Iodine Value in Breweries

STATUS QUO | Prompted by recent developments in brewhouses, especially mash filtration (see Brauwelt International no. 3, 2017: Novel Mash Filtration Process (Part 1), the importance of iodine normality in beer wort was analysed, assessed and summarised in order to evaluate brewhouse procedures.

MONITORING IODINE normality at the end of the saccharification rest during mashing is one of the simplest and yet most fundamental technical brewing analysis that brewers carry out in the brewhouse. It provides rough information about the processes of amylolytic degradation during mashing. The characteristic colouration of the iodine solution in the presence of starch can be attributed to intercalation of iodine molecules in the α-helices of starch molecules. Linear amylose gives rise to a deep blue and branched amylopectin to a purple to brown colour [1, 2]. As dextrins of a length of 9-18 glucose monomers formed during amylose no longer result in visible colouration with iodine [3, 4] – dextrins arising from amylopectin even at a length of 60 glucose monomers –, the photometric iodine value has to be used in order to make a precise, quantifiable assessment of brewhouse procedures [2, 4]. For this approach, starch and dextrins in the sample are precipitated by adding ethanol and, after a centrifugation step, dissolved in phosphate buffer. After iodine solution has been added to the sample, extinction is measured at 578 nm [5]. Based on the current MEBAK, a value of E = 0.45 [5] is considered a limit value for wort. *Narziß* considers iodine values above 0.25 as "not satisfactory" [4], whereas *Annemüller* and *Manger* recommend an iodine value of E = 0.2 in pitched wort for beers that are easy to filter [3].

Main Risks

It is well known that an elevated iodine value may give rise to problems. Common primary risks discussed are:

- risk of microbiological instability;
- turbidity ("starch turbidity"), precipitations;
- filtration problems;
- lower final attenuation;
- risk of off-flavours [18].

In general, a higher iodine value means that a quantity of non-fermentable dextrins remains in the sample, having a direct negative impact on final attenuation. If the iodine value is too high, i.e. breakdown of starch progressed only unsatisfactorily during mashing, this may have an impact on lauter turbidity which can be abnormally high. MEBAK states: "To assess development of turbidity, (...) a concomitant analytical investigation of the solids content of the pfannevoll wort and the photometric iodine value is necessary." [5].

Additionally, stubborn α-glucan turbidity can arise in unfiltered beer. This colloidal turbidity is considered non-removable or only with great effort in both kieselguhr and membrane filtration [3, 4, 6-9]. It could be shown that degradation products of branched amylopectin are the main cause of this colloidal turbidity [7]. In addition to turbidity issues, increasing molecule size and concentration of α-glucans lead to higher beer viscosity, making filtration considerably more difficult as measured by the pressure increase at the filter inlet [3, 10]. Other accounts have shown that α-glucans easily form compounds with protein polyphenol complexes via hydrogen bonds and

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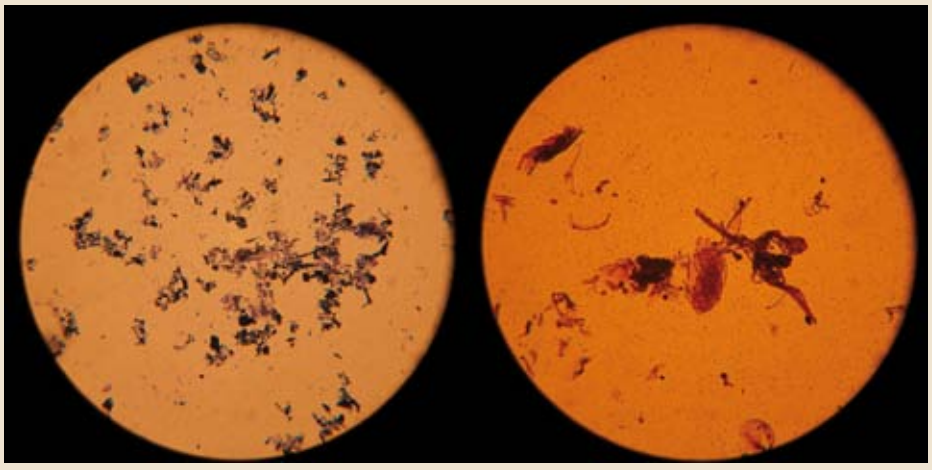

Fig. 1 Precipitations from a beer sample with small white flakes and slightly elevated turbidity, colouration is positive on neutral polysaccharides and erythrodextrins, negative on smaller carbohydrate building blocks

are thus able to reduce colloidal stability of corresponding beer further [3, 11].

The reasons for elevated iodine values can be generally attributed to technological and raw material related factors that have a negative impact on gelatinisation and saccharification of starch during mashing [8, 12]. In particular, poor grist composition as well as suboptimal pH values and temperature control during mashing are regarded as playing an important part, especially during saccharification. Moreover, excessive temperatures of sparging water as well as poorly controlled sparging timing can have a very negative impact on iodine values in the resulting wort [4, 7, 12].

