at the beginning of boiling initially showed a fine trub, which became coarser and settled. Adjustments at the end of boiling (pH 4.8) resulted in a rapidly forming, coarse trub. Compared to the unacidified wort with a recovery of 33.24% iso- α -acids, the initially acidified wort contained 19.04% and the wort acidified at the end of the boiling process 32.76%. However, the decisive factor for the bitter substance yield is that the formation of trub is also promoted by bitter substances, but the loss of bitter substances through degradation reactions is higher than the losses to the trub [64, 65]. Jaskula et al. [29] found prevailing losses of iso- α -acids with the hot trub. In further experiments by Rakete et al. [66], it was shown that incubation of trans-iso- α -acids with L-proline led to the formation of carboxylic acids and corresponding amides. Since high temperatures prevail during wort boiling and oxygen is involved, it is assumed, that this hydrolytic cleavage also takes place during boiling after the addition of hops. In the subsequent processes (fermentation, maturation, and beer filtration), the losses of α -acids predominate [56, 67].

Irwin et al. [68] studied the relationship between hopping rate (0.12 to 0.21 kg/hL), boiling time and α -acids utilization in a high-gravity (16 °P, pH 5.0) lager wort. The results indicated that the utilization of humulones, ad- and cohumulones decreases with increasing hopping rate (Figure 2, a). Actual relationship between the utilization and additions revealed to be non-linear in the study. McMurrough et al. [69] confirmed in their model system (12.0 °P, pH 4.8), that the utilization of α -acids increases with decreasing α -acids addition. 51% of the iso- α -acids produced (by adding 330 mg/L) could be detected in the hot trub, another 1.5% in cold trub.

The manifold experiments on the influences on hop isomerization consistently revealed combinatorial effects of the parameters on hop isomerization. It was shown by Bastgen et al. [70], that at high original gravity (17 °P) lower pH values were advantageous to achieve a better hop bitter substance yield. The lower the original gravity, the greater the influence of the pH value. Furthermore, an extension of the boiling time is not advisable, especially at higher pH values (pH 7.0) , because the isomerization proceeds faster due to a better solubility of the α -acids (Figure 2, a).

Application in the brewhouse

For breweries, the yield of bitter hops is of importance, since hops are paid according to their α -acids content. It is particularly noticeable in the calculations of craft breweries that hops represent a substantial part of the costs, about 12% of the raw material charges if dry yeast is used and about 20% without the application of dry yeast [71]. There is a variety of technologies, equipments, in-process methods or alternative hop products available to increase the hop bitter yield in the brewhouse. An overview is given in the following section.

In 1952, Specht [72] carried out investigations concerning an extraction process for hop bitter substances in an aqueous solution (water, wort, last runnings) at 50 °C using ultrasonic waves. The bitter substance yield could be increased by applying ultrasonic waves while the extraction rate of the hop tannins was reduced. Further publications by Arentoft et al. [73] and Hoggan [74] have also indicated that ultrasound leads to improved hop extraction in water or wort. His application in the brewhouse was not established.

The utilization of metal ions outside the brewery for the production of pre-isomerized products has been demonstrated and patented several times [75, 76]. A significantly accelerated isomerization of humulones to iso-humulones is reached by cations like Ca^{2+} , Mg^{2+} , Cd^{2+} , Mn^{2+} and Ni^{2+} [77, 78]. However, due to e.g. toxic effects, some cations are not suitable for the food sector. By using Mg^{2+} , a quantitative isomerization took place within 10 min at 70 °C. Neither a significant amount of side products nor degradation products were formed during the conversion [79]. Köller [79] concluded that Mg^{2+} is superior for the application in breweries. Lance et al. [80] found a partial isomerization without recognizable degradation reactions of antimony, barium, cadmium, cerium (III), potassium, sodium, strontium, tin (II) and zinc humulate salts, while iron (II) and iron (III) salts showed partial isomerization with simultaneous degradation.

In investigations concerning the utilization of metal ions in wort (Figure 2, b), Jaskula et al. [28] showed an increase in the isomerization rate by adding 5 mg/L chloride salts of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , and especially by Fe^{3+} . However, Fe^{3+} has a negative effect on taste stability and should therefore be avoided in the finished beer. In total, metal catalysis produced a significant reduction in the T/C ratio at the end of the wort boiling, which implies improved bitterness stability during beer storage [28].

Magnesium sulphate is mostly utilized in breweries [81]. In Germany, the addition of catalysts is not permitted according to the German Purity Law. Therefore, Plapperer [82] performed research on an alternative vessel material, soapstone (magnesium silicate hydrate), for hop isomerization. Under laboratory conditions, ground hop pellets (80 mg/L) were boiled in wort under reflux in a soapstone vessel and comparatively in an Erlenmeyer flask for 60 min. The magnesium contained in the soapstone catalyzed the isomerization reaction, resulting in higher yields. Since a soapstone vessel of the size normally used in breweries is difficult to build, stirrers with appropriate material could be alternatively applied [82].

Apart from the technologies and metal cation dosing mentioned above, there is, as already mentioned, a variety of hop products available on the market (Figure 2, c). The aim of these products is to guarantee a constant quality with low variations in composition, easy handling and a small storage area [1]. In addition, hop products are intended to increase efficiency in the brewery [83]. The following types of hop products are classified: conventional products like hop powder/pellets and hop extracts, isomerized hop products, and other hop products [7, 46, 83, 84]. In 2010, hop pellets (49%) were mainly applied in breweries (Figure 3), followed by extract (28%), isomerized products (21%) and raw hops (2%) [7].

For the manufacturing of the pre-isomerized products, catalysts such as magnesium oxide [85] or magnesium hydroxide [86] are utilized. Alternatively, there have also been studies on producing iso- α -acids by e.g. photoisomerization using an irradiator [87–89]. For pre-isomerized products, there are two application periods: in the brewhouse and after fermentation. Isomerized hop pellets and isomerized kettle extracts are utilized in the brewhouse. Downstream products and post-fermentation bittering products are intended for use after fermentation [86]. With isomerized hop products the yield can be increased to 45-80% compared to 30-35% with conventional products. The comparison of pellets type 45 and a pure ethanol resin extract, determined a slight increase by using a pure ethanol resin extract, whereby different boiling time optima must be considered [90, 91]. Pre-isomerized products in particular increase the hop bitter substance yield and reduce the boiling times in relation to the isomerization rate [84, 92, 93]. Compared to regular pellets, isomerized pellets show especially a significant increase in utilization with late hop addition in the wort kettle. The same applies for the

comparison between a CO₂-Extract and an Isomerized Kettle Extract (IKE) or Potassium-form Isomerized Kettle Extract (PIKE). Isomerized extracts generally achieved a higher yield, since fewer degradation reactions occur during production and they are therefore purer than isomerized pellets [93].

