

Some reflections on mashing – Part 2

APPLICATION | The first part of this two-part article (BRAUWELT International no. V, 2016, pp. 309-311) consists of a detailed discussion of mash parameters and how they can serve as a powerful tool for enhancing wort and beer quality. The skillful manipulation of these parameters provides a highly effective means for compensating for a particular year’s harvest and the natural fluctuations in quality which may occur. Mash parameters also afford brewers more creativity by allowing them to tailor their wort to the needs of a particular beer style through the targeted use of malt enzymes. Selected examples are presented in the second part of this essay to illustrate precisely how to bring these concepts to fruition.

THE TERM GELATINIZATION describes the transition starch molecules undergo during mashing. The crystalline form of these macromolecules is present in the starch granules found in malt. Through hydration, a colloidal solution develops, and the starch becomes accessible to malt enzymes. Therefore, gelatinization is essential for comprehensive enzymatic degradation over the short duration of mashing. The gelatinization temperature for barley malt starch under normal conditions is approximately 61 °C. Growing seasons in which the barley undergoes a hot, dry period of maturation give rise to changes in the structure of the starch. In malt produced from barley subjected to this kind of maturation, gelatinization temperatures of 65 °C or higher have been measured. If the gelatinization temperature exceeds the optimal temperature for β -amylase, the activity of the enzyme will be drastically reduced due to its short half-life [1]. This results in a low final attenuation as well as in beers

lacking a well-rounded flavor which can be raw, harsh and perhaps even oleaginous, i.e. imparting an unpleasantly thick and somewhat fatty mouthfeel. Such beers are also highly susceptible to over-attenuating beer-spoilers. The gelatinization temperature plays a rather minor role in decoction mashing procedures. The decoction mash has been thermally treated, exposing the malt starch to further enzymatic degrada-

FOR A “HIGH-SHORT” MASH PROGRAM ...	
... the required malt quality	
Friabilimeter value	> 90 %
Modification	> 90 %
Homogeneity	> 75 %
Viscosity (65 °C)	< 1.6 mPas
β -glucans (65 °C)	< 350 mg/l

Table 1

tion, and then mixed back into the main mash where the amylases remain active. Because modern mashing methods are much less intense, the gelatinization temperature is a parameter that cannot be ignored.

Decoction – For All Practical Purposes

Confronted with high gelatinization temperatures in its malt, a large German brewery has attempted to solve the problem by employing a Hoch-Kurz-Maischverfahren (literally “high-short mashing process”) with numerous steps and several amyolytic rests (a staggered maltose rest at 62/64 °C, a

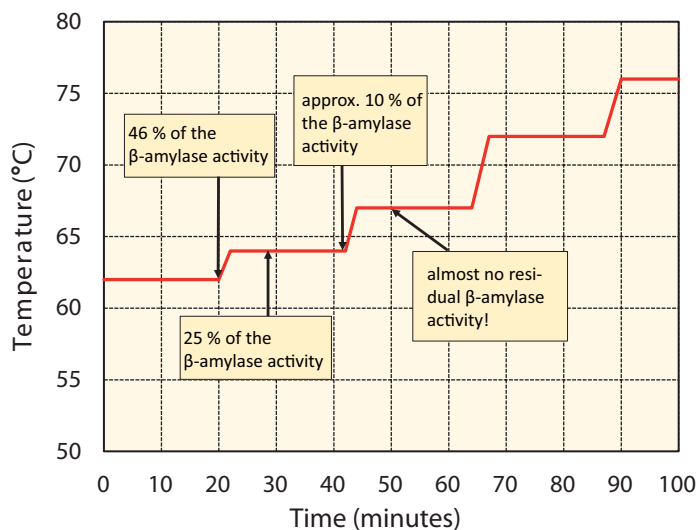


Fig. 1 Infusion mash for high gelatinization temperatures

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combination β -/ α -amylase rest at 67°C, see fig. 1). The rather short half-life of β -amylase at such temperatures (approx. 18.5 min at 62°C and 9.3 min at 64°C) brings about a fairly rapid loss in its activity (fig. 2). By the time the mash reaches 67°C, there is practically no β -amylase activity. Thus, from the standpoint of increasing the maltose content of the wort, the rest at 67°C can be deemed largely superfluous.