Useful Tool

To get to the root of potential problems affecting amylolysis during wort preparation, determination of the photometric iodine value can generally be a useful tool, a standard analytic method in breweries for decades [2, 5, 6, 8]. That said, its ability to provide information on the issue of non-fermentable dextrins mentioned above is limited. The iodine value is merely a cumulative parameter that does not differentiate between the different origins of α-glucans. This may already play a part in the brewhouse because, as mentioned above, dextrins arising from amylopectin are more involved in turbidity formation than those arising from amylose [7, 13]. Annemüller and Manger recommend differentiated α-glucan determination at 452 nm for derivatives of amylopectin, and at 565 nm for derivatives of amylose [3]. In fact, the extinction maxima of these two starch molecules are far apart due to their degree of branching [3, 7]. Moreover, the photometric iodine value is often used as a benchmark for unfiltered beer, i.e. not only in the brewhouse [6]. At this point, another α-glucan, namely glycogen originating from yeast, is also partly included in the photometric iodine value.

Implications for Filterability

It is generally known that glycogen is produced in the yeast cell as a reserve carbohydrate. It mainly gets into beer when yeast is not doing well, especially when it autolyses. Thus, this provides one of many known indications of a direct relationship between yeast vitality and potential impairment of filterability.

Glycogen, if passed over into beer in significant quantities, is – according to *Hartmann* and *Kupetz* et al. – involved to an even greater extent in turbidity formation and filtration problems than amylose residues. However, due to the fixed wavelength at 578 nm, these are more dominantly reflected in the photometric iodine value [7, 13]. Table 1 explains the link between the origin of α-glucan, extinction maxima and technical brewing problems. According to Kupetz et al., it is not possible to predict filterability of beer using the photometric iodine value alone. His work has shown instead that both the Raible and Esser tests as well as pressure increase in an industrial kieselguhr cartridge filter do not show any correlation with the photometric iodine value [13]. To provide reliable assessment of the tendency towards dextrin-induced turbidity, further tests are necessary which take the different origins of α-glucans (amylose, amylopectin, glycogen), as well as their molecular sizes, into account. Based on Hartmann and Kupetz et al., a suitable approach involves determination of the modified photometric iodine value together with gel permeation chromatography (GPC), with GPC separating the dextrins according to their molecular sizes, and the iodine value of the resulting fractions is measured at various wavelengths ranging from 400 to 700 nm [7, 13].

For the sake of completeness, determining the photometric iodine value is generally also carried out on laboratory and brewery spent grains and not only on wort and beer. Spent grains are, as a rule, macer-

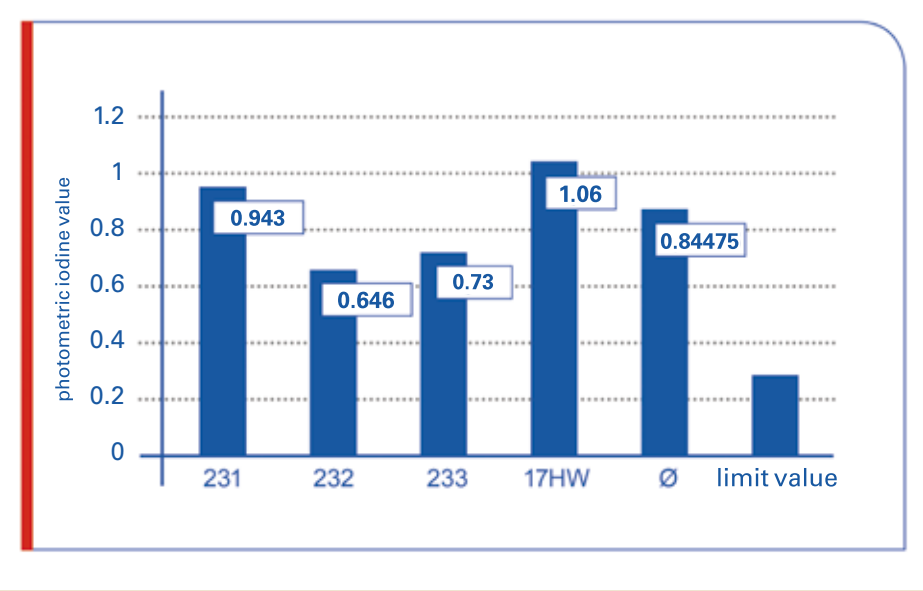

Fig. 2 Iodine values in cast wort during a brewhouse acceptance test (comparison with limit value of unbuffered method)

NON-FERMENTABLE α-GLUCANS IN BEER, ...

... their specific extinction maxima and their contribution to the tendency to cause turbidity and filtration problems; - zero or very small contribution, + large contribution, ++ very large contribution [3, 7, 13]

	Origin of non-fermentable α-glucans in beer		
	Amylose	Amylopectin	Glycogen
Origin	Malt	Malt	Yeast
Contribution to tendency to cause turbidity	-	++	+
Contribution to filtration problems	+	++	++
Extinction maximum	645 nm	545 nm	485 nm
Wavelength of photometric iodine value	578 nm		

Table 1

ated and boiled in water. After cooling and centrifugation, the iodine value in the supernatant is analysed using standard methods [5, 14]. The main purpose of analysing laboratory spent grains of congress mash is to obtain useful data about processability of the malt [15]. In brewery spent grains, the iodine value also provides information about the extent to which starch molecules could withstand enzymatic breakdown during mashing, e.g. due to clathrate formation or retrogradation [5]. As a result, iodine values of brewery spent grains – especially when compared with corresponding values from laboratory spent grains – offer insights into the quality of grist composition and the mashing process, leaching of spent grains, but also into malt quality. Taking samples from different parts of the lauter tun can additionally provide indications about the intercalation behaviour of the mash [16].