Other possibilities to increase the isomerization rate in the brewhouse are changes in the brewing process.

Jaskula et al. [60] investigated the effects of increasing the mashing-off temperature (Figure 2, d). Mashing took place at 63 °C for 30 min, 72 °C for 20 min and 1 min at 78 °C or 10 min at 95 °C. The mashing-off at 95 °C enabled the coagulation of proteins already during the mashing process and not only afterwards, during wort boiling. Consequently, the adsorption of α -acids on the hot trub during wort boiling was reduced. In addition to the higher utilization of the α -acids (plus approx. 36%) during the 90-minute boiling, an improved profile of iso- α -acids (e.g., reduced quantity of trans-iso- α -acids) was achieved. There were no effects on the taste stability of the beer depending on the mashing-off temperature. Investigations on the impact of starch washed out during the last running process, which can not be degraded due to inactivated α -amylases, were not carried out [60].

Further possibilities include changes of the brewhouse plant, parallel treatment of the hops during wort boiling up to 98 °C (patented by Ziemann Holvrieka GmbH [94–96]), pre-isomerization before wort boiling over 100 °C (patented by GEA Brewery Systems GmbH [97]) [98–101] and dynamic low-pressure boiling [102–104].

Bastgen et al. [105] compared the effects of the lautering systems available on the market (lauter tun, mash filter and continuous rotary disc filter) and their worts on hop isomerization (Figure 2, e). The results demonstrated that the boiling and dosing times of the hops have to be adjusted for each wort in order to obtain optimum isomerization rates. It was found that the total boiling time in relation to the application of the lauter system has to be increased from the continuous system via the mash filter to the lauter tun [105]. It is important to mention that the continuous lauter system separates four parallel wort flows with different compositions. This enables a separate hop isomerization with low concentrated wort (Figure 2, f). Figure 4 shows the parameters of the individual wort flows of the continuous rotary disc filter. The application of the last runnings or the low concentrated wort (depending of the lauter system) for the hop isomerization enables an improved solubility of the α -acids due to the higher pH value. In addition, the wort with its lower extract content contains fewer substances that interfere with the isomerization process. In order to avoid losses of iso-humulones during wort boiling, especially when using iso kettle products, separate hop boiling with the last runnings (Figure 2, g) is advisable according to Kappler et al. [54]. Additionally, Yamashita et al. [106] demonstrated with a fractional boiling of the first wort and the last runnings without hops and appropriate boiling times, that Strecker aldehydes in the wort can be minimized. Some of them are related to beer staling [106]. In the study of the oxidative stability of worts, Wietstock et al. [107] revealed, a hopped wort leads to significantly lower amounts of Strecker aldehydes in stored beer, compared to an unhopped wort. Since, the hop α - and β -acids minimize radicals in the wort during boiling [107].

In the pre-isomerization system presented by Hertel and Dillenburger [108], hops are heated up to 120 °C in a partial wort flow or water in a separate isomerization vessel (Figure 2, h). The temperature control follows a special scheme in order to avoid losses of bitter substances [101]. In addition, this system can be supplemented by an extraction chamber, where the bitter substances are extracted specifically by bitter substance-free wort [109]. Either the isomerized hop fluid is dosed into the wort

kettle while lautering or during wort boiling or it is added to the wort before wort cooling in order to reduce losses due to adsorption to the trub [101, 108]. Investigations proved that it is possible to reduce the hop dosage by 25% in order to achieve the same taste impression compared to conventional hopping [101, 109]. Both hop pellets and hop extract can be processed with the system. The usual extraction-related differences in the yield from pellets to extract can be reduced by the pre-isomerization in the system [110, 111]. The investigations by Takishita et al. [112] showed that pre-isomerization in the brewhouse using hop pellets in a separate vessel at pH 8.0 and a boiling time of 60 min is favourable. Additional trials showed no significant difference in the bitter quality of the beer, despite different dosing times for the pre-isomerized hops.

Dynamic low-pressure boiling (Figure 2, a) takes place at temperatures of 102-103 °C. Dynamic describes the periodic pressure build-up and reduction, which can be repeated as required up to 15 times. Due to the higher temperatures, it thus accelerates hop isomerization with a shortened boiling time. The system is particularly advantageous for breweries at high altitudes, as the boiling temperatures below 100 °C are compensated [102–104].

Another alternative to wort production in the brewhouse is the utilization of hopped wort concentrates. This method is more profitable for smaller breweries as the investment for a brewing plant is bypassed in this way. However, the production of hopped wort concentrates presents the next challenge. During the concentration of the hopped wort in the vacuum falling film evaporator losses of 15% to 25% of iso- α -acids occurred. The exact cause has not yet been clarified [71].

Conclusions

There are many strategies to increase the hop isomerization. Figure 2 summarizes the different options for hop dosing in the brewhouse. In this review, the focus lies on the isomerization of the hop α -acids in the wort, the addition of aroma hop is not considered. Within the German Purity Law the utilization of metal cations and pre-isomerized hop products is not allowed. Remaining options are the adaption of the temperature management e.g. at mashing-off as well as a preisomerization and a parallel hop systems which are utilized to increase the hop yield in the brewhouse. It is not yet clarified what effect the non-degraded starch has on the final product, as the enzymes are inactivated at a mashing-off temperature of 95 °C instead of 78 °C. The two presented hop systems for increasing hop yield in the brewhouse differ due to the prevailing temperature. At temperatures above 100 °C, present in the pre-isomerization system, the isomerization is accelerated due to the higher temperature compared to 98 °C that is present in the parallel isomerization system. However, due to the parallelism, sufficient time for the process is available. For the utilization of such systems in the brewhouse, the existing equipment must be taken into account and an appropriate selection must be made.

This review provides an overview of practical applications for increasing hop yield, but not every possibility seems to be profitable or applicable for every brewery. Basically it is a decision of philosophy and also of the existing equipment as well as the available financial means which concept a brewery should apply.