A more effective strategy for solving the problem would be a mashing process approximating decoction during which the kettle mash is not actually boiled (fig. 3). After mashing-in approx. 50 percent of the grist at 62°C directly into the kettle, it is heated to 72°C and allowed to dextrinate, meaning that many α -glucan fragments with reactive ends are formed. The depolymerization of the starch is already underway, which impedes subsequent retrogradation, the reformation of quasi-crystalline structures when the starch cools to below the gelatinization temperature. The second half of the grist is mashed-in at 52°C in the mash tun in order to preserve the β -amylase. After dextrination in the kettle, the two mashes are mixed together in the mash tun to reach a temperature of 62°C. The intense maltose formation in the pre-digested substrate increases the final attenuation to the desired level. The procedure then continues according to the high-short mashing process. The amount of time required for the whole procedure is no longer than the previously described infusion process.

■ Estery notes in Weissbier

In many breweries producing Southern German-style wheat beer, otherwise known as weissbier, after the installation of new cylindroconical fermentors, it is common for the beers to exhibit a noticeable decline in the bouquet characteristic of the style, which consists of primarily of compounds like isoamyl acetate (banana ester) [2]. The reason behind this somewhat diminished weissbier aroma is, among others, the high rate of yeast reproduction, which reduces the amount of the acetyl-coenzyme A available for ester formation. In addition, the high hydrostatic pressure in vertical vessels moderates the production of higher alcohols, thus reducing the numbers of reactants for the formation of esters. In short, the higher the liquid level is in a fermentation tank, the stronger the

