

3.2 Mashing

Mashing is the most important process in wort production. During mashing the grist and water are mixed (mashed), the contents of the malt are thereby brought into solution, and the extract is obtained with the help of enzymes.

The changes that take place during mashing are of great significance.

3.2.1 Transformations During Mashing

3.2.1.1 Purpose of Mashing

The large and small starch granules are still present in their original form contained in the barley, even after milling. Thus the purpose of mashing is to convert this starch fully into as much fermentable sugar as possible, as well as non-fermentable but soluble dextrans. All of the substances that go into solution are referred to as extract.

Examples of soluble substances are sugars, dextrans, minerals, and certain proteins. Insoluble substances include starch, cellulose, part of the high-molecular proteins, and other compounds that remain as spent grains at the end of the lautering process. One attempts to convert as much insoluble material as possible into soluble compounds, in other words to get as much extract as possible, for economic reasons. This is indicated by the brewhouse yield (section 3.5) and the spent grains extract (section 3.3.5.2).

Not only the amount but also the quality of the extract is important however, because some compounds are unwanted whereas others (such as certain sugars or protein degradation products) are particularly desirable.

During mashing, most of the extract is produced by the activity of enzymes, which are allowed to act at their optimum temperatures.

3.2.1.2 Properties of the Enzymes

The most important property of enzymes is their activity in breaking chemical bonds in the substrates (Fig. 1.23). This activity depends on various factors.

Dependence of Enzyme Activity on Temperature and Exposure Time

The activity of enzymes depends above all on the

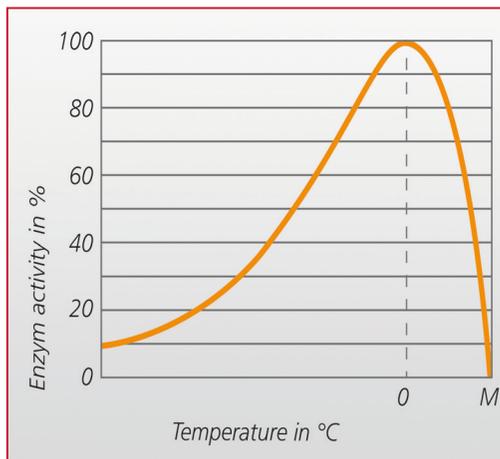


Fig. 3.23
Dependence of enzyme activity on temperature
O = optimum temperature M = maximum temperature

temperature. It increases as the temperature rises and reaches its maximum at an optimum temperature specific to each enzyme (Fig. 3.23). Rapidly increasing inactivation occurs at higher temperatures due to unfolding of the three-dimensional structure of the enzyme (denaturation).

The inactivation and destruction of enzyme activity is greater the more the optimum temperature is exceeded. Enzyme activity drops considerably when the temperature is below the optimum.

The typical enzyme activity for a particular temperature is not constant. The activity decreases rapidly with time at higher temperatures, whereas at low temperatures it remains constant almost indefinitely (Fig. 3.24).

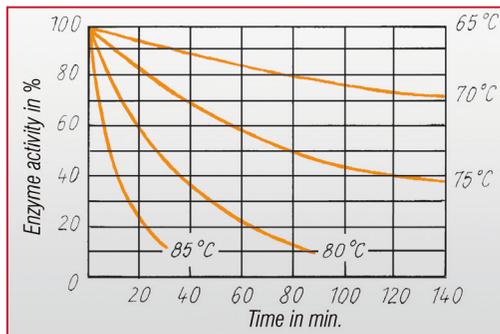


Fig. 3.24
Dependence of enzyme activity on exposure time

Dependence of Enzyme Activity on pH

Because the three-dimensional structures of enzymes also changes depending on the pH value, this influences the enzyme activity as well. It reaches its optimum at a specific value for each enzyme. The activity drops considerably at a higher and lower pH value (Fig. 3.25). The effect of pH on enzyme activity is generally not as large as the effect of temperature.

Dependence of Enzyme Activity on the Mashing Process

The activity of the enzymes and especially the β -amylases is dependent on the mashing process. Enzyme activity lasts longer in thicker mashes than in thinner mashes (Fig. 3.26). The part by weight of the grist load in the chart is in relation to the part by weight of the liquor (water).