References

1. Moir, M. Hops—A Millennium Review. *J. Am. Soc. Brew. Chem.* **2000**, *58* (4), 131–146. DOI: 10.1094/ASBCJ-58-0131.
2. Brenner, M. W.; Vigilante, C.; Owades, J. L. A Study of Hop Bitters (Isohumulones) in Beer. *Proceedings. Annual meeting - American Society of Brewing Chemists* **1956**, *14* (1), 48–61. DOI: 10.1080/00960845.1956.12006476.
3. Sanz, V.; Torres, M. D.; López Vilariño, J. M.; Domínguez, H. What is new on the hop extraction? *Trends Food Sci. Technol.* **2019**, *93*, 12–22. DOI: 10.1016/j.tifs.2019.08.018.
4. Stevens, R. The Chemistry of Hop Constituents. *Chem. Rev.* **1967**, *67* (1), 19–71. DOI: 10.1021/cr60245a002.
5. Almaguer, C.; Schönberger, C.; Gastl, M.; Arendt, E. K.; Becker, T. Humulus lupulus - a story that begs to be told. A review. *J. Inst. Brew.* **2014**, *120* (4), 289–314. DOI: 10.1002/jib.160.
6. Jaskula-Goiris, B.; De Cooman, L.; Goiris, K. Humulus Lupulus: Hop Alpha-acids Isomerization – A Review. *BrewingScience* **2018**, *71* (November/December), 85–95. DOI: 10.23763/BrSc18-12jaskula.
7. Biendl, M.; Engelhard, B.; Forster, A.; Gahr, A.; Lutz, A.; Mitter, W.; Schmidt, R.; Schönberger, C. *Hops. Their Cultivation, Composition and Usage*, 1. Aufl.; Brauwelt Knowledge; Fachverlag Hans Carl: Nürnberg, **2015**.
8. Molyneux, R. J.; Eggling, S. B. Recent developments in hop chemistry. *Tech. Q. Master Brew. Assoc. Am.* **1971**, *8* (2), 112–117.
9. De Keukeleire, D.; Vindevogel, J.; Szücs, R.; Sandra, P. The history and analytical chemistry of beer bitter acids. *Trends Analyt. Chem.* **1992**, *11* (8), 275–280. DOI: 10.1016/0165-9936(92)87089-3.
10. Lewis, M. J.; Young, T. W. Hop chemistry and wort boiling. In *Brewing*, Second Edition; Lewis, M. J., Young, T. W., Eds.; Springer Science+Business Media, LLC: New York, **2001**; 259–278.
11. Palmer, J. A Look at Isomerization Reduction Due to Altitude. *Tech. Q. Master Brew. Assoc. Am.* **2017**, *54* (3), 120–122. DOI: 10.1094/TQ-54-3-0806-01.
12. Howard, G. A. Evaluation of hops. I. A review. *J. Inst. Brew.* **1953**, *59* (36-52).
13. Hughes, P. The significance of iso- α -acids for beer quality: Cambridge prize paper. *J. Inst. Brew.* **2000**, *106* (5), 271–276.
14. Peacock, V. Fundamentals of Hop Chemistry. *Tech. Q. Master Brew. Assoc. Am.* **1998**, *35* (1), 4–8.
15. Kloppe, W. J. On head retention. *J. Inst. Brew.* **1954**, *60*, 217–222.
16. Diffor, D. W.; Likens, S. T.; Rehberger, A. J.; Burkhardt, R. J. The Effect of Isohumulone/Isocohumulone Ratio on Beer Head Retention. *J. Am. Soc. Brew. Chem.* **1978**, *36* (2), 63–65. DOI: 10.1094/ASBCJ-36-0063.

17. Kunimune, T.; Shellhammer, T. H. Foam-stabilizing effects and cling formation patterns of iso- α -acids and reduced iso- α -acids in lager beer. *J. Agric. Food Chem.* **2008**, *56* (18), 8629–8634. DOI: 10.1021/jf8011079.
18. De Keukeleire, D.; Verzele, M. The absolute configuration of the isohumulones and the humulinic acid. *Tetrahedron* **1971**, *27*, 4939–4945.
19. Jaskula, B.; Kafarski, P.; Aerts, G.; De Cooman, L. A kinetic study on the isomerization of hop α -acids. *J. Agric. Food Chem.* **2008**, *56* (15), 6408–6415. DOI: 10.1021/jf8004965.
20. Aitken, R. A.; Bruce, A.; Harris, J. O.; Seaton, J. C. Reversibility of humulone-isohumulone transformation. *J. Inst. Brew.* **1969**, *75* (2), 180–181. DOI: 10.1002/j.2050-0416.1969.tb03198.x.
21. Howard, G. A.; Slater, C. A.; Tatchell, A. R. Chemistry of hop constituents XI*. Some observations on the isomerization of humulone. *J. Inst. Brew.* **1957**, *63* (3), 237–248. DOI: 10.1002/j.2050-0416.1957.tb02923.x.
22. De Keukeleire, D.; Verzele, M. The structure and the absolute configuration of (-)humulone. *Tetrahedron* **1970**, *26*, 385–393.
23. Spetsig, L.-O.; Norman, N.; Viervoll, H.; Zackrisson, M.; Ernster, L.; Diczfalusy, E. On the Rearrangement Products of Humulone. *Acta Chem. Scand.* **1958**, *12*, 592–593. DOI: 10.3891/acta.chem.scand.12-0592.
24. Spetsig, L. O. Isolation and characterization of two isohumulone isomers. *J. Inst. Brew.* **1964**, *70* (5), 440–445. DOI: 10.1002/j.2050-0416.1964.tb02012.x.
25. De Keukeleire, D. Fundamentals of Beer and Hop Chemistry. *Quim. Nova* **2000**, *23* (1), 108–112.
26. Verzele, M.; De Keukeleire, D. Chemistry and analysis of hop and beer bitter acids. *Dev. Food Sci.* **1991**, *27* (417).
27. Liu, C.; Zong, M.; Dong, J.; Zheng, F.; Li, Y.; Li, Q.; Gu, G. Effect of boiling parameters on the ratio of trans-iso- α -acids and cis-iso- α -acids in wort. *Tech. Q. Master Brew. Assoc. Am.* **2009**, *46* (4), 1–6. DOI: 10.1094/TQ-46-4-1027-01.
28. Jaskula, B.; Aerts, G.; De Cooman, L. Potential impact of medium characteristics on the isomerisation of hop α -acids in wort and buffer model systems. *Food Chem.* **2010**, *123* (4), 1219–1226. DOI: 10.1016/j.foodchem.2010.05.090.
29. Verzele, M.; Anteunis, M. Isohumulones. *J. Inst. Brew.* **1965**, *71*, 232–239.
30. De Cooman, L.; Aerts, G.; Overmeire, H.; (Keine Angabe). Alterations of the Profiles of Iso- α -Acids During Beer Ageing, Marked Instability of Trans-Iso- α -Acids and Implications for Beer Bitterness Consistency in Relation to Tetrahydroiso- α -Acids. *J. Inst. Brew.* **2000**, *106* (3), 169–178. DOI: 10.1002/j.2050-0416.2000.tb00054.x.
31. De Clippeleer, J.; De Rouck, G.; De Cooman, L.; Aerts, G. Influence of the Hopping Technology on the Storage-induced Appearance of Staling Aldehydes in Beer. *J. Inst. Brew.* **2010**, *116* (4), 381–398. DOI: 10.1002/j.2050-0416.2010.tb00789.x.