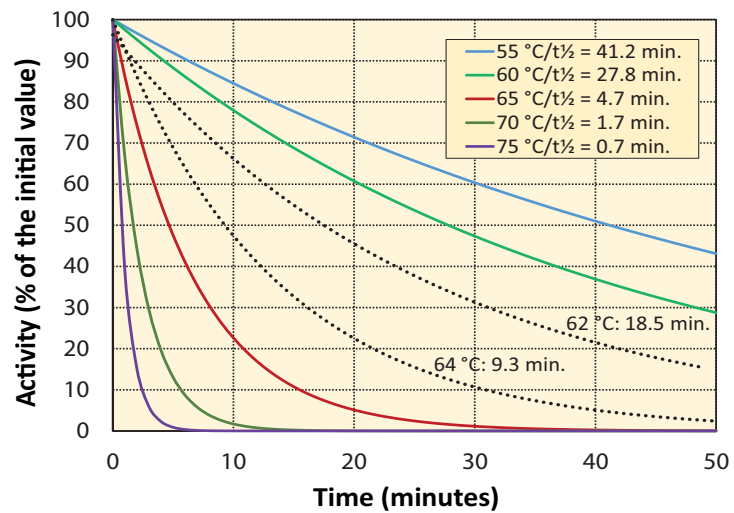


Fig. 2 Change in the β -amylase activity in barley malt at various temperatures

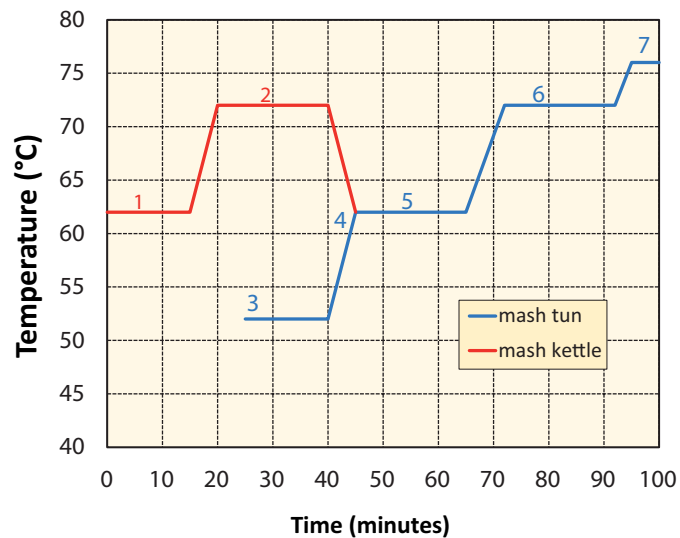


Fig. 3 "Nested" Hoch-Kurz mash program

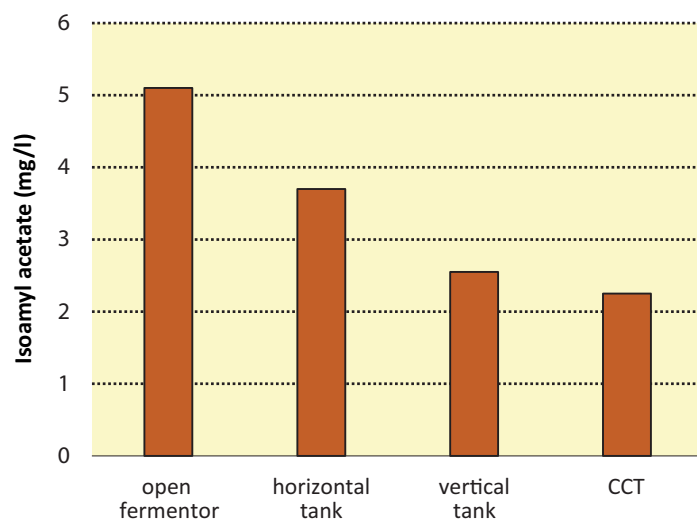


Fig. 4 Influence of the fermentation vessel on ester formation in Bavarian wheat beer