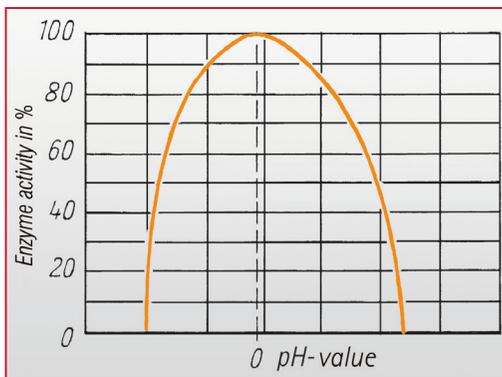


Fig. 3.25
Dependence of enzyme activity on pH value
0 = optimum value

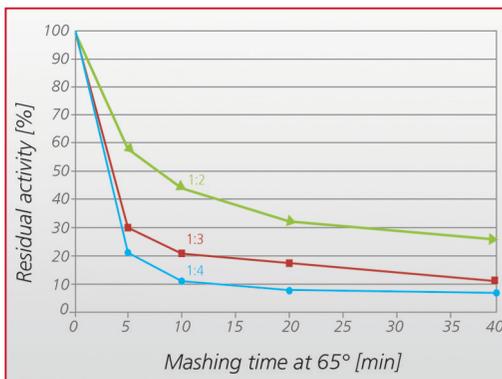


Fig. 3.26
Residual activity of the β -amylase at 65 °C depending on the liquor ratio (according to Narziß)

The degradation processes of importance for the brewer are

- the breakdown of starch,
- the breakdown of undissolved β -glucans,
- the breakdown of proteins,
- the conversion of fatty acids, and
- a number of other degradation processes.

3.2.1.3 Starch Degradation

The most important component of beer is the alcohol formed during fermentation from sugars. Therefore it is necessary to degrade the starch, primarily to maltose. Intermediate products, the dextrans, that are soluble but not fermented and remain in the beer are however always produced as well.

Starch must be degraded to sugars and limit dextrans that are not stained by iodine. Complete degradation to this state is necessary to obtain clear beer. Incomplete starch degradation leads to a higher content of dextrans and therefore to haze in the beer due to β -glucans.

Starch degradation occurs in three stages, the sequence of which is unchangeable but that merge into one another:

- Gelatinization
- Liquefaction
- Saccharification

Gelatinization

Large numbers of water molecules abruptly settle on the starch molecules at a certain temperature in a hot aqueous solution. This results in an increase in volume that causes the closely packed starch granules to swell and finally burst. The starch molecules lose their crystalline state and become amorphous (non-crystalline, unshaped) in this process. An increasingly viscous (sticky) solution is formed. The degree of the viscosity increase depends on the extent of water uptake and differs between cereal varieties. This process is called gelatinization (Fig. 3.27).

The gelatinization temperature of most cereals is between 65 – 80°C. However, the gelatinization temperature drops noticeably in the presence of starch-degrading enzymes. Malt starch normally

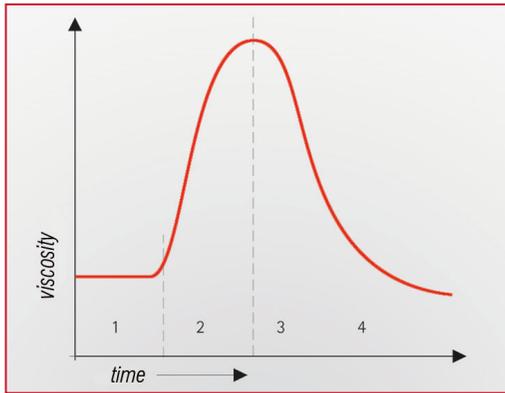


Fig. 3.27
Viscosity curve during starch degradation
(1) Mash before gelatinization
(2) gelatinization
(3) liquefaction
(4) saccharification

begins to gelatinize at 59–61°C. Small starch granules gelatinize at 1–3 K more than large granules. Complete gelatinization is the precondition for the complete breakdown of starch. If this is not the case, the results can include a lower extract yield, lower final attenuation, filtration difficulties, and starch haze. Gelatinization is not usually controlled.

Some types of starch, for example, rice starch, gelatinize at considerably higher temperatures (75–85°C) and swell up far more than malt starch. The gelatinized starch may scorch if this is not taken into account and can only be removed with great difficulty.

Rather than an enzymic reaction, gelatinization is a physical process and no catabolism occurs. Gelatinization is an important component of everyday food production (for example, when preparing pudding, making soups, or thickening sauces).

Gelatinized starch can be attacked more easily by the enzymes contained in the liquid (mash) because it is no longer packed in the solid starch granules. On the other hand, the degradation of ungelatinized starch, for example, during germination in the malting, takes several hours or even days.