32. Forster, A.; Gahr, A.; Schüll, F. What are Auxiliary Bitter Compounds in Hops and how do they Affect the Quality of Bitterness in Beer? *BrewingScience* **2017**, *70*, 203–209. DOI: 10.23763/BrSc17-21forster.
33. Cook, A. H. The outlook on hop utilization. *Tech. Q. Master Brew. Assoc. Am.* **1967**, *4* (3), 177–181.
34. De Clippeleer, J.; De Cooman, L.; Aerts, G. Beer bitter compounds – a detailed review on iso- α -acids: current knowledge of the mechanisms for their formation and degradation. *BrewingScience* **2014**, *67*, 167–182.
35. Hashimoto, N.; Tadashi, E. Oxidative degradation of isohumulones in relation to flavour stability of beer. *J. Inst. Brew.* **1979**, *85* (3), 136–140.
36. Huvaere, K.; Sinnaeve, B.; van Bocxlaer, J.; De Keukeleire, D. Photooxidative degradation of beer bittering principles: product analysis with respect to lightstruck flavour formation. *Photochem. Photobiol. Sci.* **2004**, *3* (9), 854–858. DOI: 10.1039/b403666b.
37. Hildebrand, R. P. The isomerization of humulone. *Tech. Q. Master Brew. Assoc. Am.* **1964**, *1* (2), 142–147.
38. Fritsch, A.; Shellhammer, T. H. The Bitter Qualities of Reduced and Nonreduced Iso- α -acids. *J. Am. Soc. Brew. Chem.* **2009**, *67* (1), 8–13. DOI: 10.1094/ASBCJ-2008-1028-01.
39. Dahlberg, C. J.; Harris, G.; Urban, J.; Tripp, M. L.; Bland, J. S.; Carroll, B. J. Isolation of bitter acids from hops (*Humulus lupulus* L.) using countercurrent chromatography. *J. Sep. Sci.* **2012**, *35* (9), 1183–1189. DOI: 10.1002/jssc.201101109.
40. Fritsch, A.; Shellhammer, T. H. Relative Bitterness of Reduced and Nonreduced Iso- α -Acids in Lager Beer. *J. Am. Soc. Brew. Chem.* **2008**, *66* (2), 88–93. DOI: 10.1094/ASBCJ-2008-0313-01.
41. Todd, P. H.; Johnson, P. A.; Worden, L. R. Evaluation of the Relative Bitterness and Light Stability of Reduced Iso-Alpha Acids. *Tech. Q. Master Brew. Assoc. Am.* **1972**, *9* (1), 31–35.
42. Wöllmer, W. Über die Bitterstoffe des Hopfens. *Berichte Dtsch. Chem. Ges.* **1916**, *49* (1), 780–794. DOI: 10.1002/cber.19160490185|.
43. Spetsig, L.-O. Electrolytic constants and solubilities of humulinic acid, humulone, and lupulone. *Acta Chemica Scandinavia* **1955**, *9*, 1421–1424.
44. De Clerck, J. *Lehrbuch der Brauerei. Band I; Rohstoffe, Herstellung, Einrichtungen*, 2.th ed.; Versuchs- und Lehranstalt für Brauerei: Berlin, **1964**.
45. Denk, V.; Felgentraeger, H. G. W.; Flad, W.; Lenoel, M.; Michel, R.; Miedaner, H.; Stippler, K.; Hensel, H.; Narziss, L.; O'Rourke, T. *European Brewery Convention Manual of Good Practice. Wort Boiling and Clarification*; Fachverlag Hans Carl: Nuremberg, **2002**.
46. Narziss, L.; Back, W. *Die Bierbrauerei. Band 2: Die Technologie der Würzebereitung*, 8., überarbeitete und ergänzte Auflage; Wiley-VCH: Weinheim, **2009**.
47. Wöllmer, W. *Berichte Dtsch. Chem. Ges.* **1916**, *49* (104).