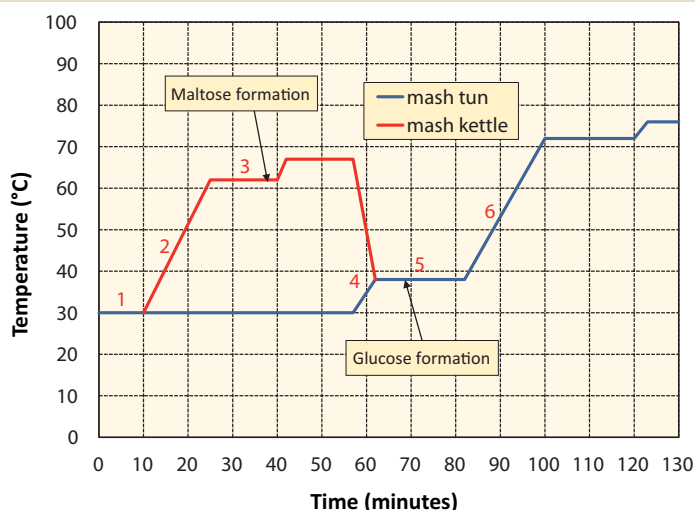


Fig. 5 Mash program for generating high concentrations of glucose

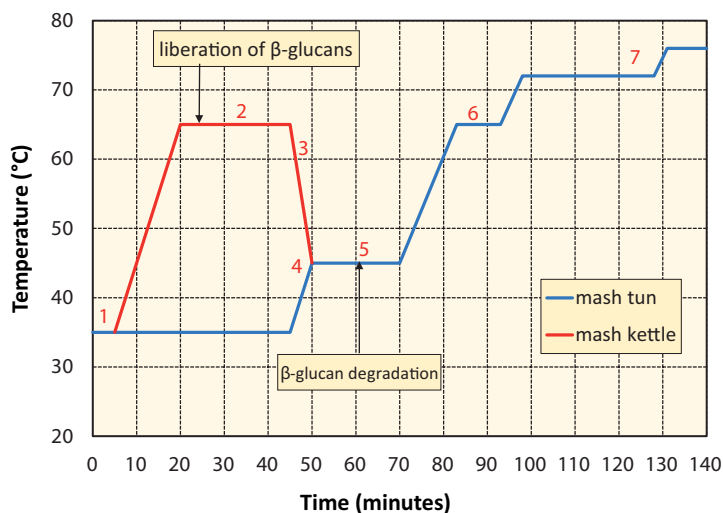


Fig. 6 Mash program for the greatest amount of β -glucan degradation

convection and homogenization, which results in a reduction in the formation of esters (fig. 4). In contrast, outside of Germany the so-called diauxic effect is known (from Greek: *dýo* = “two”, *auxáno* = “I reproduce”, meaning “reproduction using two sources of nutrition”) in wort containing high concentrations of glucose, for instance with disrupted fermentation in high gravity brewing processes in which glucose syrup is added to the boiling wort. They often exhibit a misshapen extract curve with a plateau forming after an initial, rapid decline in extract, followed by a short interval of yeast reproduction. An increased ester content expressed as fruity aroma notes, an atypical characteristic for bottom-fermented beer, is the result. The estery notes in beer have been observed to become more pronounced as the ratio of

glucose to maltose tips in favor of glucose [3]. Alcoholic fermentation with yeast in the presence of high concentrations of glucose leads to a delay in the onset of maltose metabolism after an initial rapid decline in the extract content of the wort (similar to a “second lag phase”). This explains the plateau in the extract curve. During this time, the yeast are scarcely reproducing and are compensating with the synthesis of maltose permease and maltase. The diminished yeast reproduction results in overflow of the acetyl-CoA pool and thus greater ester formation and fruitier beers. Taking advantage of these circumstances technologically would be interesting, not only for the primary fermentation of weissbier in CCTs but also for “dry beers” (estery, very highly attenuated) and for beer styles, like Oktoberfest or Märzen.

A strategy for increasing the ester content within the confines of the Reinheitsgebot targets the maltose rest (β -amylase) prior to the maltase rest for glucose formation. Owing to the gelatinization properties of barley malt starch and the temperature optima of the enzymes in question (β -amylase 60-65 °C, maltase 35-40 °C), this cannot be accomplished with infusion mashing. For this reason, the mashing process approximating decoction once again proves its utility. The mash in the kettle should not be boiled, otherwise when the kettle mash is mixed with the mash in the tun, it will rise to well above 40 °C. If the kettle mash is to be boiled, in order to achieve a more robust, grainy note, it would be better to mash-in thicker and to cool the boiling hot kettle mash with cold brewing liquor prior to mixing it with the other portion of the mash. The percentage of glucose among the fermentable sugars will double or even quadruple using this method (e.g. from 8.2 g/l to 17.4 g/l), while the concentrations of ethyl acetate and isoamyl acetate double (e.g. from 1.1 mg/l to 2.9 mg/l).

This procedure is summarized below (fig. 5):

1. Mash-in thin (pH!) at 30 °C; the ratio of malt grist to mash liquor should be 1 : 4.5 to 1 : 5 with no acidification! Objective: higher pH values favor maltase.
2. Pull a thick mash (22 %, 1 : 2.5) and transfer it to the kettle; the main mash rests at 30 °C.
3. The kettle mash undergoes a maltose rest, then is heated to 67 °C for combined β -/ α - amylase activity to maximize the maltose content.
4. Return the kettle mash to the main mash to reach a temperature of 38 °C.
5. A maltase rest ensues with glucose formation through the cleavage of maltose.
6. Heat to 72 °C, bypassing an additional maltose rest.

After the maltase rest – if it fits with the style of beer being brewed – a protein rest is also possible or even a decoction step. It is important, however, that no further maltose is generated subsequently, which is the reason the rest at 62 °C should be omitted for the entire mash.

■ Insufficient cytolytic modification

Modern mashing procedures beginning with a high mash-in temperature (e.g. 62 °C) and less overall intensity with under-

modified malt can lead to disruptions in the filtration process. Indicators are unsatisfactory friabilimeter values, and as a consequence the malt has glassy, adjunct-like tips with abundant cell walls left unmodified. Since no β -glucan degradation occurs at 62 °C (the β -glucanases are predominantly denatured), but ample β -glucans are liberated through the activity of β -glucan solubilase, the β -glucan content of the wort and beer can increase dramatically. As a result of shearing forces on the cold side of the production, the formation of β -glucan gel (“Fransen micelles”) brings about a rapid rise in the pressure difference in a diatomaceous earth filter (>0.5 bar/h), shortening filter runs and causing premature stoppage. Modern Hoch-Kurz mashing procedures necessitate very high quality malt, especially with regard to cytolytic modification (table 1). If this is an issue, for example due to a particular year’s barley crop, the mash program has to be altered to compensate for these shortcomings. This means stimulating more intense degradation of the β -glucans, for which there are three primary strategies:

- lower the mash-in temperature;
- separate a portion of the mash;
- acidify the mash at 62 °C.