Liquefaction

The long chains of unbranched and branched starch molecule chains composed of glucose residues (amylose and amylopectin) are very rapidly broken down by the α -amylase to form smaller chains (Fig. 3.28). This causes very rapid reduction of the viscosity of the gelatinized mash. The β -amylase on the other hand can only slowly degrade the long chains from the non-reducing end, and so degradation by this enzyme alone would take days. Also it would not be possible to break down the chains between the 1,6-bonds. Liquefaction means the rapid reduction of viscosity of the gelatinized starch by α -amylase.

Saccharification

The α -amylase breaks down the chains of amylose and amylopectin to form shorter chains. Each split results in two chain ends that are immediately attacked by the β -amylase by splitting off dyads of glucose residues (= maltose) (Fig. 3.28, c). Other sugars such as glucose and maltotriose are produced in this process, in addition to maltose.

In all cases the breakdown stops two or three glucose residues away from the 1,6-bonds of the amylopectin because neither α -amylase nor β -amylase can break these 1,6-bonds. Malt does contain an enzyme, limit dextrinase, that can break the 1,6-bond as well as the 1,4-bond. It has no effect during mashing however, since it has an optimum temperature of 50 °C and is therefore inactive after gelatinization.

Accordingly the following summarizes the effects of malt amylases in starch degradation:

The α -amylase breaks down the long starch chains to smaller dextrans. It acts optimally at 70–74°C and is rapidly destroyed at 80°C. The optimum pH value is 5.6–5.8.

The β -amylase splits maltose off from the non-reducing ends of chains, but it also produces glucose and maltotriose (Fig. 3.29). It acts optimally at 62°C (59–63°C) and is very sensitive to higher temperatures. At just 65°C it is inactivated relatively quickly. Thicker mash (1:2) is gentler on the β -amylase (Fig. 3.26). This is important in high-

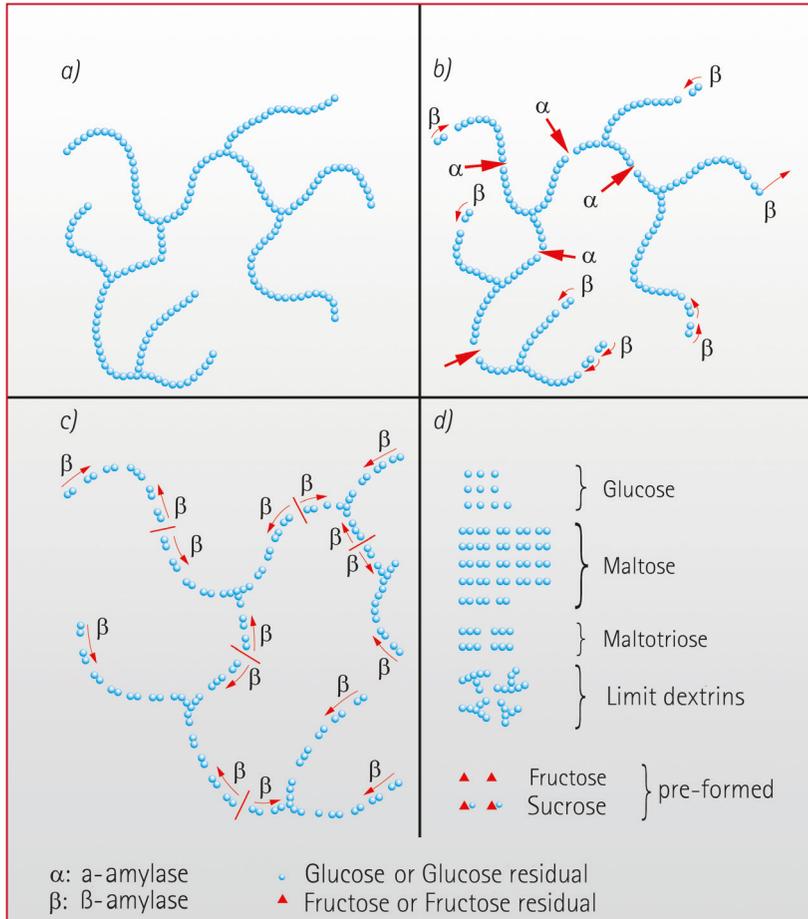


Fig. 3.28
Starch degradation during mashing using amylopectin as an example

gravity brewing. The optimum pH value is 5.4–5.5. β -amylase is more thermally stable in the presence of proteins.

Starch must be fully broken down into soluble products (sugar and limit dextrins). The complete breakdown of starch has to be monitored because residues of undegraded starch and larger dextrins cause a β -glucan haze in beer.