- 427 48. Hertel, M.; Dillenburger, M. Measures for raising yield of bitter substances in beer brewing
1 428 (Part 2): Dissolution and isomerisation processes. *Brauwelt International* **2010**, No. 3, 148-
2 429 152.
- 3
4 430 49. Back, W. *Ausgewählte Kapitel der Brauereitechnologie*, 2. aktualisierte Auflage; Brauwelt
5 431 Wissen; Fachverlag Hans Carl: Nürnberg, **2008**.
- 6
7
8 432 50. Askew, H. O. Changes in hop α acids concentrations on heating in aqueous solutions and
9 433 unhopped worts. *J. Inst. Brew.* **1964**, *70*, 503-513.
- 10
11 434 51. Malowicki, M. G.; Shellhammer, T. H. Isomerization and degradation kinetics of hop
12 435 (*Humulus lupulus*) acids in a model wort-boiling system. *J. Agric. Food Chem.* **2005**, *53* (11),
13 436 4434–4439. DOI: 10.1021/jf0481296.
- 14
15
16 437 52. Hao, J.; Speers, R. A.; Fan, H.; Deng, Y.; Dai, Z. A Review of Cyclic and Oxidative Bitter
17 438 Derivatives of Alpha, Iso-Alpha and Beta-Hop Acids. *J. Am. Soc. Brew. Chem.* **2020**, *78* (2),
18 439 89–102. DOI: 10.1080/03610470.2020.1712641.
- 19
20
21 440 53. Huang, Y.; Tippmann, J.; Becker, T. Kinetic modeling of hop acids during wort boiling. *Int. J.*
22 441 *Biosci. Biochem. Bioinforma.* **2013**, *3* (1), 47–52.
- 23
24 442 54. Kappler, S.; Krahel, M.; Geissinger, C.; Becker, T.; Krottenthaler, M. Degradation of iso- α -
25 443 acids during wort boiling. *J. Inst. Brew.* **2010**. DOI: 10.1002/j.2050-0416.2010.tb00783.x.
- 26
27 444 55. Hudson, J. R. The rationalization of hop utilization: A review. *J. Inst. Brew.* **1965**, *71*, 482–
28 445 489. DOI: 10.1002/j.2050-0416.1965.tb02076.x|.
- 29
30
31 446 56. Laws, D. R. J.; McGuinness, J. D.; Rennie, H. The loss of bitter substances during
32 447 fermentation. *J. Inst. Brew.* **1972**, *78* (4), 314–321.
- 33
34 448 57. Malowicki, M. G.; Shellhammer, T. H. Factors Affecting Hop Bitter Acid Isomerization
35 449 Kinetics in a Model Wort Boiling System. *J. Am. Soc. Brew. Chem.* **2006**, *64*(1), 29–32. DOI:
36 450 10.1094/ASBCJ-64-0029.
- 37
38
39 451 58. Lüers, H.; Baumann, A. Kolloidchemische Studien an den Hopfenbittersäuren. *Kolloid-*
40 452 *Zeitschrift* **1920**, *26* (5), 202–212. DOI: 10.1007/BF01428343.
- 41
42 453 59. Walker, T. K.; Parker, A. Report on the preservative principles of hops. Part XIX:
43 454 Quantitative studies of the changes in preservative value during the boiling and fermentation
44 455 of hopped wort. *J. Inst. Brew.* **1938**, *March*, 140–163.
- 45
46
47 456 60. Jaskula, B.; Spiewak, M.; De Cock, J.; Goiris, K.; Malfliet, S.; Poiz, S.; De Rouck, G.; Aerts,
48 457 G.; De Cooman, L. Impact of Mashing-Off Temperature and Alternative Kettle-Hopping
49 458 Regimes on Hop α -Acids Utilization upon Wort Boiling. *J. Am. Soc. Brew. Chem.* **2009**, *67*
50 459 (1), 23–32. DOI: 10.1094/ASBCJ-2008-1203-01.
- 51
52
53 460 61. Asano, K.; Hashimoto, N. Contribution of hop bitter substances to head formation of beer.
54 461 *Rept. Res. Lab. Kirin Brewery Co., Ltd.* **1976**, *19*, 9–16.
- 55
56 462 62. Howard, G. A.; Slater, C. A. Utilization of humulone and cohumulone in brewing. *J. Inst.*
57 463 *Brew.* **1957**, *63*, 478–482.
- 58
59
60 464 63. Briggs, D. E.; Boulton, C. A.; Brookes, P. A.; Stevens, R. *Brewing Science and practice*;
61 465 Woodhead Publishing Limited and CRC Press LLC: Boca Raton, Cambridge, England, **2004**.

64. Hanke, S.; Back, W.; Tauscher, F. Die Bittere ist entscheidend: Einflüsse auf die Hopfenausbeute und Trubbildung bei der Würzekochung. *Brauindustrie* **2008**, No. 2, 34–37.
65. Hanke, S. Untersuchungen zum Einfluss der Hopfungstechnologie auf die Geschmacksstabilität und Harmonie untergäriger Biere. Dissertation, Weihenstephan, **2009**.
66. Rakete, S.; Berger, R.; Böhme, S.; Glomb, M. A. Oxidation of isohumulones induces the formation of carboxylic acids by hydrolytic cleavage. *J. Agric. Food Chem.* **2014**, 62 (30), 7541–7549. DOI: 10.1021/jf501826h.
67. Jaskula, B.; Goiris, K.; Van Opstaele, F.; De Rouck, G.; Aerts, G.; De Cooman, L. Hopping technology in relation to α -acids isomerization yield, final utilization, and stability of beer bitterness. *J. Am. Soc. Brew. Chem.* **2009**, 67 (1), 44–57. DOI: 10.1094/ASBCJ-2009-0106-01.
68. Irwin, A. J.; Murray, C. R.; Thompson, D. J. An Investigation of the Relationships Between Hopping Rate, Time of Boil, and Individual α -Acid Utilization. *J. Am. Soc. Brew. Chem.* **1985**, 43 (3), 145–152. DOI: 10.1094/ASBCJ-43-0145.
69. McMurrough, I.; Cleary, K.; Murray, F. Applications of High-Performance Liquid Chromatography in the Control of Beer Bitterness. *J. Am. Soc. Brew. Chem.* **1986**, 44 (2), 101–108. DOI: 10.1094/ASBCJ-44-0101.
70. Bastgen, N.; Becher, T.; Titze, J. Influencing factors on hop isomerization beyond the conventional range. *J. Am. Soc. Brew. Chem.* **2019**, 77 (2), 126–133. DOI: 10.1080/03610470.2019.1587734.
71. Titze, J.; Huber, H. H.; Hamel, C. *The potential of wort concentrate used for beer production to enable cost optimisation in craft breweries*. Poster, 12th Trends in Brewing: Ghent, **2016**.
72. Specht, W. Zur Extraktion von Hopfenbitterstoffen durch Ultraschall. *Zeitschrift für Lebensmittel-Untersuchung und -Forschung* **1952**, 94. Band (3 (März)), 157–166.
73. Arentoft, H.; Mollering, A. Brewing Process. US 000002830904 A. **1958**.
74. Hoggan, J. Ultrasonic hop extraction. *Ultrasonics* **1968**, October, 217–219.
75. Köller, H.; Hartl, A.; Kirchner, G. Verfahren zur Herstellung von Iso humulon. DE 000001618059 C. **1967**.
76. Clarke, B. J.; Hildebrand, R. P.; Lance, D. G.; White, W.; Skinner, R. N. Preparation of water soluble isomerised hop extract. US 000003956513 A. **1976**.
77. Köller, H. Die katalytische Beschleunigung der Isomerisierung von Humulon zu Isohumulon durch Metallionen. *Tetrahedron Letters* **1968**, No. 40, 4317–4320.
78. Atlantic Research Institute Ltd. Process for the isomerisation of humulone to isohumulone by catalytic acceleration with metal salts. GB 1158697 C2. **1967**.
79. Köller, H. Magnesium Ion Catalysed Isomerization of Humulone: A New Route to Pure Isohumulones. *J. Inst. Brew.* **1969**, 75, 175–179.