Quite often, only the mash-in temperature or the temperature of the first rest is lowered to, for example, 45 °C. With under-modified malt, a rest at 45 °C has little to no effect, because after initial degradation by the β -glucanases at lower temperatures, many more high molecular weight β -glucans are liberated during the maltose rest at 62-65 °C. These can no longer be broken down, because the β -glucanases have already been denatured due to the increase in temperature. A reliable and almost complete degradation of β -glucans can be achieved, however, if the β -glucan solubilase activity is initiated in the mash before the β -glucanase rest occurs. The temperature optima of both enzymes (endo- β -1,4-glucanase: T opt. approx. 45 °C; β -glucan solubilase: T opt. approx. 62 °C) make infusion impossible. Therefore, an ample sized portion of the mash needs to be separated from the main mash, and the insoluble β -glucans must be liberated at an elevated temperature. Due to its considerable volume, this portion of the mash must be cooled with cold liquor prior to being returned to the main mash. Afterwards, β -glucan degradation occurs once the entire mash is al-

lowed to rest in the mash tun at a lower temperature. The practical implementation of this process is described below (fig. 6):

1. Mash-in thick (grist : mash liquor = 1 : 2.5) at 35 °C with a wet mill or a grist hydrating auger.
2. 25 percent of the mash should remain in the mash tun, a large portion (75%) is pulled into the mash kettle where it is heated to 62-65 °C. Aside from gelatinization of the starch and extensive saccharification (maltose formation, β -amylase), the native, high molecular weight β -glucans present in the cell walls of under-modified malt are liberated.
3. The kettle mash (65 °C) is cooled with cold liquor (12 °C, around 50% of the volume of the mash) to 47 °C.
4. The kettle mash is pumped back into the mash tun (total mash temperature after mixing: 45 °C).
5. Extensive degradation of the β -glucans occurs in the mash tun.
6. A rising temperature infusion mash program follows the rest at 45 °C,

THE EFFECT OF MASH ACIDIFICATION AT HIGHER MASH-IN TEMPERATURES ON THE

... β -glucans in beer

Extract, % d.m.	83.5	
Viscosity (mPas), adjusted to 8.6%	1.445	
Friabilimeter value, %	90.6	
Friabilimeter, completely glassy kernels, %	0.3	
β-glucans (Congress wort, Calcofluor), mg/l	225	
β-glucans (65 °C mash, Calcofluor), mg/l	509	
Mash program	Mash program A (classic infusion)	Mash program B (Hoch-Kurz with acidification)
	Mash-in at 52 °C, rest for 30 min at 52 °C	Acidify the mash to a pH of 5.35
	Heat to 62 °C (1 °C/min), rest for 30 min at 62 °C	Mash in at 62 °C, rest for 30 min at 62 °C
	Heat to 72 °C (1 °C/min), rest for 30 min at 72 °C	Heat to 72 °C (1 °C/min), rest for 60 min at 72 °C
	Heat to 76 °C (1 °C/min), rest for 10 min at 76 °C	Heat to 76 °C (1 °C/min), rest for 10 min at 76 °C
	Mash out	Mash out
Beer analyses	A	B
Foam (NIBEM)	174	181
Foam (R&C)	97	98
β-glucans (Calcofluor, mg/l)	171	198

Table 2

though the maltose rest can be reduced if not completely omitted.

- Through the dilution step, the grist to mash liquor ratio at the end of the process is approximately 1 : 3.7.

This mashing procedure takes time, but the amount of enzymatic degradation is comparable to that achieved with the addition of technical enzymes [4].