Coming back to determination of the iodine value in wort and beer, it has been reported that abnormally high values were occasionally analysed in contract analyses of intermediate and final products [17]. For instance, in modern, otherwise perfectly functioning brewhouses, iodine values in the region of 0.8 to over 1.0 have been measured during acceptance tests.

If the usual causes of higher iodine values mentioned above can be ruled out, this gives rise to the assumption that, at least in some instances, influences that are not fully known arise because parameters such as brewhouse yield and degree of final attenuation were within acceptable ranges in the worts mentioned above. In some of the beers recently sent for analysis, extremely high iodine levels were measured. It seems reasonable to assume accumulation of the "classic iodine value" and the influence of glycogen as a result of autolysis.

Summary

Analysis of the photometric iodine value is an established measurement method which is useful in many respects and able to provide good information. The method is often applied successfully in particular for monitoring breakdown of starch in the brewhouse. However, it is noticeable that the results sometimes do not appear very logical. Possible consequences of phenomena observed also do not always turn out as expected. A better understanding of relationships in terms of α-glucans to be measured and measurement techniques to be applied will help make sense of the findings. ■

The previous contribution focussed on the iodine value under the heading of analytics. In this part, the mode of action of amylolytic enzymes on the iodine value when lautering with NESSIE will be investigated in greater detail.

Brewers have been aware for a very long time that a pronounced single effect takes place: if the lautering result is very hazy, in particular in combination with elevated levels of solids, this will lead to far higher iodine values after wort boiling. Inherently, the focus will be on so-called optimum temperatures for breakdown enzymes in order to reduce this high iodine value after boiling.

It is generally known that enzymes are most effective in specific temperature ranges. These so-called optimum temperatures usually come quite close to temperature ranges that are responsible for enzyme inactivation. These inactivation temperatures are also specific for various enzymes. The following graph shows the temperature range for an alpha-amylase (here of bacterial origin).

The example in Fig. 1 indicates that inactivation sets in quite rapidly above optimum temperature but that a certain temperature range allows the enzyme to stay active though optimum temperature has been exceeded. As mentioned, the example does not show malt alpha-amylase. Therefore, the curve cannot be taken over directly but it may be assumed that it follows a similar pattern.

According to *Uhlig*, the turnover rate of an enzyme rises with temperature (about by a factor of 2 every 10 K difference in temperature) [19]. We also know from publications e.g. by *Sacher*, *Becker* and Narziß that enzymes are already rendered inactive at temperatures around the optimum range or even lower [20]. It may thus be assumed that the enzyme is progressively rendered inactive in elevated temperature ranges but that enzyme contingents that have not yet been inactivated still have a high residual activity before being inactivated and enzymatic activity has come to a standstill. These are two countereffects. Effectiveness of the enzyme rises at a higher rate below optimum temperature than inactivation proceeds but, above optimum temperature, inactivation outweighs the increase in efficiency brought about by the elevated temperature. But both effects are relative.

As a consequence, it could be shown in tests that the iodine value can still be reduced effectively at temperatures between 80 and 90 °C in a wort deliberately prepared with a high iodine value (coarse lautering and then boiling) though the well-known optimum range of amylases originating from malt was clearly exceeded. However, after a specific time at an elevated temperature, it can certainly be taken for granted that enzymes are rendered completely inactive quite rapidly.

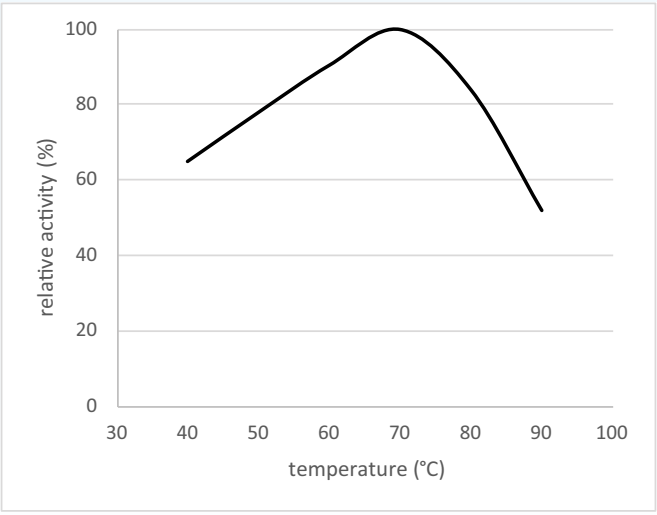

Fig. 1 Temperature spectrum of an alpha-amylase (bacterial) according to Uhlig [19]

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