80. Lance, D. G.; White, A. W.; Hildebrand, R. P.; Clarke, B. J. The effect of heat on metal humulate and isohumulate salts. *J. Inst. Brew.* **1975**, *81* (5), 364–367. DOI: 10.1002/j.2050-0416.1975.tb06406.x.
81. Holbrook, C. J. Brewhouse operations. In *The Craft Brewing Handbook: A Practical Guide to Running a Successful Craft Brewery*; Smart, C., Ed.; Woodhead Publishing Series in Food Science, Technology and Nutrition; Elsevier Science & Technology: San Diego, **2020**; 65–109.
82. Plapperer, R. F.-X. Untersuchungen zur Chiralität und Isomerisierung von Hopfenbitterstoffen. Dissertation; Technical University of Munich, Weihenstephan, **2015**.
83. Hughes, P. S.; Simpson, W. J. Production and composition of hop pellets. *Tech. Q. Master Brew. Assoc. Am.* **1993**, *30* (4), 146–154.
84. Clarke, B. J. Hop products. *J. Inst. Brew.* **1986**, *92* (March-April), 123–130.
85. Kostrzewa, D.; Dobrzyńska-Inger, A.; Rój, E.; Grzęda, K.; Kozłowski, K. Isomerization of hop extract α -acids. *J. Inst. Brew.* **2016**, *122* (3), 493–499. DOI: 10.1002/jib.349.
86. Schönberger, C. The processing of hops. In *Brewing - New Technologies*; Bamforth, C. W., Ed.; Woodhead Publishing, Cambridge, UK, **2006**; 123–148.
87. Viriot, M. L.; Andre, J. C.; Niclaude, M.; Bazard, D.; Flayeux, R.; Moll, M. Improvement of the bitterness of hops: photoreactions of alpha acids. *J. Inst. Brew.* **1980**, *86* (1), 21–24. DOI: 10.1002/j.2050-0416.1980.tb03949.x.
88. De Keukeleire, D.; Blondeel, G. M. The mechanism of the regio- and stereospecific photorearrangement of humulone to the beer bitter component trans isohumulone. *Tetrahedron Letters* **1979**, *15*, 1343–1346.
89. Sharpe, F. R.; Ormrod, I. H. L. Fast isomerisation of humulone by photo-reaction: preparation of an HPLC standard. *J. Inst. Brew.* **1991**, *97* (1), 33–37. DOI: 10.1002/j.2050-0416.1991.tb01050.x.
90. Mitter, W.; Kessler, H.; Biendl, M. Bitterhopfengabe in Form von Pellets und Extrakt und deren Einfluss auf Würze und Bier. *Brauindustrie* **1999**, No. 10, 560–563.
91. Mitter, W.; Kessler, H.; Biendl, M. Beobachtung einer Verwandlung: Isomerisierungsverlauf der Alphasäuren im grosstechnischen Massstab. *Brauindustrie* **2000**, No. 3, 142–145.
92. Hudson, J. R.; Rodin, A. D.; Howard, G. A. Metal derivatives of isohumulone: Addendum: preparation of isohumulone A. *J. Inst. Brew.* **1959**, *65* (5), 414–418. DOI: 10.1002/j.2050-0416.1959.tb01479.x.
93. Wilson, R. J. H.; Roberts, T.; Smith, R. J.; Biendl, M. Improving hop utilization and flavor control through the use of pre-isomerized products in the brewery kettle. *Tech. Q. Master Brew. Assoc. Am.* **2001**, *38* (1), 11–21.
94. Gehrig, K.; Wasmuth, K.; Becher, T.; Ziller, K.; Benninghaus, T. Verfahren zum Isomerisieren von Bestandteilen eines Hopfensubstrats in einem Bierbereitungsverfahren, entsprechende Vorrichtung und Verwendung des Isomerisats. DE 10 2016 121 014 A1. **2016**.

95. Gehrig, K.; Wasmuht, K.; Becher, T.; Ziller, K.; Benninghaus, T. Process for isomerization of constituents of a hops substrate in a beer preparation method, corresponding apparatus and use of the isomerisate. CN109963933A. **2017**.
96. Gehrig, K.; Wasmuht, K.; Becher, T.; Ziller, K.; Benninghaus, T. Process for isomerization of constituents of a hops substrate in a beer preparation method, corresponding apparatus and use of the isomerisate. EP3535379A1. **2017**.
97. Hertel, M. Method and device for the production of beer. EP 2 227 535 B1. **2008**.
98. Förster, F.; Michel, R. Die Zukunft des Brauens wird kontinuierlich: Brewery 4.0. *Brauwelt* **2017**, No. 50, 1490-1491.
99. Bastgen, N.; Wasmuht, K. A Novel Mash Filtration Process (Part 2): Fractional Wort Boiling. *Brauwelt International* **2017**, 35 (04), 270–273.
100. Bastgen, N.; Titze, J.; Becher, T. *A Novel Brewhouse Concept - How to Improve the Brewing Process and Quality by Treating Wort Fractions. Poster: Ghent*, **2018**.
101. Hertel, M.; Dillenburger, M.; Kuchler, K. Gesteuerte Isomerisierung – Praxissude mit dem Hopfenausbeuteerhöher. *Brauwelt* **2010**, 5-6, 130–132.
102. Hackensellner, T. Würzbereitung mit dynamischer Niederdruckkochung. *Brauindustrie* **2001**, No. 3, 14–16.
103. Kantelberg, B.; Hackensellner, T. Zeitgemäße Würzekochung. *Brauindustrie* **2001**, No. 9, 18-22.
104. Bühler, T.; Michel, R.; Kantelberg, B.; Baumgärtner, Y. Die dynamische Niederdruckkochung – systematisch qualitätsoptimiert. *Brauwelt* **2003**, No. 38, 1173–1178.
105. Bastgen, N.; Becher, T.; Titze, J. The effects of three mash separation systems on the isomerisation of hop alpha-acids. *J. Inst. Brew.* **2020**, 126 (2), 148–154. DOI: 10.1002/jib.605.
106. Yamashita, H.; Kühbeck, F.; Hohrein, A.; Herrmann, M.; Back, W.; Krottenthaler, M. Fractionated boiling technology: wort boiling of different lauter fractions. *Monatsschrift f. Brauwissenschaft* **2006**, July/August, 130–147.
107. Wietstock, P.; Kunz, T.; Shellhammer, T.; Schön, T.; Methner, F.-J. Behaviour of Antioxidants Derived from Hops During Wort Boiling. *J. Inst. Brew.* **2010**, 116 (2), 157–166.
108. Hertel, M.; Dillenburger, M. Measures for raising yield of bitter substances in beer brewing (Part 4): New equipment for raising hop yield. *Brauwelt International* **2010**, No. 5, 278-282.
109. Hertel, M.; Dillenburger, M.; Schönberger, C. Gezielte Isomerisierung: Untersuchungen zur Erhöhung der Hopfenausbeute. *Brauindustrie* **2010**, No. 10, 38–40.
110. Hertel, M.; Dillenburger, M.; Schönberger, C. Der Hopfenausbeuteerhöher bei Verwendung von Ethanolextrakt. *Brauwelt* **2011**, No. 36, 1092–1097.
111. Hertel, M.; Dillenburger, M.; Schönberger, C. Der Hopfenausbeuteerhöher bei Verwendung von Pellets Typ 45. *Brauwelt* **2011**, No. 41, 1232–1235.