The fact that the acidification of the mash was originally employed to stimulate proteolytic activity has been largely forgotten, in part because of the high enzymatic capacity of modern malt. For example, lowering the pH of the mash in order to increase protein degradation and raise the FAN content of the wort is no longer necessary and, in fact, can be counterproductive. Moreover, mash acidification does not benefit α -amylase (pH opt. 5.6-5.8), which is essential as a “pace setting” enzyme in starch degradation and thus for its influence on the iodine value and the limit of attenuation of pale beers. Modern water treatment methods allow for the creation of almost any type of brewing liquor,

thus basically eliminating the need to correct the pH of the mash through the addition of natural lactic acid. Furthermore, through mash acidification coupled with mashing-in at low temperatures (45-52 °C), the buffering capacity of the wort increases, thereby causing the pH of the finished beer to end up somewhat higher than it would if the mash had not been acidified (acid phosphatase: T opt. approx. 52 °C, pH opt. 5.0-5.3), which is attributable to the buffered, less precipitous drop in pH during fermentation.

However, mash acidification can also be very advantageous, one benefit being that it renders softer, more satisfyingly full-bodied beers with a pleasingly rounded character. Producing beers with these attributes is possible even with very abbreviated mash programs, such as those frequently employed in brewhouses equipped with mash filters. Lactic acid produced by means of natural fermentation using bacteria also introduces reductones, providing protection against oxidation. In the end, the negative impact of increasing the buffering capacity is of

no concern at a high mash-in temperature (62 °C) because phosphatases are no longer active at that temperature. On the other hand, inhibition of β -glucan solubilase increases as the pH drops (pH optimum = 6.8). This represents the greatest hurdle to β -glucan solubilase activity, which experiences a steep drop as the pH approaches 5.4, where it is all but non-existent. Malt samples exhibiting exceptionally high β -glucan values in wort produced in an isothermal 65 °C mash in the laboratory, nevertheless yield acceptable values in wort produced in an actual brewhouse (table 2), as was found in research conducted at the end of the 1990s. At that time, the central question was whether or not mash acidification could round out the character and serve to enhance the body and possibly the values for foam stability in beers suffering from a lack of malt protein. Although the foam characteristics were not improved, mash acidification did compensate for the absence of colloids, which are responsible for mouthfeel. Even more surprising was that by acidifying the mash in conjunction with an abbreviated, high temperature mashing method (Hoch-Kurz), the β -glucan content actually dropped to a normal, technically manageable level. At the time, malt produced from the problematic barley variety Scarlett tended to possess an excessive amount of β -glucans, though for all other cytolytic attributes the values were fine. Brewing with a mash filter confers one further advantage: more β -glucans are liberated at 62 °C from the huge surface area of the fine malt flour than from the coarser grist employed in a lauter tun. However, the liberation of these β -glucans can be significantly reduced through mash acidification.

A knowledge of the relevant enzymes, their optima and the degradation processes they bring about as well as an awareness of the mash parameters as boundary conditions for the targeted regulation of enzymatic activity enables brewers to design mashing procedures to compensate for fluctuations in the quality of raw materials, thereby ensuring consistent product quality. Decoction mashing methods are considered obsolete, because they are time and energy intensive and also due to the thermal stress associated with the boiling a portion of the mash. Decoction is now largely limited to the production of specialty beers. However, this approach to mashing brings with it myriad benefits through clever and more efficient combinations of enzymatic activity, which

are simply not available with infusion. Boiling the kettle mash is, in fact, not necessary. Most often, it is sufficient to target the “pace setting” enzymes through rests and to allow the degradation processes to run their course prior to mixing the kettle mash with the portion still in the mash tun. Issues one may currently experience with barley malt, such as high gelatinization temperatures or difficulties stemming from under-modification, can be elegantly solved with these kinds of procedures – still within the confines of the Reinheitsgebot – since the enzymatic

degradation achieved using these methods cannot otherwise be accomplished without utilizing technical enzymes.

Additionally, a mashing process approximating decoction permits the creation of beers with a distinctive character, which is not feasible with a simple infusion method, as with the production of glucose-rich wort to elicit a fruity note in beer. ■

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