With a normal mashing process, about two thirds (65.5 %) of the sugar that goes into solution can be expected to consist of maltose, about 17.5 % maltotriose, and the same amount of saccharose, glucose, and fructose [3-8].

Starch degradation is monitored using 0.02N tincture of iodine (a solution of iodine and potassium

iodide in alcohol). This procedure is called the *iodine test* and is always performed on a cooled mash sample. The iodine test is based on the fact that the iodine solution makes a blue to red color at room temperature with gelatinized starch and

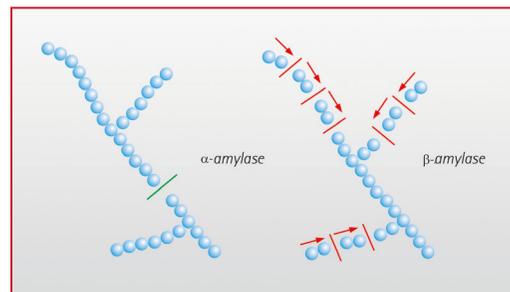


Fig. 3.29
Differences in the effect of α - and β -amylase

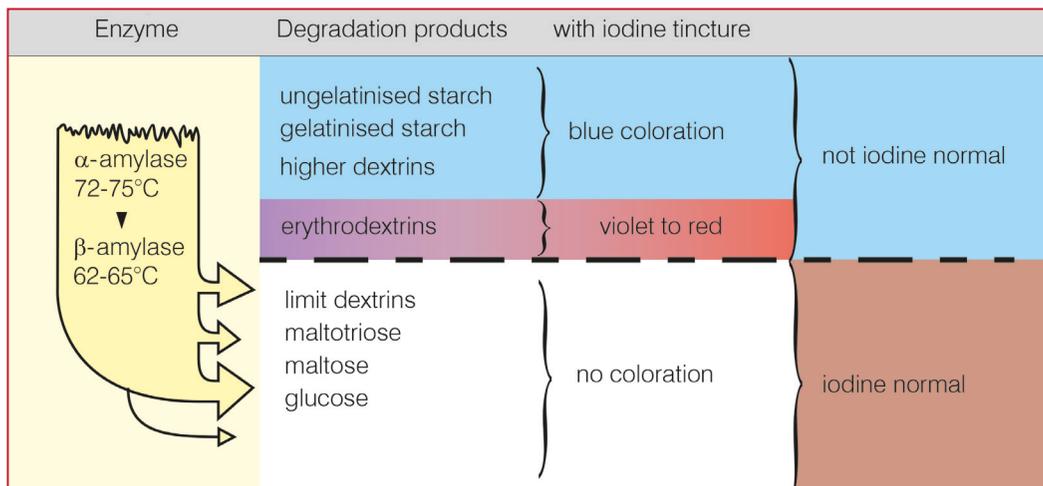


Fig. 3.30
Starch degradation to iodine normality

larger dextrins with more than 10 glucose residues, whereas all sugars and smaller dextrins from four to about ten glucose residues do not cause a discoloration of the yellow-brown tincture of iodine (Fig. 3.30). Higher to medium dextrins with about 11–12 glucose residues still produce a red to violet iodine coloration. This coloration is not always easy to see but it indicates a wort that is still not iodine normal.

A stricter iodine test according to W. Windisch monitors the presence of these dextrins by precipitation with ethanol, removal of the ethanol, redissolving, and coloration with iodine (iodine value). This method is used in problem cases.

The brewer must be able to evaluate the iodine test correctly. If discoloration of the iodine tincture no longer occurs when it is mixed with the mash sample, the mash is said to be iodine normal. Degradation of the starch molecules until the iodine normal condition is reached is called saccharification. Saccharification means complete degradation of the liquefied starch to maltose and iodine normal dextrins by the amylases.

The starch degradation products formed during mashing differ substantially with regard to fermentability by brewing yeast:

Dextrins are not fermented. These include all glucose chains up to 10 glucose residues.

Maltotriose is fermented by all top-fermenting yeast strains. However, maltotriose is not fermented by yeast until the maltose has been fermented, so preferably only during storage (late fermentation sugar).

Maltose and other disaccharides are easily and rapidly fermented by yeast (main fermentation sugar).

Glucose is the first sugar used by yeast (initial fermentation sugar).

The percentage of fermentable sugar in the total extract of the wort determines the final attenuation ($V_{s\text{end}}$). Since the final attenuation establishes the potential alcohol content of the beer, it has a decisive influence on its character.

The proportion of fermentable sugars is determined by the variable activity of the enzymes during mashing (Table 3.4). Thus the final attenuation that is subsequently possible is established while mashing.