112. Takishita, S.; Imashuku, H.; Krottenthaler, M.; Becker, T. *Increasing the hop alpha-acids utilization by hop pre-isomerization and the evaluation of the bitter quality of beer*. Proceedings; 2012 World Brewing Congress: Portland, Oregon, USA, **2012**.

113. Bastgen, N.; Becher, T.; Wasmuht, K. Achieving enhanced hop utilization by fractional wort boiling. *Tech. Q. Master Brew. Assoc. Am.* **2018**, *55* (2), 33–38. DOI: 10.1094/TQ-55-2-0614-01.

Captions:

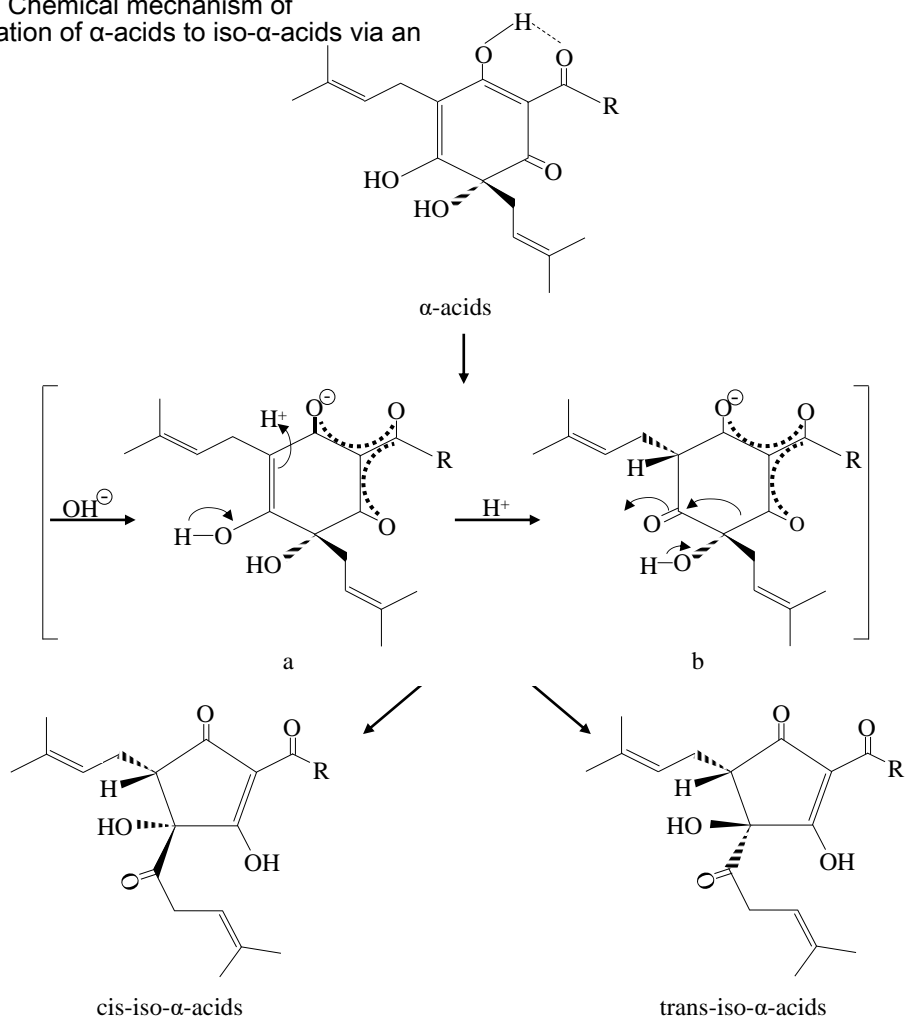
Figure 1: Chemical mechanism of isomerization of α -acids to iso- α -acids via an acyloin ring contraction [18, 19].

Figure 2: Technological possibilities of hop dosing to increase the isomerization rate of hop α -acids in the brewhouse. The letters a-h are mentioned at the corresponding positions in the text.

Figure 3: Utilized cone hops on the world market 2010, divided into hop products [7].

Figure 4: Wort flow parameters of each module of the continuous rotary disc filter. In comparison a preboil wort of a lauter tun (n = 2 samples; n = 1 lauter tun) [113].

Figure 1: Chemical mechanism of isomerization of α -acids to iso- α -acids via an



R=	α -acids	cis-iso- α -acids	trans-iso- α -acids
CH(CH ₃) ₂	cohumulone	cis-isocohumulone	trans-isocohumulone
CH ₂ CH(CH ₃) ₂	humulone	cis-isohumulone	trans-isohumulone
CH(CH ₃)C ₂ H ₅	adhumulone	cis-isoadhumulone	trans-isoadhumulone

Figure 2: Technological possibilities of hop dosing to increase the isomerization rate of hop α -acids in the brewhouse. The letters a-h are mentioned at the corresponding positions in the text.

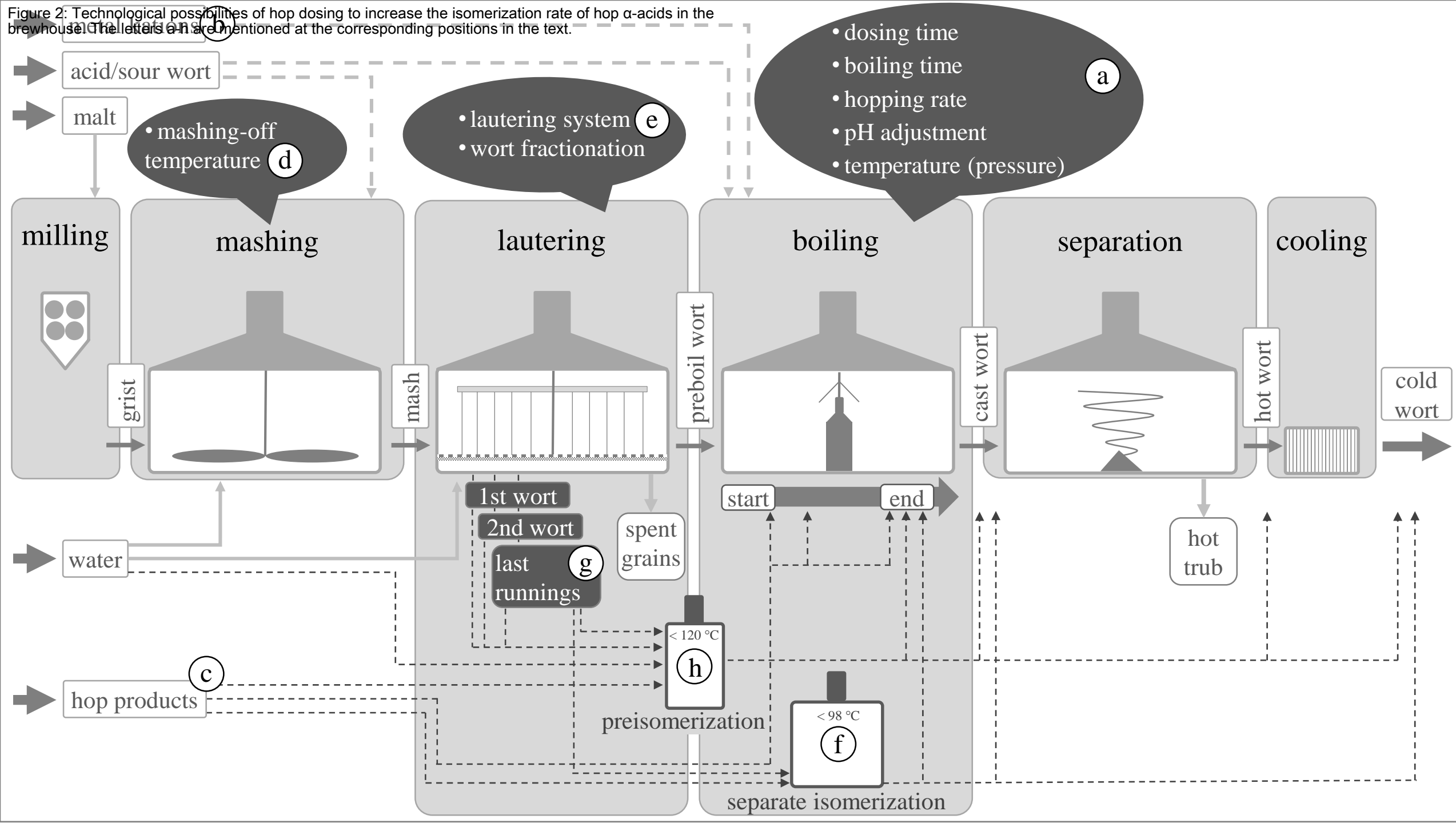


Figure 3: Utilized cone hops on the world market 2010, divided into hop products [7]

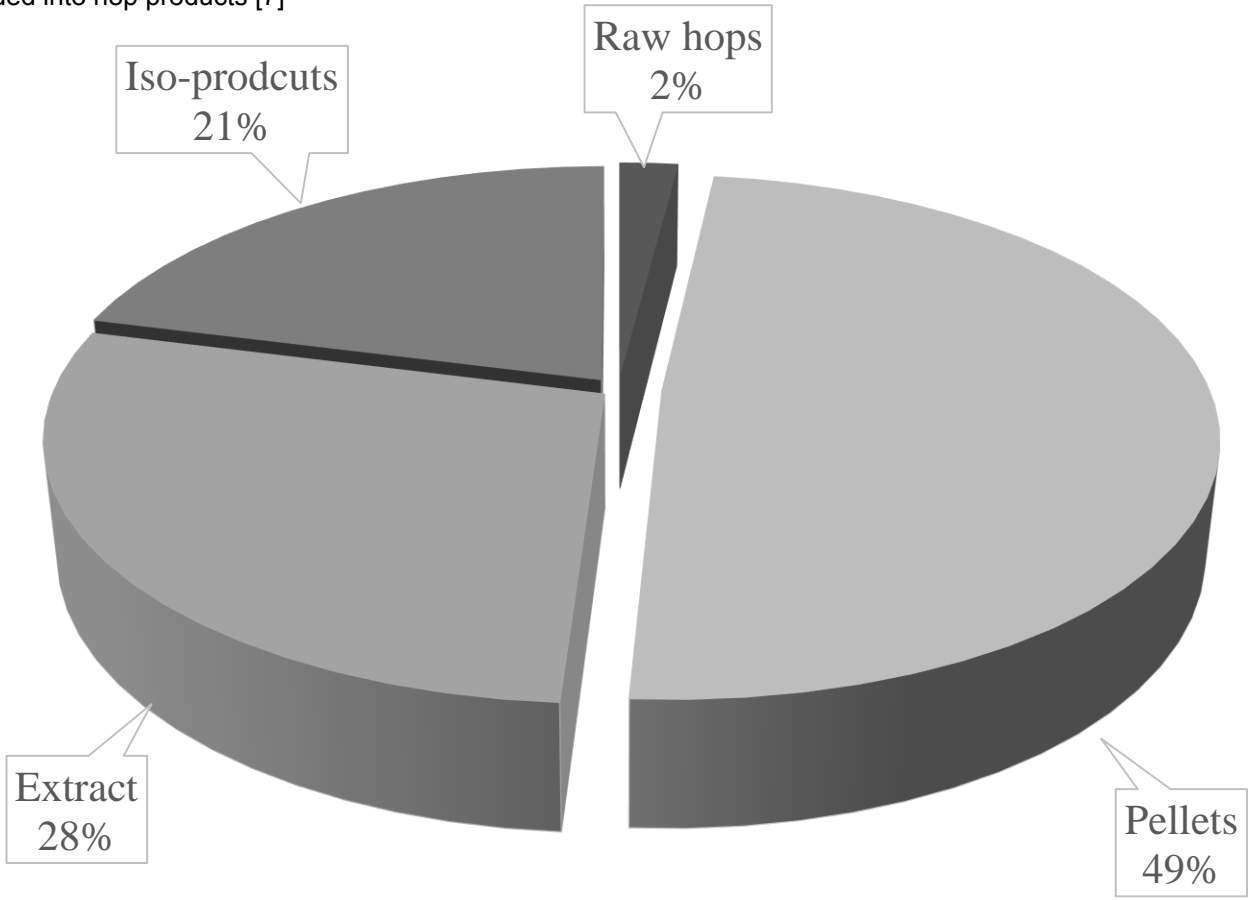


Figure 4: Wort flow parameters of each module of the continuous rotary disc filter. In comparison a preboil wort of a lauter tun (n = 2 samples; n = 1 lauter tun) [105].

